

## In Vitro Corrosion of Stainless Steel and Nickel-Free Brackets after Exposure to Fluoride Agents

Natsinee Pipatvadekul<sup>1</sup>, Kanlaya Insee<sup>1,2\*</sup>, Samroeng Inglam<sup>2,3</sup>, Awiruth Klaisiri<sup>4,5</sup>

1. Division of Orthodontics, Faculty of Dentistry, Thammasat University, Pathumthani, Thailand.
2. Thammasat University Research Unit in Dental Biomechanics, Thammasat University, Pathumthani, Thailand.
3. Division of Oral Diagnostic Sciences, Faculty of Dentistry, Thammasat University, Pathumthani, Thailand.
4. Division of Restorative Dentistry, Faculty of Dentistry, Thammasat University, Pathumthani, Thailand.
5. Thammasat University Research Unit in Restorative and Esthetic Dentistry, Thammasat University, Pathumthani, Thailand.

### Abstract

This in vitro study aimed to analyze the nickel ions release, surface morphology and surface roughness of stainless steel, and nickel-free brackets after exposure to fluoride agents.

Twelve samples of stainless steel and nickel-free brackets were used and divided into three groups for exposing different fluoride agents by following each product's instructions; acidulated phosphate fluoride (APF) solution, fluoride varnish, and artificial saliva without fluoride as a control group. After that, all brackets were detracted from their respective solutions and submerged in artificial saliva for seven days. Inductively coupled plasma mass spectrometry was used to determine the amount of nickel ion concentration. A scanning electron microscope and a non-contact optical 3-dimensional profilometer were used to evaluated surface morphology and surface roughness, respectively. The Shapiro–Wilk test was used to determine the distribution of nickel ion concentration and surface roughness values. The data were presented as means and standard deviations. Differences between groups of each type of bracket were analyzed by one-way analysis of variance (ANOVA) followed by Dunnett's test. The results were considered significant at  $P < 0.05$ .

Nickel ions concentration and surface roughness from stainless steel brackets significantly increased after exposure to fluoride products. In contrast, nickel-free brackets released similar amounts of nickel ions among groups. There were no significantly different in the amounts of nickel ions and the surface roughness between groups of nickel-free brackets.

Nickel-free brackets are a choice for orthodontic patients who need a topical fluoride supplement. APF gel and fluoride varnish should not be used with stainless steel brackets in orthodontic patients for minimal clinical side effects.

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### Introduction

The most frequently metallic bracket material used in orthodontics is austenitic stainless steel, for example, type 304 and 316L of the American Iron and Steel Institute (AISI), which contains around 8–12 % nickel and 17–22 % chromium.<sup>1,2</sup> The corrosion resistance of

stainless steel alloys is based on chromium oxide layer along the surface. Nickel is cooperated into alloys to compete with chromium for the formation of salts, providing more chromium to create a passive layer. Nickel enhances ductility, stiffness, and resistance to crevice corrosion.<sup>3</sup> However, the link between the nickel atoms and the intermetallic compounds is so weak that the nickel is removed from the alloy surface.<sup>3,4</sup> Moreover, nickel is frequently known as an immunologic sensitizer that causes both short- and long-term sensitivity reactions.<sup>5</sup> Nickel-induced contact dermatitis is a hypersensitive immunological response that takes at least 24 hours to manifest.<sup>6</sup>

Orthodontic appliances must be retained in the oral environment for a long time, two years

#### \*Corresponding author:

Asst.Prof. Kanlaya Insee,  
Division of Orthodontics, Faculty of Dentistry, Thammasat University, 99 M. 18, Paholyothin road, Klongluang, Pathumthaini 12120, Thailand.  
E-mail: [ikanlaya@tu.ac.th](mailto:ikanlaya@tu.ac.th)

on average. Although these alloys have high corrosion resistance, when exposed to the oral environment, they can be corrosive and release metal ions including nickel ions into the oral cavity.<sup>7</sup> These released nickel ions can induce allergic reactions. Consequently, alternative materials for nickel hypersensitive orthodontic patients which do not contain or contain a lower amount of nickel were developed such as titanium brackets, ceramic brackets, and nickel-free (or sometimes called low-nickel stainless steel brackets, less than 5%). When compared to conventional alloys, nickel-free brackets were reported to cause fewer allergic reactions<sup>8</sup> and to have a greater corrosion resistance.<sup>9-11</sup>

