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Surface Analysis and Corrosion Resistance of Different Stainless Steel Orthodontic Brackets in Artificial Saliva

Mau-Chin Lin;[a] Sheng-Chieh Lin;[b] Tzu-Hsin Lee;[c] Her-Hsiung Huang[d]

ABSTRACT

The purpose of this study was to investigate the variation in corrosion resistance of commercial stainless steel (SS) brackets with different brands and types for the same application, using the electrochemical technique. The linear polarization test was used to evaluate the corrosion resistance, in terms of polarization resistance (R_p), of as-received commercial SS brackets in acidic artificial saliva. A two-way analysis of variance was used to analyze the R_p with the factors of brand and type. A scanning electron microscope and an atomic force microscope were used to analyze the surface morphology and roughness, respectively. The X-ray photoelectron spectroscopy was used to identify the chemical composition of the passive film on SS brackets. Results showed that different brands of SS brackets had a statistically significant difference in R_p ($P < .0001$), whereas there was no statistical difference between the bracket types ("Roth" and standard) ($P = .27$). Different surface topography, including surface roughness and defect, was present among the tested SS brackets. The same passive film structure, containing Cr_2O_3/Fe_2O_3 with small amounts of NiO, was observed on all SS brackets. The surface topography of the commercial SS brackets with identical surface passive film structure did not correspond with the difference in corrosion resistance.

KEY WORDS: Surface, Corrosion resistance, Polarization resistance, Stainless steel, Orthodontic bracket.

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INTRODUCTION Return to TOC

Fe-Cr-Ni–based stainless steel (SS) is one of the most popular materials used for orthodontic bracket because of its favorable mechanical properties and suitable corrosion resistance.[1] Although a protective passive film exists on the SS alloy, the Fe, Cr, or Ni (or all) ions may still be released from the metal surface in the acidic oral environment through the corrosion processes.[2]

The metallic brackets are normally placed in the oral cavity of patients for 1–2 years and may suffer from corrosion processes.[3] Studies have shown that the metal ions, such as Fe, Cr, and Ni, released from orthodontic appliances in artificial saliva because of corrosion phenomena, are much higher (five- to sevenfold) than those in saline solutions.[4,5] The potential hazard associated with corrosion in the use of Ni- or Cr-containing (or both) alloys comes from the biological and cytotoxical side effects of the Ni and Cr ions released.[6–12] Therefore, the Ni/Cr-containing SS bracket with good corrosion resistance is crucial to the biocompatibility of an orthodontic appliance.

Research on the corrosion resistance of SS orthodontic brackets has been carried out.[13–17] The study by Staffolani and his coworkers[13] showed that the quantities of metal ions released from SS bracket in acidic solution should not be the cause for concern in using the orthodontic appliance. Huang et al[14] stated that the recycled SS brackets release more metal ions than the new SS brackets. However, the total metal ions released after 12-week immersion in artificial saliva does not exceed the recommended daily intake (300–500 μg). Furthermore, Maijer and Smith[15] reported that the presence of voids, together with poor oral hygiene, leads to the occurrence of crevice corrosion of SS brackets and the formation of colored products, which results in enamel stains. Gwinnett[16] found that pitting corrosion can occur on SS brackets, and in some cases large amounts of metal are missing, leading to the existence of considerable amounts of Fe, Cr, and Ni elements in the bonding, discolored resin.

On the other hand, the sliding mechanisms are usually used in the fixed orthodontic devices. Loreille[17] claimed that one of the main reasons for the unpredictable control of orthodontic forces can be the surface corrosion of wires and brackets. Therefore, it is of no doubt that the SS brackets with good corrosion resistance are clinically important to the esthetics and integrity of the orthodontic appliance as well as to the biocompatibility as mentioned above.

