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Metal ion release from new and recycled stainless steel brackets

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SUMMARY As orthodontic appliances can corrode with time in the oral environment, the aim of this study was to compare the release of metal ions from new and recycled brackets immersed in buffers of different pH values over a 48 week period. To simulate commercial recycling, the stainless steel brackets were divided into two groups: new and recycled. The bases of the latter were coated with adhesive and the brackets were heat treated before being immersed in the test solution for 48 weeks. The release of nickel, chromium, iron, copper, cobalt and manganese ions was analysed by atomic absorption spectrophotometry. Differences were compared using one-way analysis of variance.

The results showed that recycled brackets released more ions than new brackets ($P < 0.05$). Brackets immersed in solutions of pH 4 released more ions than those immersed in solutions of pH 7, and the total amount of ions released increased with time over the 48 week period ($P < 0.05$). This study demonstrates that both new and recycled brackets will corrode in the oral environment. To avoid clinical side-effects, metal brackets should be made more resistant to corrosion, and recycled brackets should not be used.

Introduction

In the oral environment, orthodontic appliances are exposed to potentially damaging physical and chemical agents which may cause metallic corrosion. Corrosion will occur continuously in the mouth, due to the release of ions with abrasion by foods, liquids and tooth brushes (Geis-Gerstorfer, 1994). Orthodontic appliances may corrode over time. Electrochemical breakdown of corrosion-resistant high-nickel and titanium wire can also occur (Maijer and Smith, 1986).

Recycled orthodontic brackets may be used in the clinic for several reasons, including cost. A survey of 300 members of the British Orthodontic Society found that 47.5 per cent of respondents recycled metal brackets, and this was carried out more by specialist practitioners than consultants (Coley-Smith and Rock, 1997). The use of recycled brackets can accelerate the corrosion process, which in turn can be responsible for the failure of orthodontic appliances, either fixed or removable (Muller, 1986).

Grimsdottir *et al.* (1992a) proposed that corrosion of the bracket can cause the uptake of metal ions into the body. The major corrosion products of stainless steel are iron (Fe), chromium (Cr) and nickel (Ni). Although all three elements potentially have adverse effects, Ni and Cr have received the most attention because of their reported potential for producing allergic, toxic, or carcinogenic reactions (Pereira *et al.*, 1999). Cobalt (Co) has been found to impair the phagocytosis of bacteria by human polymorphonuclear leucocytes *in vitro* (Haynes *et al.*, 2000). Approximately 10 per cent of the general population exhibit hypersensitivity to Ni, with females being reported to be 10 times more sensitive than males (Peltonen, 1979). Moffa (1982) found that 31.9 per cent of females and 20.7 per cent of males in a population of 403 found a positive hypersensitivity reaction in a similar patch test of nickel sulphate. *In vitro* experiments on cultured human gingival fibroblasts showed that ions released from implanted Ni–Cr alloys caused altered cellular functions (Messer and Lucas, 2000). In addition, other studies have reported decreased DNA synthesis and inhibition of enzymes in cultured cells following exposure to Ni-based alloys (Wataha *et al.*, 1991; Bumgardner and Lucas, 1995).

High-gold alloys are extremely resistant to corrosion, due to their thermodynamic stability (Canay and Oktermer, 1992; Lucas and Lemons, 1992). In low-gold alloys, corrosion occurs primarily in silver-rich regions and secondarily in Cu-rich regions (Laub and Stanford, 1982). In the oral environment, different levels of moisture, changes in pH and variations in oxygen pressure exist. The type and level of ions degraded from new and recycled metal bracket appliances introduced into the mouth need to be investigated. There is a lack of studies that compare the behaviour of new and recycled brackets in a long-term corrosive environment, in terms of ion leakage from the metal brackets.

The aim of this study was to compare the metal ions released from new and recycled metal brackets following immersion in artificial saliva under controlled conditions of pH over an extended time interval.

Materials and methods

Four different types of metal bracket were investigated: Unitek DynaLock twin-torque brackets, Tomy metal base brackets, Ormco standard edgewise brackets and

Table 1 Details of the metal brackets.