The importance of good oral hygiene in orthodontic treatment cannot be disregarded. Many orthodontists prescribe topical fluoride therapy to treat poor oral hygiene.<sup>12-14</sup> On the other hand, fluoride prophylactic agents might decrease the alloys or metal brackets' resistance to corrosion. The presence of fluorides has been documented by several researchers to reduce corrosion resistance.<sup>11-19</sup> However, the effect of fluoride agents on nickel-free brackets has not been widely evaluated.

This study aimed to analyze the corrosion resistance of stainless steel and nickel-free brackets after exposure to fluoride agents in aspects of nickel ions released, surface morphology, and roughness.

## Materials and methods

### Sample and solutions preparation

Two categories of brackets were used 1) stainless steel brackets (Gemini, 3M™ Unitek™, United States) composed of 18–20 % chromium, 8–12 % nickel, 2.0% manganese (maximum) and 1.0 % silicon (maximum) and 2) nickel-free brackets (Forestadent®, Pforzheim, Germany) composed of 16-20 % chromium, 16-20 % manganese, ≤ 1.0 % silicon, ≤ 0.1 % carbon, 1.8-2.5 % molybdenum, ≤ 0.3 % nickel, ≤ 0.05 % sulfur, and ≤ 0.05 % phosphorus.<sup>10</sup> The 0.022 inches bracket slot size was used. The brackets were weighed using a semi-micro analytical balance (Denver instrument TB-214).

Each sample consisted of twenty orthodontic brackets and four molar tubes. Twelve samples of each type of brackets were prepared and divided into three groups depending on the solutions exposed including

fluoride varnish, acidulated phosphate fluoride (APF) solution, and artificial saliva as a control. The composition of artificial saliva was potassium chloride 0.75 g, calcium chloride 0.199 g, magnesium chloride 0.07 g, dipotassium hydrogen phosphate 0.965 g, potassium dihydrogen phosphate 0.439 g, sodium benzoate 2.4 g, and sodium carboxymethylcellulose 6 g in 1,200 mL of deionized water.<sup>19</sup> Then, adjust artificial saliva to a pH of 6.5.

Following their instruction, the samples were exposed to fluoride-containing items. For the varnish groups, four samples were directly applied with fluoride varnish (Colgate Duraphat®, having 22,600 ppm fluoride) and submerged in artificial saliva for 30 minutes. The APF solution was produced by mixing APF gel (60 Second Taste®, having 12,300 ppm fluoride) and artificial saliva at a 1:1.4 (v/v) ratio for APF groups.<sup>19</sup> Four samples were submerged in the APF solution for four minutes before being dried for thirty minutes. Lastly, four samples were submerged in artificial saliva for thirty minutes in control groups. A pH meter was used to determine the pH of each solution (FiveEasy Plus FEP20, Mettler Toledo, Switzerland). After that, all brackets were removed from the solutions, then cleaned with deionized water, and submerged in 8 mL of artificial saliva for 7 days at 37 °C.

### Measurement of nickel ion released

At the end of the immersion period, 5 mL of artificial saliva was collected, and added 50 microliters of 65 % HNO<sub>3</sub> to stabilize the ions. The concentration of nickel ion released was performed by using inductively coupled plasma mass spectroscopy (ICP-MS) (NexION® 350, PerkinElmer, USA). For nickel ions, the minimum detection limits of ICP-MS utilized in this investigation were 0.1 g/L.

### SEM observation of the surface morphology

The submerged brackets were cleaned with deionized water and dried after being submerged in artificial saliva. The right maxillary central incisor bracket was selected for surface morphology observation. The slot floor was then examined using a scanning electron microscope (SEM) (JEOL® JCM-6000 Benchtop SEM) at 15 kV and 500x magnification to determine the qualitative surface roughness (Figure 1).