Recently, Kao et al[18] investigated the anticorrosion ability of TiN plating on a SS bracket and found that the surface TiN-coating does not improve the corrosion resistance of SS bracket in the acidic artificial saliva. In the present practice, the as-received commercial SS bracket without surface coatings or treatments is still one of the most popular orthodontic appliances. The as-received SS brackets may have different corrosion resistance in an acidic oral environment because of the different manufacturing processes. The related information regarding the comprehensive differences in corrosion resistance among the as-received commercial SS brackets from various manufacturers is clinically important but still limited. Furthermore, the difference in bracket type may also play an important role in the corrosion resistance of SS brackets and is worth further investigation.

In this study, the dissimilarity in corrosion resistance in acidic artificial saliva of as-received commercial SS brackets of different types produced by different manufacturers was studied. The surface analysis results were compared, and the correlation was also studied with the corrosion resistance.

MATERIALS AND METHODS Return to TOC

Ten different commercial Fe-Cr-Ni–based SS orthodontic brackets (as-received condition) were chosen in this study. Among the brackets investigated, five different "Roth" type twin SS brackets (slot size: 0.022 inch) were used and designated as follows.

- U-R (3M Unitek, Puchheim, Germany),
- D-R (Dentaurum, Pforzheim, Germany),
- O-R (Ormco, Scafati, Italy),
- R-R (RMO, Denver, Colo), and
- T-R (Tomy, Tokyo, Japan).

Furthermore, five different standard type twin SS brackets (slot size: 0.022 inch) were also used and designated as follows.

- U-S (3M Unitek, Puchheim, Germany),
- D-S (Dentaurum, Pforzheim, Germany),
- O-S (Ormco, Scafati, Italy),
- R-S (RMO, Denver, Colo), and
- T-S (Tomy, Tokyo, Japan).

Chemical compositions (in wt%) of the as-received SS brackets were analyzed using an energy-dispersive spectrometer (EDS) (EX-200, Horiba, Kyoto, Japan). The EDS analysis was carried out using area analysis with the size of about 10 × 10 μm. Three brackets for each type of bracket and one area for each bracket were analyzed.

A scanning electron microscope (SEM) (S-3000N, Hitachi, Tokyo, Japan) was used to observe the wing surface morphologies of the SS brackets. The SEM examination was performed at a magnification of 1200× and with the area size of about 125 × 80 µm. At least three areas for each type of bracket were examined by SEM. A three-dimensional surface roughness (R_a) of the wing surface of SS brackets was evaluated using an atomic force microscope (AFM) (Nanoscope III, Digital Instruments Inc, Santa Barbara, Calif) with the detection limit close to atomic size. The AFM analysis was carried out with the area size of 20 × 20 µm, and two areas were examined for each type of bracket. The outermost surface chemical analyses of the passive film on the wing surface of SS brackets were assessed from X-ray photoelectron spectroscopy (XPS) (ESCALAB 210, VG Scientific Ltd, East Grinstead, UK). For XPS analysis, two spots were analyzed for each type of bracket.

A potentiostat (AUTOLAB PGSTAT 30, Eco Chemie BV, Utrecht, The Netherlands) was used to perform the linear polarization test. The wing surface of the SS brackets was chosen as the test region, indicated by arrows in Figure 1. During the corrosion test, the bracket surface except the test region (area:0.25 cm^2) was isolated by epoxy resin. A saturated calomel electrode (SCE) and platinum sheet were used as the reference electrode and counter electrode, respectively. Modified Fusayama artificial saliva[19] was used as the corrosion test electrolyte, which consisted of NaCl (400 mg/L), KCl (400 mg/L), $CaCl_2 \cdot 2H_2O$ (795 mg/L), $NaH_2PO_4 \cdot H_2O$ (690 mg/L), KSCN (300 mg/L), $Na_2S \cdot 9H_2O$ (5 mg/L), and urea (1000 mg/L). The electrolyte had a pH of 5.0 and was maintained at 37 ± 1°C.

