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# Galvanic corrosion between orthodontic wires and brackets in fluoride mouthwashes

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SUMMARY The aim of this investigation was to determine the influence of fluoride in certain mouthwashes on the risk of corrosion through galvanic coupling of orthodontic wires and brackets. Two titanium alloy wires, nickel-titanium (NiTi) and copper-nickel-titanium (CuNiTi), and the three most commonly used brackets, titanium (Ti), iron-chromium-nickel (FeCrNi) and cobalt-chromium (CoCr), were tested in a reference solution of Fusayama–Meyer artificial saliva and in two commercially available fluoride (250 ppm) mouthwashes, Elmex® and Meridol®. Corrosion resistance was assessed by inductively coupled plasma-atomic emission spectrometry (ICP-MS), analysis of released metal ions, and a scanning electron microscope (SEM) study of the metal surfaces after immersion of different wire-bracket pairs in the test solutions. The study was completed by an electrochemical analysis.

Meridol® mouthwash, which contains stannous fluoride, was the solution in which the NiTi wires coupled with the different brackets showed the highest corrosion risk, while in Elmex® mouthwash, which contains sodium fluoride, the CuNiTi wires presented the highest corrosion risk. Such corrosion has two consequences: deterioration in mechanical performance of the wire-bracket system, which would negatively affect the final aesthetic result, and the risk of local allergic reactions caused by released Ni ions.

The results suggest that mouthwashes should be prescribed according to the orthodontic materials used. A new type of mouthwash for use during orthodontic therapy could be an interesting development in this field.

## Introduction

Wire-bracket systems are commonly used in orthodontics to move teeth. Practitioners can choose from a wide range of wires and brackets made from different alloys. Stainless steel (iron-chromium-nickel: FeCrNi), titanium (Ti) and Elgiloy (cobalt-chromium: CoCr) are frequently used in the manufacture of brackets, while wires may be made from stainless steel and CoCr as well as from titanium-molybdenum (TMA) and nickel-titanium (NiTi) alloys, and niobium. Thus, various bracket-wire combinations can be chosen. Although several authors have studied the best combination from a mechanical point of view (frictional behaviour; Kusy *et al.*, 1991; Michelberger *et al.*, 2000; Clocheret *et al.*, 2004; Grosgogeat *et al.*, 2005), few have investigated their biological implications (Mockers *et al.*, 2002; Jacobsen and Hensten-Pettersen, 2003; Eliades *et al.*, 2004a,b). In recent years it has been reported that in an acidic environment (buccal cavity) and in the presence of fluoride ions (mouthwashes) the corrosion resistance of certain materials, particularly Ti and Ti alloys, can deteriorate (Boere, 1995; Toumelin-Chemla *et al.*, 1996; Reclaru and Meyer, 1998; Nakagawa *et al.*, 1999, 2001; Fernandez Lorenzo de Mele and Cortizo, 2000; Schiff *et al.*, 2002, 2004, 2005). It is important to recommend regular use of products containing fluoride, in particular gels and mouthwashes, during the course of orthodontic treatment in order to help prevent dental caries (Marinho *et al.*, 2003).

The aim of the present study was to assess the risk of corrosion caused by galvanic coupling between wires and brackets in different solutions: artificial saliva and fluoride mouthwashes.

## Materials and methods

### *Specimens*

Three types of brackets and two types of wire were tested. Their composition and origin are shown in Table 1. Elastic bands made from electrochemically neutral material were used to attach the wires to the brackets. To comply with ISO (International Organization for Standardization, Geneva, Switzerland) Norm NF EN 10271 (2002), four brackets and four wires of each type of material were shaped into a cylindrical form to constitute the cap of a rotating disk electrode (a total of 20 specimens). The metal part was inserted into a polytetrafluoroethylene (PTFE) ring, adaptable to the working electrode. In order to prevent infiltration of the electrolyte, the space between the metal and the PTFE was filled with a resin with inert electrochemical properties. The exposed surface of the metal disk constituted