### Surface roughness measurement

A non-contacting 3D microscope (Alicona® InfiniteFocus SL, Graz, Austria) was

used to measure the quantitative surface roughness (Ra) of the same bracket as well as in the same area observed for the surface morphology. InfiniteFocus MeasureSuite software ( Alicona®, Graz, Austria) was used to analyze the surface roughness. All brackets were scanned three times and calculated the mean values.

**Statistical analysis**

The data were analyzed using the Statistical Package for Social Sciences version 23.0 (SPSS Inc., Chicago, Illinois, USA). The Shapiro–Wilk test was used to determine the distribution of nickel ion concentration and surface roughness values. The data were presented as means and standard deviations. Differences between groups of each type of bracket were analyzed by one-way analysis of variance (ANOVA) followed by Dunnett’s test. The results were considered significant at  $P < 0.05$ .



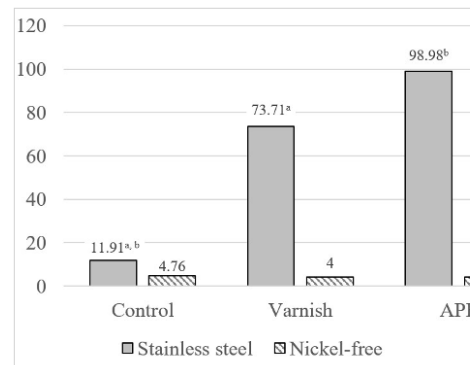
**Figure 1.** X demonstrates the area scanned by SEM.

**Results**

**The nickel ion released**

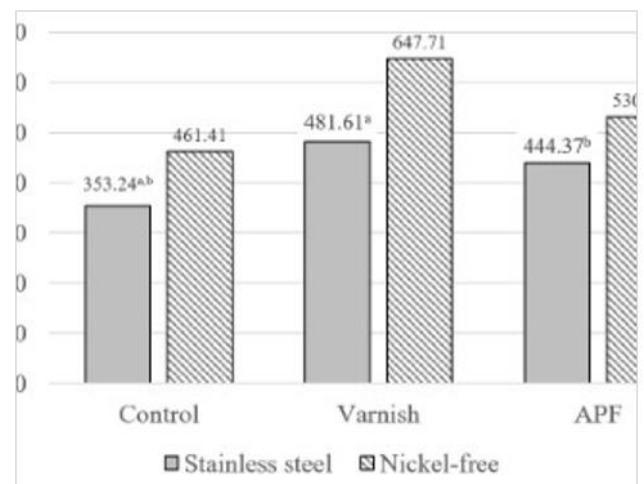
For stainless steel brackets, the highest quantity of nickel ions was found in the APF group ( $98.98 \pm 7.10 \mu\text{g/L}$ ), followed by the varnish group ( $73.71 \pm 15.10 \mu\text{g/L}$ ) and the control group ( $11.91 \pm 0.88 \mu\text{g/L}$ ), respectively, as demonstrated in figure 2. The concentration of nickel ions in the varnish and APF groups were significantly higher than in the control group ( $P < 0.01$ ). Whereas those from nickel-free brackets, the number of nickel ions in all groups was

similar and there were no significantly different between groups ( $P = 0.12$ ). The detected concentrations of nickel ions were  $4.76 \pm 0.30 \mu\text{g/L}$  in the control group,  $4.00 \pm 0.18 \mu\text{g/L}$  in the varnish group, and  $4.06 \pm 0.26 \mu\text{g/L}$  in the APF group (Figure 2).



**Figure 2.** The concentration of nickel ions released from stainless steel and nickel-free brackets from different solutions.

\* Significant differences ( $P < 0.05$ ) between the groups are indicated by lowercase letters.



**Figure 3.** Average surface roughness (Ra) of two types of bracket compared within group (control, varnish, and APF groups).

\* Significant differences ( $P < 0.05$ ) between the groups are indicated by lowercase letters.

**Bracket surface roughness measurement**

The results showed that stainless steel brackets in the varnish groups had the highest surface roughness ( $481.61 \pm 23.44 \text{ nm}$ ), followed by the APF groups ( $444.37 \pm 26.97 \text{ nm}$ ) and the control groups ( $353.24 \pm 44.90 \text{ nm}$ ), respectively.

