

# Galvanic Corrosion of Metal Injection Molded (MIM) and Conventional Brackets with Nickel-Titanium and Copper-Nickel-Titanium Archwires

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## ABSTRACT

**Objective:** To compare the galvanic coupling of conventional and metal injection molded (MIM) brackets with commonly used orthodontic archwires.

**Materials and Methods:** Six of each type of bracket were suspended in lactic acid along with a sample of orthodontic wire (three nickel-titanium and three copper-nickel-titanium) for 28 days at 37°C. The potential differences between the wires and brackets were recorded per second throughout the duration of the experiment.

**Results:** The MIM brackets exhibited potential differences similar to those seen for the conventional brackets. The greatest potential difference was found for MIM brackets with nickel-titanium wires (512 mV), whereas MIM brackets with copper-nickel-titanium wires had the smallest difference (115 mV). Scanning electron microscope (SEM)–energy-dispersive spectroscopic analysis of the tie-wing area of each bracket type indicated similar elemental composition in both brackets, but in slightly different percentages by weight. The MIM bracket exhibited extensive internal porosity, whereas the conventional bracket was more solid internally.

**Conclusion:** The composition and manufacturing processes involved in fabricating MIM brackets impart corrosive properties similar to those seen in the bracket-wing area of conventional brackets and may provide a measurable benefit when taking into account the increased corrosion between the bracket and brazing alloy of conventional brackets.

**KEY WORDS:** Brackets; MIM; Galvanic corrosion

## INTRODUCTION

The resistance to corrosion of orthodontic appliances is important for prevention of ion release into the

oral cavity.<sup>1</sup> Some of these ions, such as iron (Fe), chromium (Cr), and nickel (Ni), have been associated with allergic, toxic, or carcinogenic effects when taken up by the human body.<sup>2–4</sup> In orthodontic treatment, galvanic interaction commonly exists between the archwire and bracket,<sup>4</sup> but can also occur within a bracket's own components.<sup>5</sup> Conventional metal brackets are designed with different stainless steel alloys in the bracket base and tie wings, which are then brazed together with a silver, Ni, or gold (Au) alloy.<sup>5</sup>

The base alloy is of a softer metal to facilitate easier debonding of the bracket, whereas the tie-wing metal requires greater hardness in order to withstand the forces applied by the archwires.<sup>6</sup> The distinct elemental compositions of these two types of stainless steel and the brazing alloy give rise to differences in their corrosion potentials.<sup>7</sup> If the potential difference between two types of metals is high enough, the less-stable metal tends to corrode and to oxidize releasing ions into the solution as it disintegrates.<sup>7,8</sup> Elemental

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**Table 1.** Commercial Names, Lot Numbers, Manufacturers, and Types of Brackets and Archwires Included in This Study<sup>a</sup>

Combination	Brackets	Bracket type	Archwires
MIM-CuNiTi	MiniTwin (3M/Unitek, Lot #010294300)	MIM	Cu-Ni-Ti (Ormco, Lot #00A213A)
MIM-NiTi	MiniTwin (3M/Unitek, Lot #010294300)	MIM	Ni-Ti (Ormco, O1E485E)
Con-CuNiTi	OptiMESH (Ormco, Lot #00F660F)	Con	Cu-Ni-Ti (Ormco, Lot #00A213A)
Con-NiTi	OptiMESH (Ormco, Lot #00F660F)	Con	Ni-Ti (Ormco, O1E485E)

<sup>a</sup> MIM indicates metal injection molded; CuNiTi, copper-nickel-titanium; NiTi, nickel-titanium; Con, conventional.

analysis of in vivo-aged brackets has shown that ionic release occurs under clinical conditions.<sup>9</sup>

In an effort to prevent this ion release, metal injection molding (MIM) has introduced single-unit brackets with uniform elemental distribution, thereby eliminating the possibility of galvanic corrosion that can occur within a bracket's components. However, all brackets, regardless of composition, will be in the presence of metallic archwires, thus providing the essential conditions for the development of a galvanic couple.