**Table 1** Origin and composition of the materials used in this study.

| Material | Composition (wt %) | Supplier |
|---|---|---|
| First bracket | Fe: 65.5, Cr: 18.5, Ni: 12.3, Mo: 2.4 | Ormodent, Montreuil, France |
| Second bracket | Co: 60.3, Cr: 31.6, Mo: 8, Fe: 1.2 | OrthoPlus, Igny, France |
| Third bracket | Ti: 92.7, Al: 3.98, V: 2.57 | Ormodent |
| NiTi wire | Ni: 55, Ti: 45 | Ormodent |
| CuNiTi wire | Cu: 5.5, Ni: 48, Ti: 46.5 | Ormodent |

Al, aluminium; Co, cobalt; Cr, chromium; Cu, copper; Fe, iron; Mo, molybdenum; Ni, nickel; Ti, titanium; V, vanadium.

the working electrode (the areas concerned were 0.02 cm$^2$ for each bracket and 0.005 cm$^2$ for each wire). The working electrodes were wet-ground with 120, 240, 620, 800 and 1200 grit abrasive papers (ESCIL, Lyon, France). They were then polished and degreased in acetone and alcohol. Prior to corrosion testing, the electrodes were cleaned using ultrasound and demineralised water.

### *Tests solutions*

The reference electrolyte used was Fusayama–Meyer artificial saliva (Venugopalan and Lucas, 1998; Huang, 2003). All the reagents were supplied by Sigma Chemical Company, St Louis, USA. The composition of the artificial saliva, which closely resembles natural saliva, was: KCl (0.4 g/l), NaCl (0.4 g/l), $CaCl_2.2H_2O$ (0.906 g/l), $NaH_2PO_4.2H_2O$ (0.690 g/l), $Na_2S.9H_2O$ (0.005 g/l), urea (1 g/l). pH was measured with an XC601 glass electrode (Radiometer Analytical, Villeurbanne, France) connected to a PHM 220 pH meter (Radiometer Analytical). The pH of this reference saliva, corresponding to the first test solution, was 5.3.

The two ready-to-use mouthwashes were Elmex® and Meridol® (Gaba, Müchenstein, Switzerland). The active ingredients were 100 ppm amine fluoride Olafluor and 150 ppm sodium fluoride, and 125 ppm amine fluoride Olafluor and 125 ppm stannous fluoride, respectively. The pH was 4.3 and 4.0, respectively.

### *Electrochemical set-up*

A glass electrochemical cell (Metrohm, Courtabeuf, France) with three openings in the cover, allowed the insertion of the different electrodes (Radiometer Analytical): a TC 100 saturated calomel electrode (SCE), a platinum counter electrode, and an EDI 101 rotating disk as the working electrode. The corrosion tests were carried out in ambient air in order to best simulate clinical conditions. The entire three-electrode assembly was placed in a Faraday cage to limit noise disturbance and then connected to an EG&G PAR 273A computer-controlled potentiostat (Perkin Elmer, Evry, France).

The thermostat (Bioblock, Illkirch, France) was set at 37 ± 0.1°C and the rotating speed of the disk electrode was 500 rpm.

### *Corrosion resistance study: released ions, surface analyses and electrochemistry*

Corrosion tests were performed by immersing the specimens (orthodontic elastics were used to fasten each wire-bracket pair together): for each combination bracket-wire, four pairs were immersed in 10 ml of solution for two months. At the end of this immersion period the four solutions were recovered (40 ml) and analysed by inductively coupled plasma-atomic emission spectrometry (ICP-MS; Jobin-Yvon, Ultima 2000, Longjumeau, France; Gil *et al.*, 1997; Huang *et al.*, 2001; Noar *et al.*, 2003). The ICP-MS parameters included 1000W applied power and a 0.05 ppm detection limit. The reagents were standard solutions for atomic absorption spectrometry, diluted to 1 ppm. The results of the released ion measurements are given in µg/l. Ti, Co and Cu were not measured since these ions can precipitate and distort the results.