ANOVA showed a significantly different in the bracket surface roughness between groups ( $P = 0.006$ ). The results of Dunnett's posthoc test showed that the surface roughness values of the varnish and the APF groups were significantly greater than in the control groups ( $P = 0.0004$ , and  $P = 0.026$ , respectively).

For nickel-free brackets, Ra values were  $647.71 \pm 70.70$  nm in the varnish groups,  $530.79 \pm 39.86$  nm in the APF groups, and  $461.41 \pm 13.79$  nm in the control groups. We can notice that after being exposed to fluoride agents and submerged in the artificial saliva for seven days, both types of brackets had increased average surface roughness in a very similar pattern (Figure 3). But there was no significantly different between groups for nickel-free brackets ( $P = 0.06$ ).

stainless steel bracket surfaces. Especially in the varnish group, a little deposition of surface residues was seen.

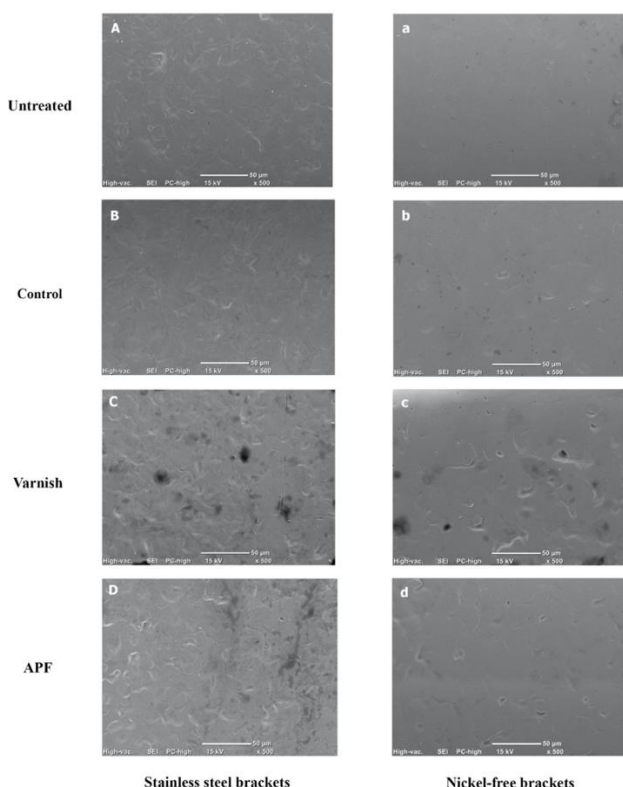
For the nickel-free brackets, bracket surfaces exposed to fluoride-containing products became rougher. Shallow surface marks and grooves were obviously seen in the varnish group as well as in the APF group.

### Discussion

Previous studies reported the corrosion resistance of brackets or archwires in different environments such as artificial saliva,<sup>9,20,21</sup> acidic solutions,<sup>22,23</sup> and fluoridated solutions.<sup>11,16,18,24-26</sup> The release of nickel ion was emphasized in many studies because nickel has been associated to allergic reactions in the oral cavity.<sup>5</sup> However, there have been few cases of nickel-free brackets corroding in a fluoride environment. Therefore, this present study was conducted to investigate the corrosion resistance of stainless steel and nickel-free brackets that exposed to different fluoride agents in three aspects including the nickel ion released, surface roughness and morphology.

According to Yanisarapan and co-workers' study, the corrosion resistance of stainless steel brackets with several archwire types could be reduced by APF gel.<sup>19</sup> The resistance of archwires was reduced in direct response to increases in fluoride concentration, according to Hevari and co-workers.<sup>15</sup> Hence, we included APF gel and fluoride varnish which contain high concentrations of fluoride ions in our study (12,300 and 22,600 ppm, respectively). Kuhta and co-workers reported that the most metal ions were discharged in the first week of immersion.<sup>27</sup> Consequently, nickel ions concentration measurements were done after 7-day immersion in this present study.