Because the corrosion potential of brackets is affected by material composition, manufacturing process, and microstructure, it is logical to assume that MIM brackets may behave differently from conventional brackets.<sup>8,10</sup> It is already known that MIM-made appliances may be an improvement over conventional brackets in that their single-unit fabrication removes the potential for galvanic corrosion that may occur between the stainless steel and brazing material.<sup>11</sup> As a result of the manufacturing process involved, a different metallic composition or microstructure is formed, which may noticeably decrease the possibility of corrosion and ionic release into the oral cavity, thus reducing adverse biological consequences. The aim of this study is to compare the galvanic corrosion potential of MIM brackets to that of conventional brackets under similar in vitro conditions with commonly-used orthodontic archwires.

## MATERIALS AND METHODS

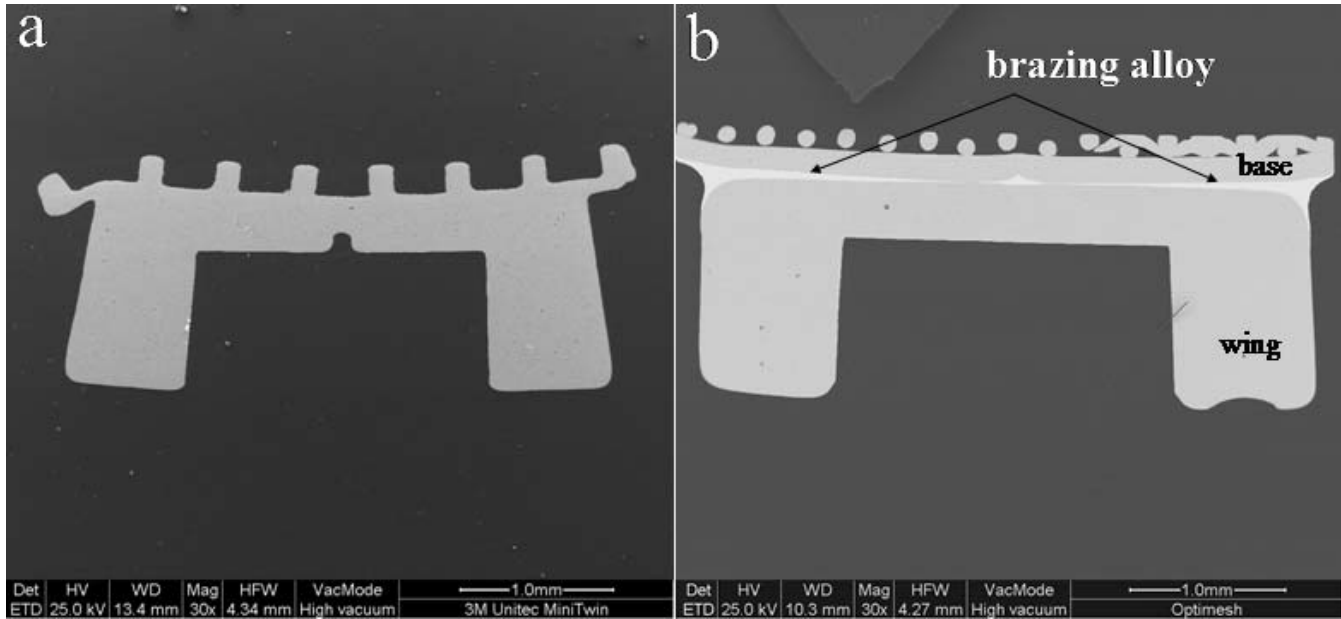
For the present study, seven MIM brackets (0.022-inch slot, MiniTwin, 3M/Unitek, Monrovia, Calif) and seven conventional brackets (0.018-inch, OptiMESH, Ormco, Glendora, Calif) were embedded in epoxy resin (Caldofix, Struers, Copenhagen, Denmark; 1 vertically and 6 horizontally) (Table 1). Next, each vertically embedded bracket was ground with silicon carbide (SiC) papers (80–4000 grid) under continuous water cooling until the interface between the tie wings and bracket base was exposed. The horizontally embedded brackets (six of each type) were ground so that only the bracket wing was exposed. All brackets were