Company	Bracket type	Position	Size	Order no.
Tomy Co. (Tokyo, Japan)	Micro-LOC bracket, standard edgewise	Upper premolar	0.018″	920-45
Ormco Co. (Orange, CA, USA)	Diamond bracket, standard edgewise	Upper premolar	0.018″	340-0604
Unitek 3M Co. (Monrovia, CA, USA)	Twin-torque bracket, Andrew	Upper premolar	0.018″	018-203
Dentaurum Co. (Pforzheim, Germany)	Discovery direct bond bracket, System Ricketts Universal	Upper premolar	0.018″	790-136-00

Dentaurum Rickett brackets (Table 1). In total, 320 brackets were used in this experiment. They were divided into new and recycled groups. The new brackets were used as received from the manufacturers and recycling of the brackets was mimicked by applying adhesive to the bracket base and once set, heating the bracket to 350°C for 30 minutes to burn off the adhesive (Maijer and Smith, 1986). This was to simulate the heat treatment at a commercial recyclers.

New and recycled brackets were immersed in the relevant solutions and incubated at 37°C for 48 weeks. The artificial saliva (Sinphar, Taiwan; Table 2) was adjusted with 1 mM $NaHNO_3$ to pH 4 and pH 7 buffer solutions. Each polypropylene tube contained 5 ml of buffer solution and four metal brackets. Five independent samples were prepared for each time point, 1 hour and 48 weeks. Following incubation times of 1 hour and 48 weeks, 0.5 ml of the immersion solution was removed and tested using graphite atomic absorption spectrophotometry (Perkin-Elmer AAS model 372, Norwalk, CT, USA). The solution was analysed for Ni, Cr, Cu, Co, Fe, and manganese (Mn) ions. Controls were prepared in equivalent solutions to counteract any buffer effects. The pre-treatment and atomization temperatures recommended by the manufacturers were used in the furnace programmes to ensure that linear standard curves were obtained for each element. Each sample was analysed for all six ions, and concentrations in μg/ml were averaged across the five replicates.

Results

The results of the graphite atomic absorption analysis of the solutions are presented in Figures 1–6. The results were compared using one-way analysis of variance (ANOVA). Differences in the treatment means were analysed with the Student–Newman–Keul's test and were considered to be significant at $P < 0.05$.

Table 2 Contents of the artificial saliva (Sali Lube).

Sodium chloride	0.844 mg
Potassium chloride	1.2 mg
Calcium chloride anhydrous	0.146 mg
Magnesium chloride $6H_2O$	0.052 mg
Potassium phosphate dibasic	0.34 mg
Sorbitol solution 70%	60 mg
Methyl paraben	2 mg
Hydroxyethyl cellulose	3.5 mg

Release of Ni ions

Following immersion in the pH 4 buffered solution (Figure 1a), more Ni was released from the recycled