The electrolyte was deaerated with argon gas for one hour before the specimen was dipped into the electrolyte for the following corrosion test. The linear polarization curves of the test specimens were measured from −10 to +10 mV (vs corrosion potential) with a scan rate of 0.1 mV/second after dipping the specimen into the test electrolyte for two hours. The polarization resistance (R_p), which is inversely proportional to the corrosion rate, is defined as the slope of the potential vs the current density near corrosion potential in the linear polarization curves.[20] The R_p was statistically analyzed using two-way analysis of variance (ANOVA) for analyzing the factors of bracket brand and type ($\alpha = .05$). The number of SS bracket specimens for each corrosion test group was 10.

RESULTS Return to TOC

Chemical compositions (in wt%) of the wing surface of the as-received commercial SS brackets were identified using EDS. The Cu-containing R-R and T-R specimens were Fe-based alloys with 19.9% Cr, 3.0% Ni, 2.1% Cu, 1.0% Si, 0.5% Mn, and other elements (<1.0%) and with 16.3% Cr, 4.3% Ni, 2.9% Cu, 0.4% Si, 0.4% Mn, and other elements (<1.0%), respectively. The other tested brackets (except the R-R and T-R specimens) were Fe-based alloys with 16.7–21.6% Cr, 7.5–10.5% Ni, <2.0% Mn, <2.0 Si, and other elements (<1.0%).

Figure 2 shows the SEM observations of the as-received commercial SS brackets. Figure 3 shows the AFM observations and corresponding surface roughness (R_a:nm) of the as-received commercial SS brackets. Surface defect produced during the manufacturing processes was noticeably observed on the U-R, U-S, O-R, O-S, R-R, T-R, and T-S specimens (Figure 2). A rougher surface was visible on the R-R (R_a:79 nm) and T-R (R_a:112 nm) specimens, whereas the D-R and R-S specimen had the lower surface roughness (R_a < 30 nm) (Figure 3). XPS surface analysis results, which are not shown here, indicated that the outermost surface of the passive film on all tested SS brackets was the same and contained mainly Cr_2O_3/Fe_2O_3 with small amounts of NiO.

Table 1 shows the stable open-circuit potential (OCP) of the as-received commercial SS brackets after two hours immersion in acidic artificial saliva. The OCP values of the tested specimens could reach stable values after the two-hour immersion in acidic artificial saliva. All the stable OCP values of the tested specimens were very close and in the range between −634 and −593 mV (SCE).

Table 2 shows the R_p of the as-received commercial SS brackets after linear polarization tests in acidic artificial saliva. The ranking of the mean R_p was as follows: T-S (2.3×10^4 Ω cm^2) > D-R (2.0×10^4 Ω cm^2) > D-S (8.4×10^3 Ω cm^2) > U-R (7.9×10^3 Ω cm^2) > T-R (6.1×10^3 Ω cm^2) > R-S (4.7×10^3 Ω cm^2) ≅ O-S (4.6×10^3 Ω cm^2) > R-R (4.0×10^3 Ω cm^2) > O-R (3.6×10^3 Ω cm^2) > U-S (2.1×10^3 Ω cm^2). Results of two-way ANOVA for the R_p showed that the brand had a statistically significant influence on the R_p of SS bracket ($P < .0001$), whereas the bracket type had no statistical influence on the R_p ($P = .27$). Further comparison with Tukey's test for the factor of bracket brand revealed that two different groups, namely (A) Tomy and Dentaurum brand and (B) 3M Unitek, RMO, and Ormco brand, were observed.

DISCUSSION Return to TOC

Reports regarding the in vitro corrosion resistance of SS orthodontic brackets have focused mainly on the metal ions release using a time-consuming immersion test.[13,14,18,21] In this study, from the linear polarization test, taken as a nondestructive, fast, and precise electrochemical technique, the R_p could be rapidly calculated and used as a parameter for corrosion resistance evaluation. Although the XPS analysis results showed that the outermost surface structure of the passive film on all SS brackets was the same, a statistically significant difference was found in R_p (or corrosion resistance) among the tested SS brackets from different manufacturers ($P < .0001$).