The surface of each wire-bracket pair after immersion for 2 months in the different test solutions was examined using a scanning electron microscope (SEM; Leica, Cambridge, UK; Huang *et al.*, 2003; Watanabe and Watanabe, 2003). The SEM photomicrographs show the average surface topography of the specimens.

In parallel, an electrochemical analysis was carried out for each material (four specimens of each) in the three solutions. Using the electrochemical set-up described above, the corrosion potential (Ecorr) was measured over 24 hours (independent of the 2-month immersion period). The galvanic coupling potentials (Egalv) were computed on the basis of the Ecorr. Values are shown in mV/SCE.

## Results

### *Fusayama–Meyer artificial saliva*

Released ion measurements for the wire-bracket pairs with NiTi wire showed (Figure 1) that Ni ion concentrations were highest when this wire was coupled with the CoCr bracket (109 µg/l), followed by the FeCrNi bracket (54.2 µg/l) and finally the Ti bracket (16.7 µg/l), where concentrations of this element in the solution were six times lower than with the CoCr bracket. Cr ions released in this solution were negligible (<5 µg/l). The NiTi-FeCrNi pair released 34.8 µg Fe ions into the solution.

Measurements for the wire-bracket pairs using CuNiTi wire showed that Ni ion release was lowest (19.8 µg/l) for the CuNiTi-Ti combination. The Ni ion concentrations measured for the CuNiTi-CoCr and CuNiTi-FeCrNi pairs were higher by a factor of almost ×2 (34.1 and 32.6 µg/l, respectively). Cr released ion concentrations were also

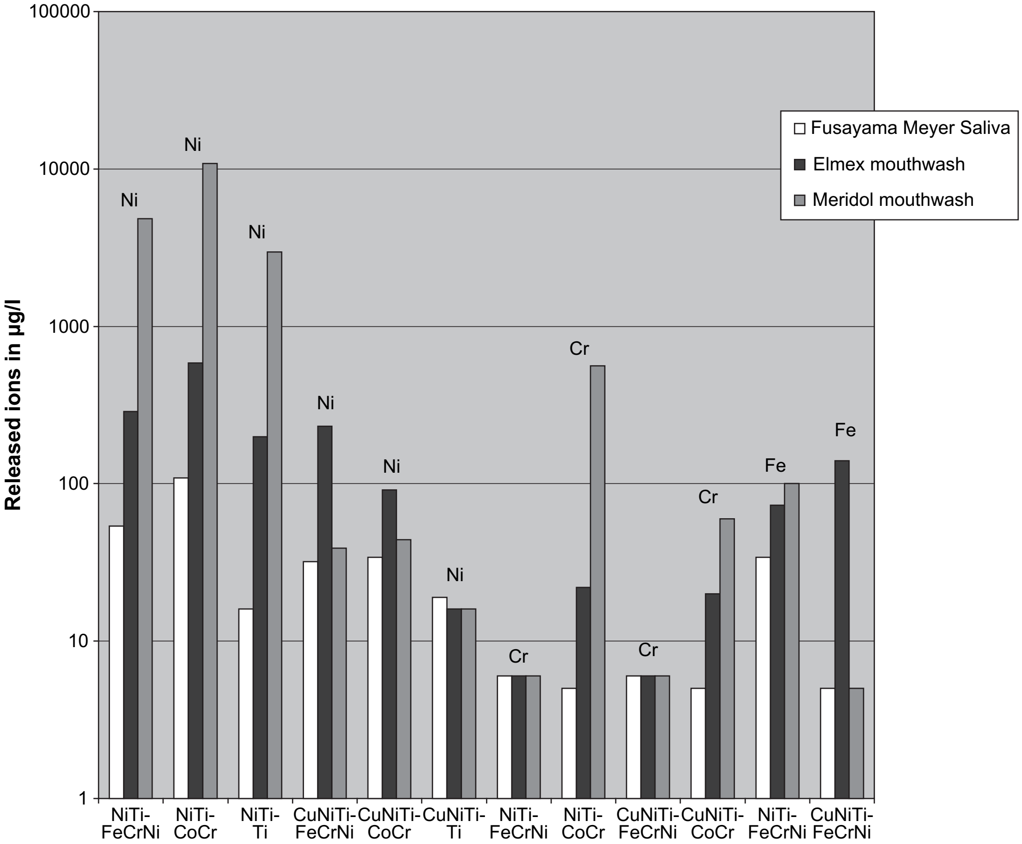

**Figure 1** Metal ions (in µg/l) released by wire-bracket combinations in the different solutions.

negligible in this solution (<5 µg/l ). For the CuNiTi-FeCrNi pair a negligible amount of Fe was released (<5 µg/l ).