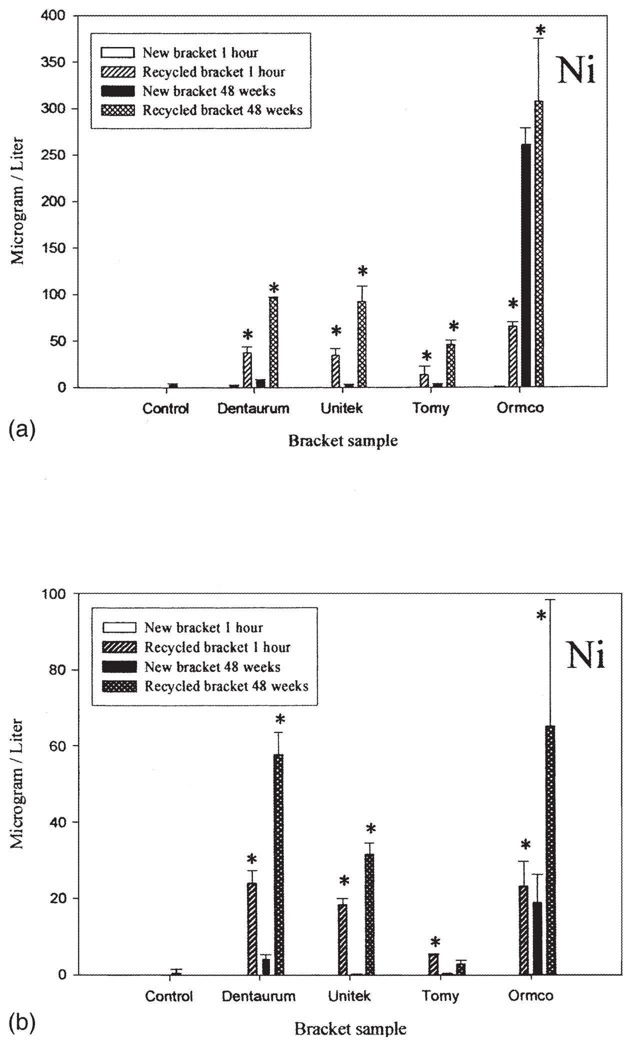


Figure 1 Nickel (Ni) ions released from the new and recycled metal brackets after 1 hour and 48 weeks' immersion. (a) Immersion in buffer at pH 4. (b) Immersion in buffer at pH 7. Each column and bar represents the mean and standard deviation of five replicates. The means and standard deviations were calculated by one-way analysis of variance. *Statistically different at $P < 0.05$.

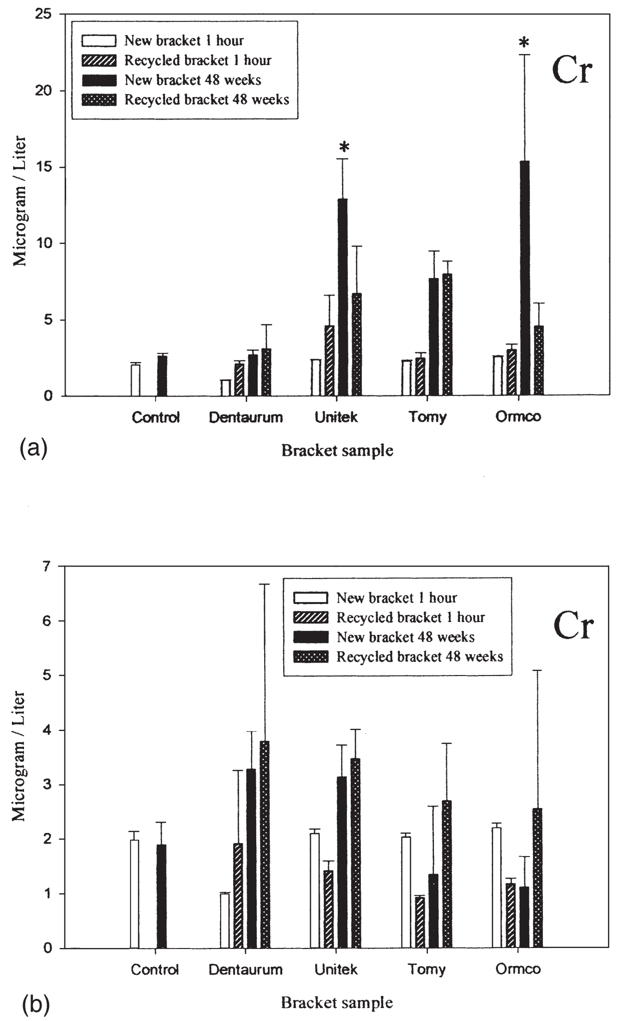


Figure 2 Chromium (Cr) ions released from the new and recycled metal brackets after 1 hour and 48 weeks' immersion. (a) Immersion in buffer at pH 4. (b) Immersion in buffer at pH 7. Each column and bar represents the mean and standard deviation of five replicates. The means and standard deviations were calculated by one-way analysis of variance. *Statistically different at $P < 0.05$.