polished with diamond paste (DM Paste, Struers, Copenhagen, Denmark) up to 1  $\mu$ m in a grinding-polishing machine (Ecomet III, Bueler, Lake Bluff, Ill). One of each type of bracket was used to analyze the brackets' elemental composition. The vertically embedded brackets were then coated with carbon in a sputter-coating unit (SCD004 Sputter-Coater with OCD 30 attachment, Bal-Tec, Vaduz, Liechtenstein). The bracket surfaces were examined with a scanning electron microscope (Quanta 200, FEI, Hillsboro, Ore) equipped with a super ultra-thin Be window x-ray energy-dispersive spectroscopic (EDS) detector (Sapphire CDU, Edax Intl, Mawhaw, NJ).

For the study of the elemental composition, one EDS spectrum was obtained from the wing area of each bracket under 25 keV accelerating voltage, 100  $\mu$ A beam current, and 0.215  $\times$  0.215-mm sampling window. The quantitative analysis of the percentage of weight concentration was performed by the relevant software (Genesis, version 3.5, Edax) under a non-standard analysis using the atomic number, absorption, and fluorescence correction method (ZAF). A line scan analysis was employed in order to determine the variation of each element from the base to the tie-wing (slot) area.

The galvanic potential of the two bracket types was determined by using the 12 remaining brackets (six MIM brackets and six conventional brackets), which had been previously embedded in epoxy resin. Each embedded bracket was suspended in its own glass container (Ilmabor TGI, Scientific Glass Laboratories Ltd., Staffordshire, UK), which contained 125 ml of 1 M lactic acid solution (pH = 1.3) by an insulated wire that was connected to a recording device (Logoscreen 500, JUMO Instrument Co., Harlow, Essex, UK). A segment of 10 mm of either copper-nickel-titanium (0.017  $\times$  0.025-inch, Ormco) or nickel-titanium archwire (0.017  $\times$  0.025-inch, Ormco) was also submerged in the solution (Table 1). The brackets' cables were connected to the anode and the wires' cables to the cathode.

There were a total of four different bracket-archwire



**Figure 1.** Secondary electron images from the cross sections of (a) a single-piece bracket (MIM) and (b) a bracket consisting of base and wing components joined together by a brazing alloy (indicated by the lighter zone between base and wing). Original magnification 30×.

combinations, and each was tested three times (Table 1). The bracket and wire combinations were kept in solution for 28 days, during which the temperature was maintained at a steady  $37 \pm 0.2^\circ\text{C}$  in a water bath. Throughout the duration of the experiment, the potential difference between the anode (brackets) and cathode (archwire) was continuously monitored and recorded each second by the recording device. After 28 days, graphs of the potential difference between the anode and cathode were produced for each of the bracket and wire combinations tested.

**RESULTS**

SEM analysis of the conventional and MIM brackets verified that MIM brackets are one solid unit (Figure 1a) whereas conventional brackets are comprised of two components joined together by a brazing alloy (Figure 1b). The EDS analysis found that the tie-wing components of both brackets are composed of the same elements, but in slightly different percentages by weight. The only elemental difference between the two is that the conventional brackets contain manganese (Mn) whereas the MIM brackets do not (Table 2). This analysis was also able to identify the presence of each element in specific bracket regions. In the conventional bracket (Figure 2a), certain elements appear in equal proportions in both the base and wing areas, but their proportions are different in the brazing alloy, whereas others are found in different proportions in each of the three possible regions.