SEM observations after corrosion showed slight changes in the surfaces of the CuNiTi and NiTi wires when coupled with the CoCr and Ti brackets. On the other hand, the surface of the FeCrNi bracket showed greater corrosion when coupled with the NiTi wire (Figure 2a) than with the CuNiTi wire (Figure 2b), where the surface condition remained unchanged.

Electrochemical investigation yielded Ecorr and Egalv values that indicated that the wires acted as the anode and the brackets as the cathode (Table 2).

### *Elmex® mouthwash*

Released ion (Figure 1) in Elmex® for the wire-bracket pairs with NiTi wire showed that Ni ion concentrations were highest (586.3 µg/l) when this wire was coupled with the CoCr bracket, followed by the FeCrNi bracket (288 µg/l) and finally the Ti bracket (199.1 µg/l). This classification according to the highest and lowest quantities of Ni ions released was the same as for Fusayama–Meyer artificial saliva. However, the values themselves were distinctly higher than those obtained in artificial saliva: ×6 higher for the NiTi-FeCrNi pair and the NiTi-CoCr pair, and ×12 higher for the NiTi-Ti pair. Fe ion release was high for the NiTi-FeCrNi pair in Elmex®: 73.4 µg/l, which was twice that for this wire-bracket pair in Fusayama–Meyer artificial saliva. The concentration of Cr ions released into Elmex® was negligible with FeCrNi (6 µg/l) and 22.3 µg/l with CoCr.

For the CuNiTi wire, the highest concentrations of released Ni ions were found when it was coupled with the FeCrNi bracket (232.9 µg/l). For the CuNiTi-CoCr pair, the concentration of released Ni ions was 91.2 µg/l. These values were distinctly higher than those measured in Fusayama–Meyer artificial saliva, in particular for the CuNiTi-FeCrNi pair where the Ni ion concentration was ×7 higher. For the CuNiTi-Ti pair, the concentration of Ni ions released into the Elmex® solution was negligible (6 µg/l). For the CuNiTi-FeCrNi pair, the concentration of Fe ions released into Elmex® was 140.7 µg/l, whereas for the same wire-bracket pair in Fusayama–Meyer artificial saliva, Fe ion release was negligible (6 µg/l). Cr ion release was negligible overall for the CuNiTi-FeCrNi pair (6 µg/l), while for the CuNiTi-CoCr pair it was 20.2 µg/l.

SEM observations of the NiTi and CuNiTi wires did not reveal any more significant surface damage when they were coupled with the CoCr or Ti brackets than was found in Fusayama–Meyer artificial saliva.

However, there was more marked corrosion of the FeCrNi bracket when coupled with the CuNiTi wire (Figure 3a) compared with the FeCrNi bracket coupled with the NiTi wire (Figure 3b).

The Ecorr measurements in the electrochemical studies (Table 2) confirmed that the NiTi and CuNiTi wires acted as anodes. The potentials obtained for the NiTi-CoCr and CuNiTi-CoCr pairs showed that the bracket was the anode.