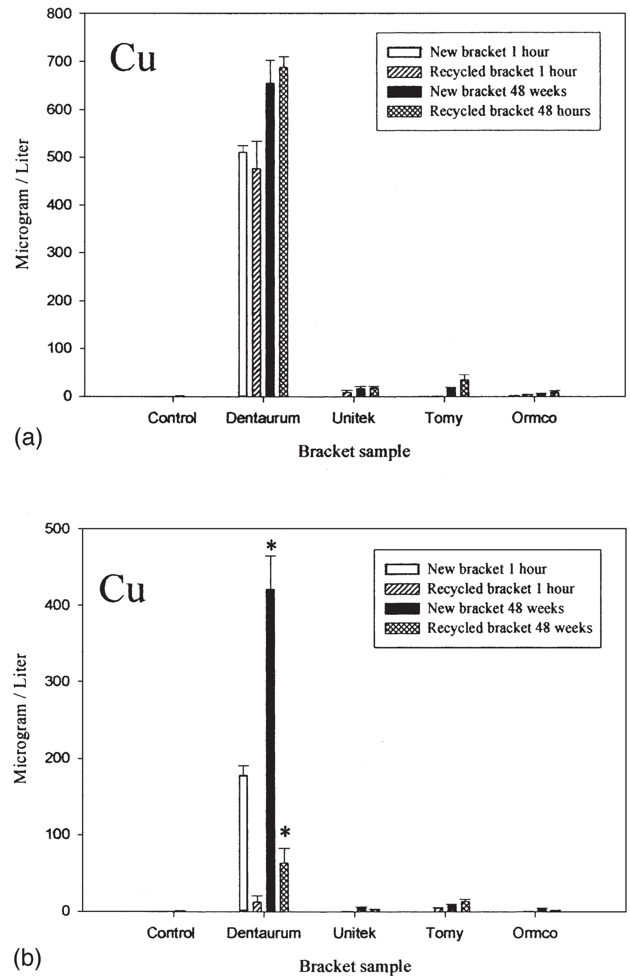


Figure 3 Copper (Cu) ions released from the new and recycled metal brackets after 1 hour and 48 weeks' immersion. (a) Immersion in buffer at pH 4. (b) Immersion in buffer at pH 7. Each column and bar represents the mean and standard deviation of five replicates. The means and standard deviations were calculated by one-way analysis of variance. *Statistically different at $P < 0.05$.

brackets than from the new brackets, and this was greater after 48 weeks than after 1 hour, for all samples tested. The Ormco brackets immersed for 48 weeks released the highest level of Ni, with the recycled group [307.3 μg/ml, standard deviation (SD) 67.5] releasing more than the new brackets (260.5 μg/ml, SD 17.9). More Ni was released in the pH 4 solution (Figure 1a) than in the pH 7 solution (Figure 1b). At pH 7, the recycled samples released more ions than the new samples, with the highest levels being recorded for the recycled Dentaurum (57.82 μg/ml, SD 5.82) and Ormco (65.0 μg/ml, SD 33.4) brackets, both after immersion for 48 weeks.

Release of Cr ions

At pH 4 (Figure 2a), new brackets from Unitek (12.86 μg/ml, SD 2.64) and Ormco (15.29 μg/ml, SD 7.00) immersed for 48 weeks showed the highest levels of Cr release. There was no significant difference between new and recycled samples from Dentaurum and Tomy.

Brackets immersed in the pH 7 solutions (Figure 2b) showed no statistical difference ($P > 0.05$) between the new and recycled groups for Cr release, in either those immersed for 1 hour or 48 weeks.

Release of Cu ions

At pH 4 (Figure 3a), all Dentaurum samples showed higher Cu (689.31 μg/ml, SD 22.13) release than any of the other brands, regardless of the type of bracket or immersion period. There was no statistical difference between the amount of Cu ions released from the new and recycled Dentaurum brackets, with more released after 48 weeks.