It appears that Au is the predominant element in the

**Table 2.** Elemental Compositions (in Percentage of Total Weight) of Alloys From Wing Area of the Brackets Tested, as Determined by EDS Analysis<sup>a</sup>

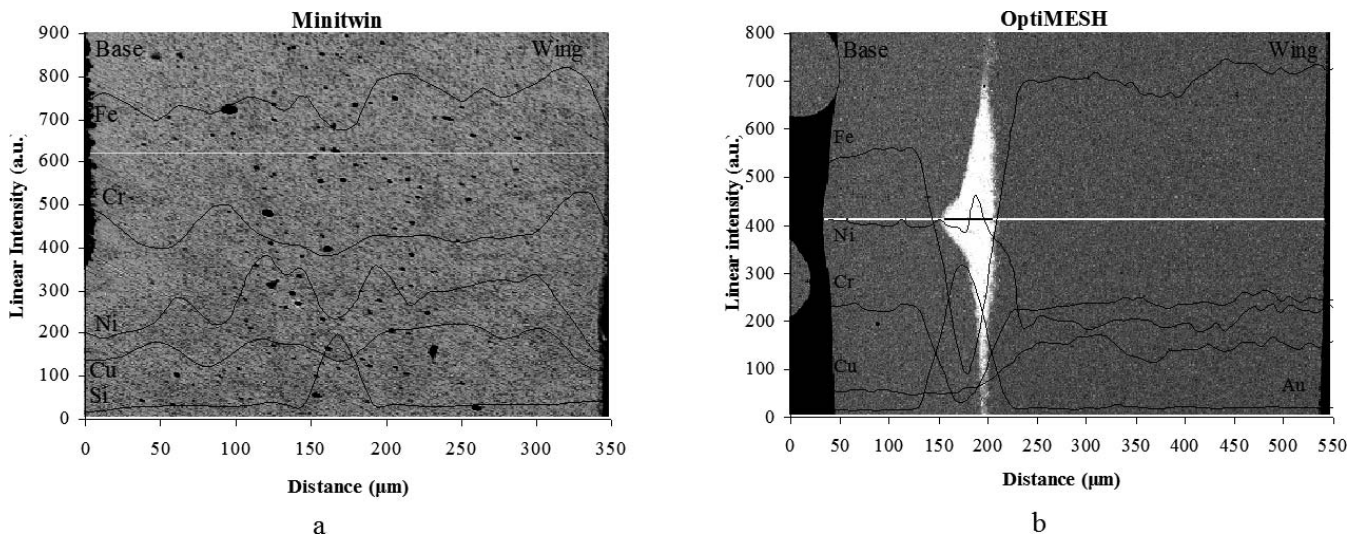
Element	OptiMESH	Minitwin	CuNiTi <sup>b</sup>	NiTi <sup>b</sup>
Fe	75.81	73.12		
Cr	15.30	16.84		
Ni	3.72	4.45	48.00	55.00
Cu	3.54	3.84	5.50	
Si	0.85	1.65		
Mn	0.79			
Ti			46.50	45.00

<sup>a</sup> For comparison purposes, the elemental compositions of archwires included in this study are also presented (as given by the manufacturer). CuNiTi indicates copper-nickel-titanium; NiTi, nickel-titanium; Fe, iron; Cr, chromium; Ni, nickel; Cu, copper; Si, silicon; Mn, manganese; Ti, titanium.  
<sup>b</sup> Elemental composition as given by the manufacturer.

brazing area, whereas Fe, Cr, Mn, and silicon (Si) are found in only the base and tie-wing regions and are evenly distributed throughout those components of conventional brackets. There is a greater concentration of Ni in the tie wings than in the base, whereas the opposite is true for copper (Cu).

In the MIM bracket, it is evident that the elements are more uniformly distributed throughout the bracket cross section, although some small deviations in the concentrations of Fe, Cr, Ni, and Cu were noted. In contrast, Si appears to increase towards the center of the bracket. Regarding the internal structure of both bracket types, it was noted that conventional brackets are more solid with a limited number of pores, whereas





**Figure 2.** Line scan analysis demonstrating the variation of each element from the base to the tie-wing (slot) area. (a) Minitwin; (b) OptiMESH.

MIM brackets appear to have a significant amount of internal porosity. The presence of these pores seems to increase towards the center of the cross section (Figure 2a).