Our findings demonstrated that the number of nickel ions released from stainless steel brackets significantly increases after exposure to fluoride varnish and APF gel. The highest amount was detected in the APF group, followed by the varnish and the control groups, respectively. Though, the detected concentrations were lower than the threshold amount required to cause allergic and lower than the daily dietary intake level (200 - 300  $\mu$ g). In contrast to stainless steel brackets, those from nickel-free brackets were found to be similar in all



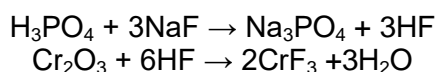
**Figure 4.** SEM observations of two types of the bracket in different solutions (500x magnification).

### SEM analysis

SEM observations at 500x magnification of two types of brackets in the different solutions are shown in figure 4. Both stainless steel and nickel-free untreated brackets presented smoother surfaces than those trial groups. After exposure to fluoride-contain products, irregularities were obviously observed on

groups and the results were not significant ( $P = 0.12$ ).

The corrosion resistance of dental alloys is based on the construction of a passive oxide along the surface (called passivation). This protective film is not certain because it can be damaged by both mechanical and chemical destruction.<sup>3</sup> Acidic conditions, chloride ions, or fluoride ions can enhance the corrosion process via the damage of the passive oxide layer. The results of this study have shown that the concentration of nickel ions from stainless steel brackets was the greatest in the APF group. This finding can explain that hydrofluoric acid (HF) is formed after stainless steel alloys are subjected to acidulated topical fluoride, and dissolved the passive chromium oxide layers according to the equation below,



From SEM observations, surface defects are shown in the varnish and APF groups in both stainless steel and nickel-free brackets. These findings are consistent with the previous experiments.<sup>11,19,28</sup> The qualitative surface roughness demonstrated that the surfaces of nickel-free brackets are rougher than stainless steels, although the number of nickel ions released was lower and more constant. This is most probably due to bracket manufacturing. The qualitative surface roughness coincided with the quantitative surface roughness from the non-contact surface profilometer which showed that the varnish group had the greatest Ra, followed by APF and control groups, respectively. The possible explanation for these results is that the pH of the APF solution was low and the concentration of fluoride ions in APF gel and fluoride varnish is very high, these conditions accelerate the corrosion process following the equation mentioned above. Besides sodium fluoride varnish has a sticky consistency that promotes adhesion to the tooth's surface. This could result in some products being left on the bracket's surface and leading to increased surface roughness. Many studies have proved that surface roughness is one of several factors of friction that affects the sliding of tooth movement, resulting in increased treatment time.<sup>29</sup> Moreover, increased surface roughness leads to greater biofilm adhesion.<sup>30</sup>

In this study, we used this device for surface roughness measurement because it needs no sample preparation and provides 3D images. Moreover, it is a non-destructive method.<sup>31</sup> The results revealed that stainless steel brackets' surface roughness significantly increased after being exposed to fluoride agents ( $P = 0.006$ ). But for nickel-free brackets, even if it is not significant ( $P = 0.06$ ), bracket surfaces in the trial groups were rougher than in the control group with a high standard deviation. Therefore, we suggest increasing the sample size to decrease the standard deviation.

In the aspect of surface roughness and nickel ion release, nickel-free brackets present higher corrosion resistance than stainless steel brackets in a fluoride environment. Nickel ions release minimal which is opposite to stainless steel brackets. APF gel and fluoride varnish are not recommended in patients treated with fixed stainless steel brackets. Consequently, nickel-free brackets can be chosen as an alternative appliance for an orthodontic patient who has nickel hypersensitivity and needs topical fluoride treatment.

## Conclusions

Stainless steel brackets exposed to fluoride agents (APF gel and fluoride varnish) significantly released nickel ions more than those not exposed to fluoride solutions. However, there were no significantly different in the concentration of nickel ions in nickel-free brackets. The surface roughness of both brackets in the varnish and APF groups was higher than in the control group, however, only stainless steel brackets showed significant differences. Therefore, we suggest that nickel-free brackets are a good choice for nickel-sensitive patients who required a topical fluoride supplement. On the other hand, using fluoride varnish and APF gel should be avoided in orthodontic patients who wear fixed stainless steel appliances.

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### Declaration of Interest

All authors have no conflicts of interest.

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