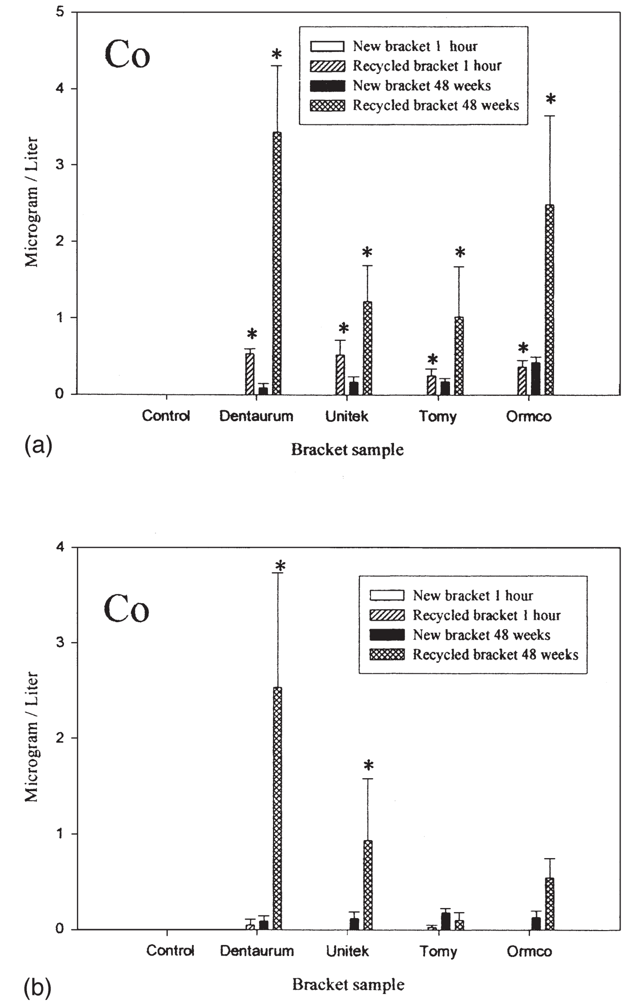


Figure 4 Cobalt (Co) ions released from the new and recycled metal brackets after 1 hour and 48 weeks' immersion. (a) Immersion in buffer at pH 4. (b) Immersion in buffer at pH 7. Each column and bar represents the mean and standard deviation of five replicates. The means and standard deviations were calculated by one-way analysis of variance. *Statistically different at $P < 0.05$.

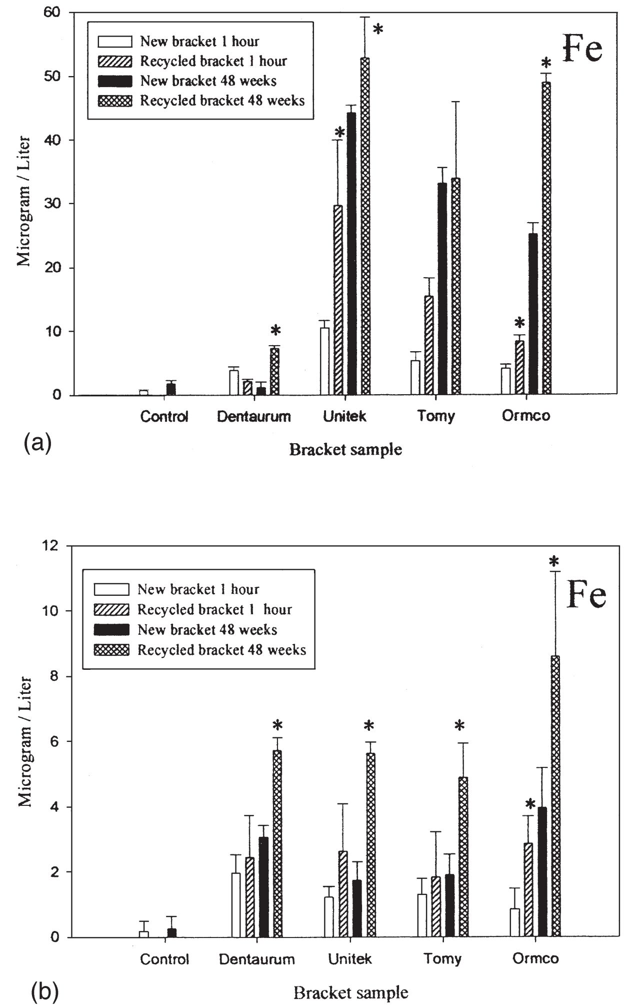


Figure 5 Iron (Fe) ions released from the new and recycled metal brackets after 1 hour and 48 weeks' immersion. (a) Immersion in buffer at pH 4. (b) Immersion in buffer at pH 7. Each column and bar represents the mean and standard deviation of five replicates. The means and standard deviations were calculated by one-way analysis of variance. *Statistically different at $P < 0.05$.

After immersion in the pH 7 buffered solution (Figure 3b), the new Dentaurum brackets released the highest levels of Cu (421.75 μg/ml, SD 42.95), with over twice as much released after 48 weeks than after 1 hour immersion. These figures were approximately two- and five-fold higher, respectively, than that of the recycled Dentaurum bracket immersed for 48 weeks. The Unitek, Tomy, and Ormco brackets showed comparatively very small amounts of Cu release.

Release of Co ions

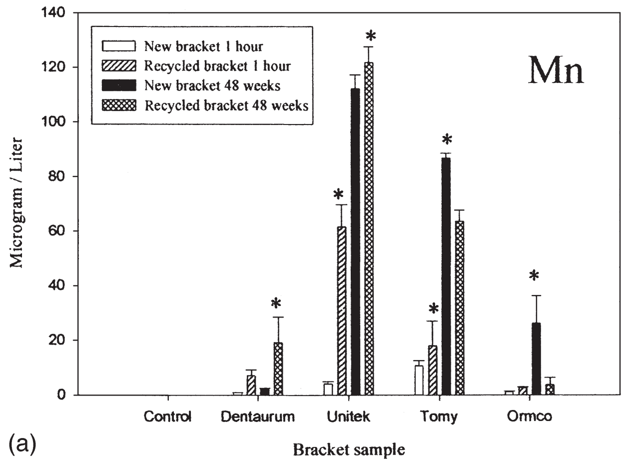
At pH 4 (Figure 4a), the recycled brackets showed higher levels of Co release than the new brackets for all four brackets and at both time points.