Figure 3 demonstrates representative plots of potential vs. time for each combination tested. The potential difference stabilized quickly (after less than 2 days) for MIM–copper–nickel–titanium (MIM–CuNiTi; Figure 3b), whereas this occurred towards the midpoint of the experimental time for the remaining combinations (Figure 3a, c, d). The mean values of the final potential obtained after 28 days were determined for each group and plotted in decreasing order as shown in Figure 4. The deviations of the mean values are within the range of 0.512 for the MIM–NiTi combination and 0.115 for the MIM–CuNiTi pairing.

## DISCUSSION

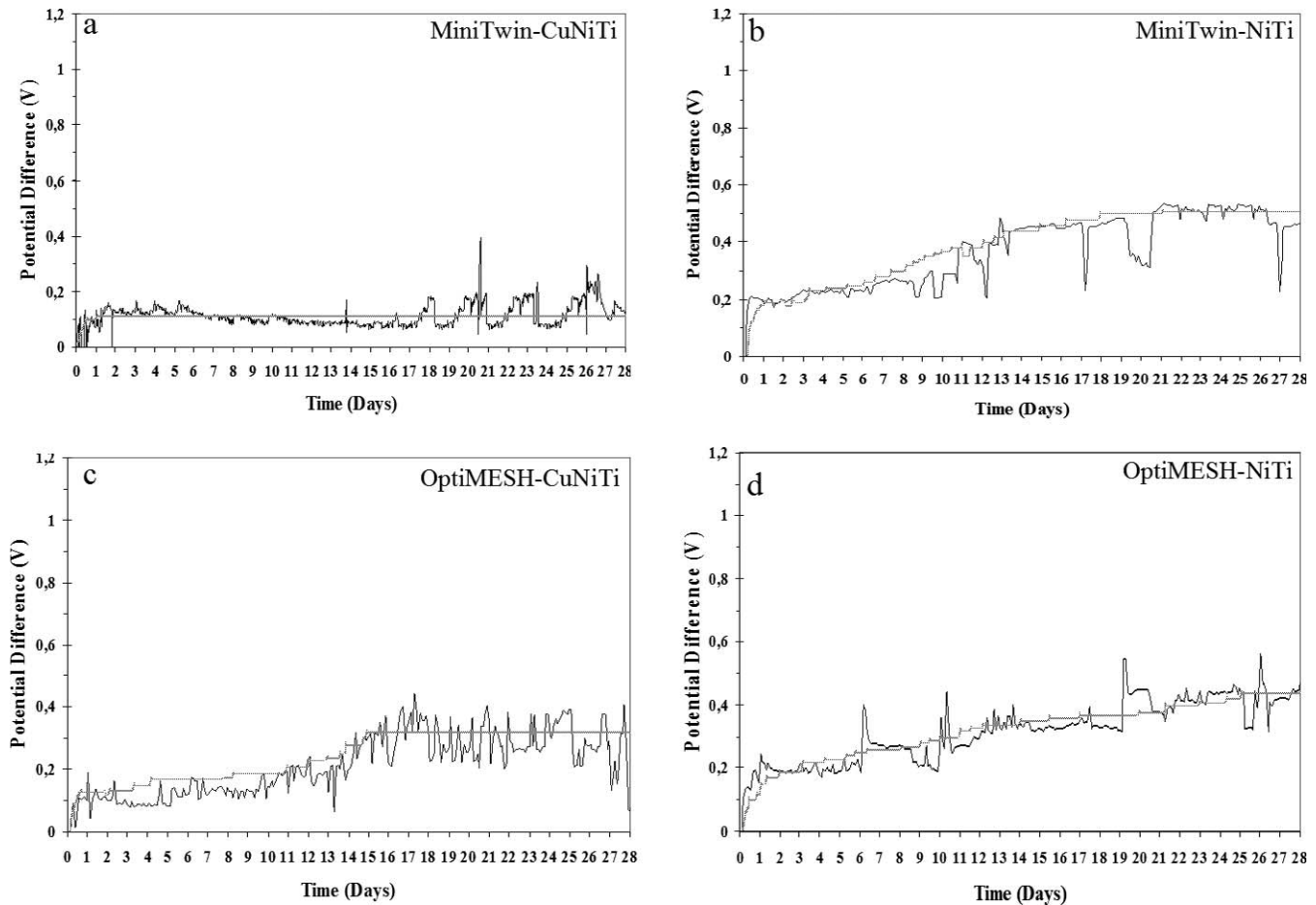
Elemental analysis showed that the conventional bracket (OptiMESH) consists of two parts (base and wing) joined together with a Au-based soldering alloy. The wing material contained increased Cu and decreased Ni concentration compared to the base alloy, a finding that is in agreement with previous studies.<sup>6,9</sup> The elemental composition of this alloy is very close to that of the PH 17-4 SS (also known as S 17400) precipitation-hardening alloy, which has a nominal composition of 0.07 carbon, 0.70 Mn, 1.00 Si, 1–17.5 Cr, 3.0–5.0 Ni, 3.0–5.0 Cu, 0.04 phosphorus, 0.04 sulfur, and 0.15–0.45 tantalum and niobium (by percentage of weight).<sup>12</sup>