Studies regarding the influence of surface characterization on the corrosion resistance of commercial orthodontic wires have been reported.[22–25] However, the dissimilarity in the corrosion resistance of commercial orthodontic brackets of different brands and types was very limited. In this study, the SS bracket (such as the T-R specimen) with obvious surface defects (Figure 2) and higher roughness (Figure 3) did not exhibit a lower R_p (Table 2) or a lower corrosion resistance.

It has been reported that the corrosion phenomenon for metallic brackets can be increased by the internal stress in the alloy or in the inhomogeneous microstructure of the alloy, or both.[12] Therefore, the difference in R_p (or corrosion resistance) among the tested SS brackets with the same surface passive film might be related to the different surface characterizations, such as surface residual stress and metallurgical factors, produced during the various manufacturing processes, instead of the surface roughness and preexisting defect.

As for the Fe-Cr-Ni–based SS alloy, it is well known that the Cr element in the SS alloy can form a thin and adherent Cr_2O_3-based passive film which provides the corrosion resistance of a substrate alloy.[26] A minimum Cr content of around 11% is required to form a protective passive film on SS alloy, and all the SS brackets used in this study have met the minimal requirement. On the other hand, the strengthening effect of SS alloy can be achieved by adding such element as Cu, which forms intermetallic precipitates during heat treatment. This precipitation-strengthened SS alloy, normally with a lower Ni content of 3–5%, has corrosion resistance similar to that of the austenitic SS alloy, which contains higher Ni content of 8–12%.[26]

In this study, according to the American Iron and Steel Institute (AISI) standard grades of stainless steels, the Cu-containing R-R (RMO brand with Roth type) and T-R (Tomy brand with Roth type) specimens were classified as the precipitation-strengthened SS brackets, whereas the others as the austenitic SS brackets. However, according to the results of Tukey's test for the factor of bracket brand, a significant difference in corrosion resistance was obtained between the precipitation-strengthened and austenitic SS brackets, such as RMO brand vs Dentaurum brand, Tomy brand vs 3M Unitek brand, and Tomy brand vs Ormco brand.

It is known that the biocompatibility of a metal is related mainly to the character of the surface passive film.[27] Therefore, a SS bracket with long-term good corrosion resistance, namely with a durably protective Cr_2O_3-based passive film, in an acidic oral environment is crucial to biocompatibility. In this study, the T-S and D-R specimens showed a higher R_p (or a more protective Cr_2O_3-based passive film) in the acidic artificial saliva compared with the other specimens. Namely, the passive film on the T-S and D-R specimens had a higher ions transfer resistance, although no difference in the outermost surface structure of the passive film was present among the tested brackets.

The R_p values for different commercial SS orthodontic wires have been measured in the acidic artificial saliva and are around 10^3–10^4 Ω cm^2.[2] These R_p values are close to those obtained in this study, as shown in Table 2. However, for very high corrosion-resistant biomaterials (eg, Ti metal), the R_p in the artificial saliva may even reach 10^6 Ω cm^2.[28] This implied that the TiO_2-based passive film formed on Ti metal has better corrosion resistance in acidic artificial saliva than the Cr_2O_3-based passive film on SS. Generally speaking, the investigated SS brackets in the acidic artificial saliva seemed not to be highly corrosion resistant, although they have long been used for orthodontic treatments.

Further investigation on the development of highly corrosion-resistant SS brackets is suggested when the biocompatibility, integrity, and esthetics of orthodontic appliance are taken into consideration. Different surface characterizations, such as surface residual stress and metallurgical factors, produced on the brackets during the manufacturing processes might play an important role in corrosion resistance, which, however, needs further investigation. The avoidance of acidic dietary for patients with orthodontic treatments is highly recommended.