### *Meridol® mouthwash*

Measurements for NiTi wires coupled with the different brackets showed that in Meridol®, Ni ion release was considerably higher than in the two previous solutions. The highest Ni ion concentration measured in Meridol® was for the NiTi-CoCr pair (10 822 µg/l) where the value was ×18 higher than in Elmex® and ×100 higher than in Fusayama–Meyer artificial saliva. For the NiTi-FeCrNi pair, the Ni ion concentration was 4841 µg/l, which was ×16 higher than in Elmex® and ×90 higher than in Fusayama–Meyer artificial saliva. Finally, for the NiTi-Ti pair, the Ni ion concentration was 2971 µg/l, i.e. ×15 higher than in Elmex® and ×200 higher than in Fusayama–Meyer artificial saliva. This classification of the wire-bracket pairs according to the highest and lowest quantities of Ni ions released was the same as in the two previous test solutions. Fe ion release measured for the NiTi-FeCrNi pair was 100 µg/l, almost identical to the value measured in Elmex®, but nevertheless almost three times the concentration measured in Fusayama–Meyer artificial saliva. The amount of Cr ions released into Meridol® was negligible for the NiTi-FeCrNi pair (6 µg/l for Elmex® and Fusayama–Meyer artificial saliva). On the other hand, when the NiTi wire was coupled with the CoCr bracket in Meridol®, Cr ion release was very high (563.5 µg/l), and ×25 higher than in Elmex®.

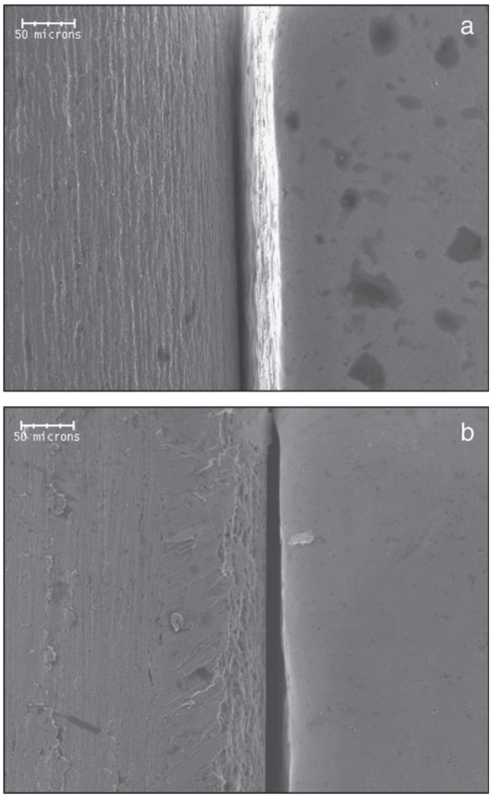

**Figure 2** Scanning electron microscopy photomicrographs (×200) of coupling of (a) NiTi wire and FeCrNi bracket, and (b) CuNiTi wire and FeCrNi bracket in Fusayama–Meyer saliva.

For the CuNiTi wire, the quantity of Ni ions released into Meridol® was similar to that found in Fusayama–Meyer artificial saliva, with the same classification from highest to lowest values: 44.1 µg/l for the CuNiTi-CoCr, 39 µg/l for the CuNiTi-FeCrNi pair and 16.2 µg/l for the CuNiTi-Ti pair. Concentrations of released Fe ions were negligible for the CuNiTi-FeCrNi pair, at 6 µg/l (whereas in Elmex® this concentration was very high). However, the CuNiTi-CoCr pair released 59.7 µg/l of Cr ions, which was ×3 higher than the concentration measured for this wire-bracket pair in Elmex®.

SEM observations revealed considerable differences in surface condition for specimens immersed in Elmex® and Fusayama–Meyer artificial saliva. For the NiTi-CoCr pair (Figure 4a), vertical marks were observed on the surface of the NiTi wire as well as localized corrosion of the bracket. For the NiTi-FeCrNi pair (Figure 4b) a change in the surface condition of the NiTi wire was clearly seen, while the FeCrNi bracket seemed to be unaffected by corrosion. The surface condition of the CuNiTi-FeCrNi appeared unchanged. The photomicrograph of the CuNiTi-CoCr pair