At pH 7 (Figure 4b), the brackets immersed for 48 weeks showed the only noteworthy levels of Co release, with the Dentaurum (2.54 μg/ml, SD 1.20) and Unitek (1.23 μg/ml, SD 0.46) samples releasing the highest amounts.

Release of Fe ions

At pH 4, more Fe was released from all the bracket types after 48 weeks than after 1 hour (Figure 5a), with the recycled brackets consistently releasing more Fe than the new brackets, except for the Tomy brackets where the difference between new and recycled brackets at 48 weeks was not statistically significant. The highest Fe was released from the Unitek (52.9 μg/ml, SD 6.3) and Ormco recycled bracket (48.9 μg/ml, SD 1.3) after 48 weeks' immersion.

There was less Fe released in the pH 7 buffered solution (Figure 5b) than in the pH 4 solution. The



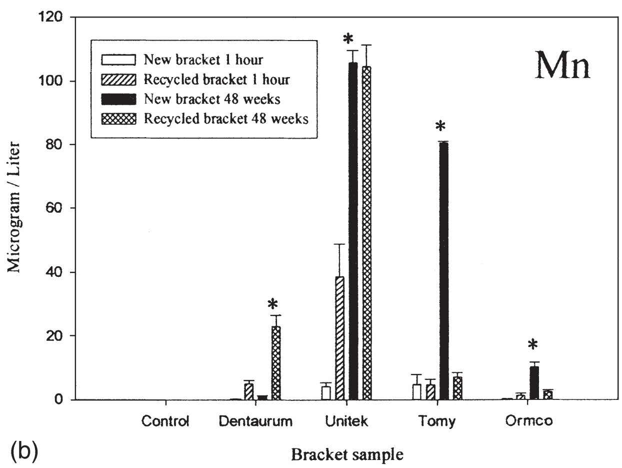


Figure 6 Manganese (Mn) ions released from the new and recycled metal brackets after 1 hour and 48 weeks' immersion. (a) Immersion in buffer at pH 4. (b) Immersion in buffer at pH 7. Each column and bar represents the mean and standard deviation of five replicates. The means and standard deviations were calculated by one-way analysis of variance. *Statistically different at $P < 0.05$.

recycled brackets released more Fe than their new counterparts. The Ormco recycled brackets at 48 weeks' immersion showed the highest Fe release (8.6 µg/ml, SD 2.6).

Release of Mn ions

At pH 4 (Figure 6a), the Tomy and Ormco recycled brackets released less Mn than their new counterparts at 48 weeks' immersion, whereas the Unitek and Dentaurum recycled brackets released more Mn than the new samples. The new and recycled Unitek brackets released the highest concentrations of Mn (112.2 µg/ml, SD 5.1 and 121.9 µg/ml, SD 5.7, respectively).

At pH 7 (Figure 6b), the new brackets from Ormco and Tomy released higher amounts of Mn than the recycled brackets at 48 weeks' immersion. The highest concentration released overall at this pH was found for the new (105.7 µg/ml, SD 3.9) and recycled (104.53 µg/ml, SD 6.7) Unitek brackets following 48 weeks' immersion.

Discussion

Metal brackets immersed in buffered solutions for 48 weeks released more ions than those immersed for only 1 hour. This result was independent of the pH of the solution or whether the bracket was new or recycled, and demonstrated that corrosion of a metal surface increases over time.

In general, recycled brackets released more ions than new ones, with the exception of the following: Cr from Unitek and Ormco new brackets immersed in the pH 4 solution for 48 weeks; Mn from new Tomy brackets in both the pH 4 and pH 7 solutions; and Mn from new Ormco brackets immersed in the pH 4 solution for 48 weeks.