CONCLUSIONS Return to TOC

- The brand of the as-received commercial SS brackets had a significant influence on the corrosion resistance in the acidic artificial saliva ($P < .0001$), whereas there was no statistical difference in the corrosion resistance between the brackets with Roth and standard types ($P = .27$).
- Among the tested SS brackets, the standard type Tomy brand and the Roth type Dentaurum brand showed a higher corrosion resistance (R_p:2.0–2.3 × 10^4 Ω cm^2).
- The surface roughness and preexisting defect of SS brackets with identical surface passive film structure (Cr_2O_3/Fe_2O_3 with amounts of NiO) did not correspond with the difference in the corrosion resistance.

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TABLES Return to TOC

TABLE 1. Stable Open-circuit Potential, OCP (mV, SCE), of the As-received Commercial Stainless Steel Brackets With Different Brands and Types After 2-h Immersion in Acidic Artificial Saliva

	U-R	U-S	D-R	D-S	O-R	O-S	R-R	R-S	T-R	T-S
OCP	−634 (25)[a]	−627 (39)	−593 (12)	−602 (54)	−620 (19)	−631 (9)	−613 (61)	−596 (7)	−611 (47)	−625 (18)

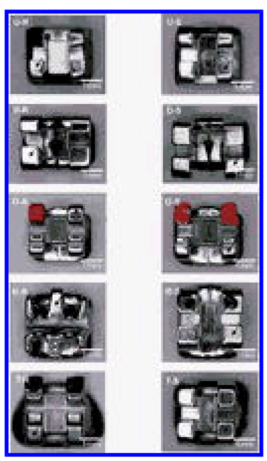
[a] Standard deviations are given in parentheses.

TABLE 2. Polarization Resistance, R_p (Ω cm^2), of the As-received Commercial Stainless Steel Brackets With Different Brands and Types After Linear Polarization Tests in Acidic Artificial Saliva

	U-R	U-S	D-R	D-S	O-R	O-S	R-R	R-S	T-R	T-S
R_p	7.9×10^3 (382)[a]	2.1×10^3 (187)	2.0×10^4 (1233)	8.4×10^3 (370)	3.6×10^3 (190)	4.6×10^3 (97)	4.0×10^3 (465)	4.7×10^3 (179)	6.1×10^3 (382)	2.3×10^4 (1735)

[a] Standard deviations are given in parentheses.

FIGURES Return to TOC



Click on thumbnail for full-sized image.

FIGURE 1. Optical microscope micrographs of the as-received commercial stainless steel brackets, showing the corrosion test regions as indicated by arrows

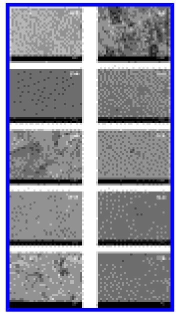


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FIGURE 2. Scanning electron microscope observations of the as-received commercial stainless steel brackets with different brands and types

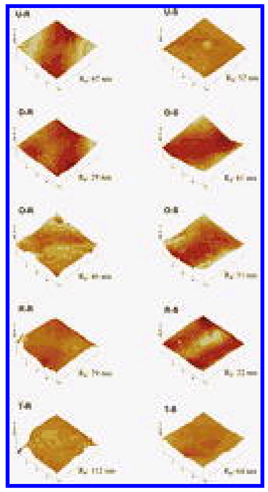

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FIGURE 3. Atomic force microscope observations and corresponding surface roughness (R_a:nm) of the as-received commercial stainless steel brackets with different brands and types

[a]Instructor, Department of Dental Laboratory Technology, Central Taiwan University of Science and Technology, Taichung, Taiwan

[b]Instructor, Department of Dental Laboratory Technology, Shu-Zen College of Medicine and Management, Kaohsiung, Taiwan

[c]Assistant Professor, Department of Dentistry, Chung Shan Medical University Hospital, Taichung, Taiwan

[d]Professor, School of Dentistry, National Yang-Ming University, Taipei, Taiwan

Corresponding author: Dr. Her-Hsiung Huang, School of Dentistry, National Yang-Ming University, Taipei 112, Taiwan (E-mail: biomaterial@msn.com)