**Table 2** Corrosion (Ecorr) and coupling (Egalv) potentials (mV/SCE) of test materials in the different solutions.

| Wire/bracket Anode* | Fusayama–Meyer saliva | | Elmex® | | Meridol® | |
|---|---|---|---|---|---|---|
| | Ecorr | Egalv | Ecorr | Egalv | Ecorr | Egalv |
| NiTi/FeCrNi | *−150/0 | −137 | *−90/+40 | −213 | *−350/−170 | −193 |
| NiTi/CoCr | *−150/+20 | −28 | −90/−200* | −213 | *−350/+40 | −312 |
| NiTi/Ti | *−150/+50 | −27 | *−90/0 | −212 | *−350/−220 | −294 |
| CuNiTi/FeCrNi | *−140/0 | −74 | *−150/+40 | −147 | −100/−170* | −161 |
| CuNiTi/CoCr | *−140/+20 | −133 | −150/−200* | −47 | *−100/+40 | −67 |
| CuNiTi/Ti | *−140/+50 | −133 | *−150/0 | −147 | −100/−220* | −161 |

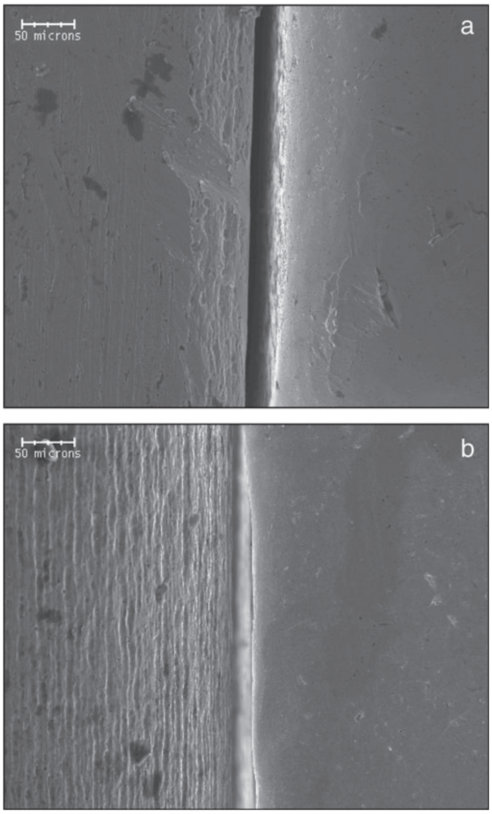

**Figure 3** Scanning electron microscopy photomicrographs (×200) of coupling of (a) CuNiTi wire and FeCrNi bracket, and (b) NiTi wire and FeCrNi bracket in Elmex® mouthwash.

(Fig 4c) demonstrated a change in surface condition of the CuNiTi wire in the form of vertical marks, while the surface of the CoCr bracket seemed to be unaffected. No changes in surface condition were observed when the NiTi and CuNiTi wires were coupled with the Ti bracket.

The Ecorr results (Table 2) showed that the NiTi wire (−350 mV/SCE) acted as an anode when coupled with the three different brackets. In the CuNiTi pairs, the electrochemical results showed that the FeCrNi and Ti brackets acted as anodes while the CuNiTi wire was the anode when coupled with the CoCr bracket.

## Discussion

According to the ion release results, it would appear that for the NiTi-CoCr and NiTi-Ti pairs in Fusayama–Meyer saliva, the NiTi wire was the anode and was consequently at risk of corrosion. For the NiTi-FeCrNi pair in this solution, the FeCrNi bracket could be the anode, while Carroll and Kelly (2003) found that NiTi was anodic. For CuNiTi in Fusayama–Meyer saliva, Huang *et al.* (2004) obtained a similar finding of Cr released ion concentrations. It would appear that in all pairs the CuNiTi wire was the anode and, therefore, susceptible to corrosion.