The general mechanism for the corrosion and subsequent release of metal ions from stainless steel involves loss of the passivated layer of chromium oxide and chromium hydroxide which forms on the surface upon contact with oxygen. Heat treatment of a metal bracket can alter the surface protection of the alloy. If the steel is heated to between 400 and 900°C, a chromium carbide precipitate is formed and, as a result, becomes susceptible to intragranular corrosion, leading to a general weakening of the structure (Philip, 1973; Matasa, 1995; Kerosuo *et al.*, 1997). During recycling, the brackets are heated to between 300 and 500°C, which decreases the corrosion resistance (Grimsdottir *et al.*, 1992b). Such heat can cause intergranular corrosion due to a loss of chromium carbide at the grain boundaries (Park and Shearer, 1983). This is why most of the recycled brackets investigated in the present study showed higher amounts of ion release than the new samples. Thus, if a bracket undergoes heat treatment it is less able to resist corrosion.

Most metal brackets are not cast or fabricated in one piece. Instead, the wing and the base portion of the metal bracket are connected by solder, which is primarily comprised of Cu. The Dentaurum brackets released more Cu than all the other brands, in either the pH 4 or pH 7 solutions. In the pH 4 solution, the new and recycled Dentaurum brackets released similar amounts of Cu, but in the pH 7 solution more Cu was released from the new brackets than the recycled brackets. Berge *et al.* (1982) reported that silver solder introduces a galvanic couple which influences both the stainless steel and the solder by facilitating the release of Ni as well as other metals. In the present study, large amounts of Ni, Cu and Mn were released from some brackets following long-term immersion, with relatively lower amounts of Cr released. It is presumed that this was due to the heat applied to the bracket during the fabrication process.

The corrosive environment can be discriminated into atmospheric, water, chemical, temperature and microbiological corrosion. Acid solutions that cause chemical corrosion can be divided into inorganic, organic or mineral acid. During the fabrication process, the corrosive ability of inorganic acid is stronger than that of organic acid (Matasa, 1995). In the present study, the buffer solution consisted of $NaHNO_3$ and the pH was adjusted using HCl or NaOH, making the solution an inorganic acid and, therefore, highly corrosive to metal alloys. More metal ions were released in the pH 4 solution than in the solution at pH 7, showing that bracket corrosion can be influenced by solution condition.

Cr in an alloy can increase its corrosion-resistant properties (Philip, 1973). Cr is added to Ni-based alloys to improve their ability to form a protective oxide film on their surface. Generally, the alloy surface consists of a chromium oxide layer. It has been suggested that a Cr content of 16–27 per cent will provide the optimal corrosion resistance for Ni-based alloys, while the addition of molybdenum will further enhance the corrosion resistance (Brune, 1986). In this study, more Cr was released from the brackets immersed in the pH 4 solution than in the pH 7 solution, with the new Unitek and Ormco samples releasing the highest levels at pH 4. At pH 7, there was no difference between brands. Gil *et al.* (1999) found that more ions were released from Ni–Cr alloys than from palladium and gold–silver alloys in lactic acid *in vitro*. They suggested that Ni–Cr alloy microstructures are not single phase and, thus, do not present chemical homogeneity throughout their structure. Therefore, the alloy structure would act as if it was an electrochemical cell, making the corrosion properties higher than those of other alloys. Most orthodontic brackets are made of Ni–Cr alloy, containing 8–12 per cent Ni and 17–22 per cent Cr. Recently, titanium brackets have been developed and, according to the manufacturers' descriptions, have many benefits, such as no patient hypersensitivity. Titanium is also highly corrosion resistant and appears to bind Ni, making the alloy corrosion resistant (Dunlap *et al.*, 1989). Whether these new titanium brackets are more corrosion resistant than other alloy brackets warrants further investigation.

In the present study the metal brackets were immersed in buffered solutions, which is a static condition. In the clinical setting, the brackets are used in the oral cavity where they are mechanically activated to enable movement of the teeth. That is a dynamic situation, as opposed to the static condition used in the present experiment. Thus, movements of wires and friction in the brackets might result in other types of corrosion, for example, fretting, which might further enhance the release of ions from the appliance (Magnusson *et al.*, 1982). Further studies are needed to simulate this additional variable in the analysis of ion release from brackets.

Conclusions

Metallic brackets immersed in a pH 4 solution released more ions than those immersed in a buffered artificial saliva solution at pH 7. The release of metal ions increased with long-term immersion of the brackets, with Ni being the most predominant metal ion released. The highest level of Cu ion release was found with the Dentaurum brackets following immersion for 48 weeks. The results of this study indicate that metal brackets used in orthodontic appliances will corrode in an acid or neutral environment after long-term use.

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