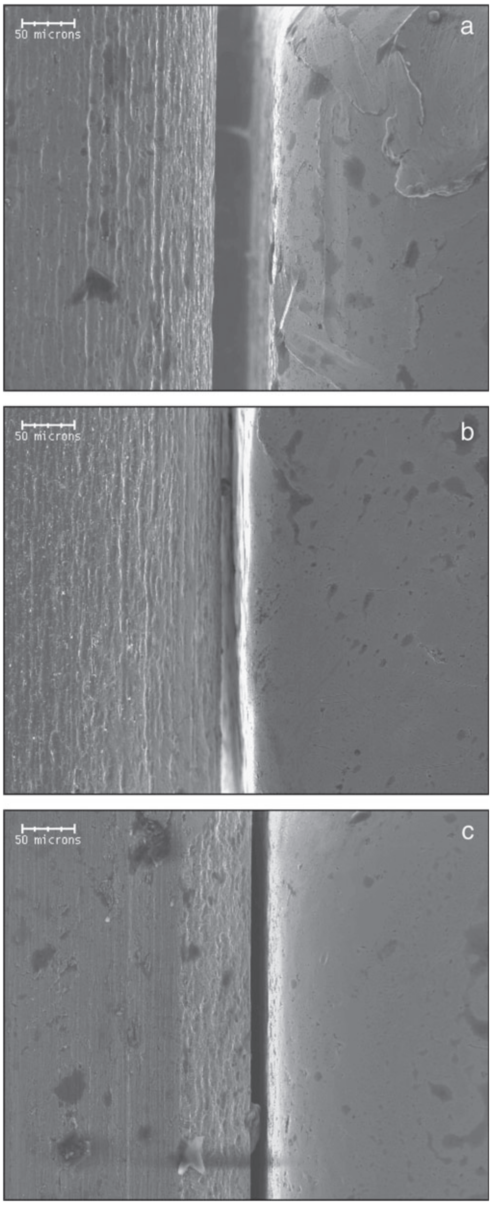

**Figure 4** Scanning electron microscopy photomicrographs (×200) of coupling of (a) NiTi wire and CoCr bracket, (b) NiTi wire and FeCrNi bracket, and (c) CuNiTi wire and CoCr bracket in Meridol® mouthwash.

For the wires with the CoCr bracket and the Ti bracket in Fusayama–Meyer saliva, SEM analyses showed that the surface changes were uniform and non-significant: this result was also reported by Es-Souni *et al.* (2003). However, for NiTi-FeCrNi and CuNiTi-FeCrNi pairs, SEM observations corroborated the ion release measurements and confirmed that the FeCrNi bracket was subject to corrosion when coupled with NiTi wire.

Electrochemical findings in Fusayama–Meyer saliva are in agreement with the ion release measurements and SEM observations, except for the NiTi-FeCrNi pair. In this case, the Ecorr measurements indicated that the anode was the

NiTi wire and not the FeCrNi bracket, as suggested by the ICP-MS results. This discrepancy has two possible explanations: (1) there was a general phenomenon involving polarity reversal over time, bearing in mind that the ion release measurements were obtained after two months' immersion whereas the electrochemical results were instantaneous, which could create a difference in the long term with reversal of the couplings, or (2) there was localized dissolution (Platt *et al.*, 1997) resulting from heterogeneity of the components in the cathode where certain phases would oxidize.

In Elmex® mouthwash, it would appear that the NiTi wire was the anode in the NiTi-Ti pair and was susceptible to corrosion. For the NiTi-FeCrNi and NiTi-CoCr pairs, the brackets seemed to act as the anodes, given the respective amounts of Fe and Cr ions measured in the solution. A similar result was also observed for the CuNiTi wire.

Regarding SEM analyses in Elmex® mouthwash, the surface observations corroborate the ICP-MS results showing a released Fe ion concentration for the CuNiTi-FeCrNi pair that was double the concentration for the NiTi-FeCrNi pair, suggesting more marked corrosion.

Electrochemical studies showed that wires were subject to more or less significant corrosion when coupled with the Ti bracket in Elmex® mouthwash, but when they were coupled with the CoCr bracket, the potentials confirm the ICP-MS results (it was for these two wire-bracket pairs that Cr ion release concentrations were the highest). On the other hand, with the FeCrNi bracket, the electrochemical measurements did not corroborate the ICP-MS results. As in the case of the tests in artificial saliva, as described earlier, there are two possible explanations for this disparity.

In Meridol® mouthwash, it would appear that the NiTi was the anode when coupled with the Ti bracket. For NiTi wires coupled with CoCr and FeCrNi brackets, the brackets could act as the anode. It was observed that the CuNiTi wire acted as the anode when it was coupled with the Ti bracket or the FeCrNi bracket, but when it was coupled with the CoCr bracket, the bracket would be the anode.

Regarding SEM analyses, in Meridol® mouthwash the localized corrosion surface observed with NiTi-CoCr pair confirm the ICP-MS results that indicated considerable release of Ni and Cr ions in this solution. The surface condition of the CuNiTi-FeCrNi pair was unchanged, as suggested by the ICP-MS analysis.

Electrochemical studies showed that in Meridol® mouthwash the NiTi wire acted as an anode when coupled with the different brackets: this is not strictly in agreement with the results obtained by ICP-MS, which indicated that the CoCr and FeCrNi brackets could act as the anode in the wire-bracket system. Also, electrochemical studies showed that CuNiTi wire was the anode when it was coupled with the CoCr bracket: this result does not corroborate the released ion measurements. As mentioned earlier, this disparity has two possible explanations: either a general phenomenon of polarity reversal over the long term (taking the example of the CuNiTi-Ti pair, the Ti anode oxidizes and the oxide protects it, leading to polarity reversal in favour of the CuNiTi), or localized dissolution resulting from heterogeneity of the cathode components.

The results reported in this study indicate that the NiTi wires are more susceptible than the CuNiTi wires to corrosion through galvanic coupling between wires and brackets. This is true for the three test solutions. However, Meridol® mouthwash appears to be the solution in which the NiTi wires coupled with the different brackets presented the highest corrosion risk. This mouthwash contains 125 ppm stannous fluoride which might, in the presence of additives, be one cause of NiTi degradation (Schiff *et al.*, 2005). However, it was in Elmex® mouthwash that the CuNiTi wire-bracket pairs presented the highest corrosion risk. The sodium fluoride in this mouthwash, along with the additives, could be the cause of deterioration of this material. Practitioners should therefore recommend the most appropriate mouthwash for the particular wire-bracket combinations used. Thus, Meridol® mouthwash is recommended for patients with wire-bracket combinations using CuNiTi wire, and Elmex® for patients with wire-bracket combinations using NiTi wire. In both cases, and even though the risk is minimal, it is nevertheless advisable to rinse the mouth after using these mouthwashes to limit any residual topical action of the fluoride which could corrode the alloys. Degradation of the materials through corrosion could negatively affect the mechanical operation of the wire-bracket system and lead to unsatisfactory therapeutic results (Michelberger *et al.*, 2000).

Finally, Ni and Cr were the ions most frequently found and in the highest quantities. Some authors (Mockers *et al.*, 2002; Es-Souni *et al.*, 2003) have alerted practitioners to the possibility of hypersensitivity reactions to released Cr and Ni ions. They have been shown to cause lesions such as stomatitis, erythema, oedema, burning sensations, loss of taste and angular cheilitis (Jacobsen and Hensten-Pettersen, 2003). Particular care should therefore be taken concerning the use of fluoride-containing mouthwashes that might release allergens (Staerkjaer and Menné, 1990; Ağaoğlu *et al.*, 2001).

## Conclusions

The present study clearly identifies the risk of corrosion caused by galvanic coupling between the wire and bracket when fluoride mouthwashes are used. The results indicate that NiTi wires released the most ions in the presence of Meridol® mouthwash while CuNiTi wires released the most ions in the presence of Elmex® mouthwash. Although the risks are minimal, the clinical consequences of corrosion of orthodontic devices are quite plausible: impaired mechanical performance can lead to unsatisfactory aesthetic results, while Ni and Cr ions released in the organism can cause allergic reactions (Kusy, 2004). It is important to eliminate these risks.

Fluoride mouthwashes are advised in the prevention of dental caries during orthodontic treatment. However, the results suggest that dental practitioners should take into account the types of wires used during orthodontic treatment when prescribing mouthwashes. There appears to be a need for a new type of mouthwash containing both fluoride and corrosion inhibitors which could be used without restriction by young patients undergoing orthodontic therapy.

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