Although the elemental composition of the MIM bracket (MiniTwin) demonstrates slight differences from that of the conventional bracket (Table 2), it does not match any previous alloy reported for the produc-

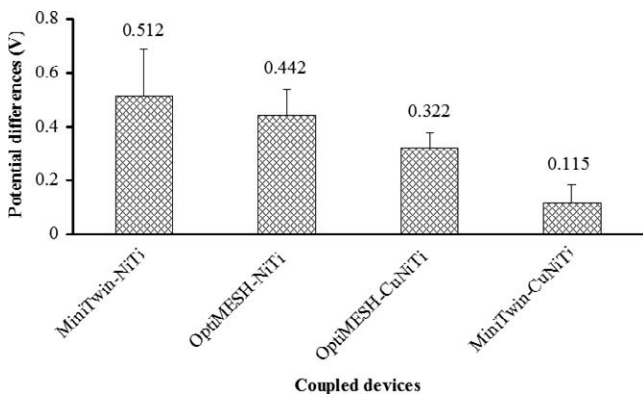
tion of MIM brackets.<sup>11</sup> This finding can be attributed to the fact that each company uses different materials for the manufacturing of their brackets, and thus the biological, corrosive, physical, and clinical properties can vary considerably among the available products. MiniTwin brackets present a significant amount of internal porosity, which is a common problem induced by the sintering process.<sup>11</sup> Porosity was found to increase toward the center of the cross section, possibly because of the entrapment of gases during the de-vesting and/or sintering processes.

Although MIM brackets, as single-unit appliances, are free from the galvanic corrosion that occurs between the bracket and brazing alloys in conventional brackets, their increased porosity may augment their tendency towards pitting corrosion.<sup>4,11</sup> The abrupt increase of Si concentration at the center (Figure 2a) may be appended to segregation as sintering is initiated at the external surfaces of the brackets because of temperature gradients during thermal processes.

The galvanic couples were tested in triplicate because this is the maximum number of replications proposed by ASTM G 71-81.<sup>13</sup> Figure 4 shows the mean galvanic potential for each combination after 28 days in decreasing order. The highest potential differences were found for MiniTwin–NiTi and the lowest for MiniTwin–CuNiTi, with galvanic susceptibility decreasing from the former to the latter couple. All potential differences (Figure 4) were found to be positive, indicating that the archwires were consistently the cathode and the brackets were the anode of the galvanic cell. This implies that, in all cases, brackets undergo accelerated corrosion in order to protect archwires. The last statement can readily explain the results of retrieval analysis in which ionic release was identified



**Figure 3.** Potential difference (V) throughout duration of experiment. (a) Minitwin with CuNiTi wire; (b) Minitwin with NiTi wire; (c) OptiMESH with CuNiTi wire; and (d) OptiMESH with NiTi. Dash lines represent the trend curve among the experimental data.



**Figure 4.** Mean values and standard deviations of potential differences after 28 days of all couples tested in lactic acid. Results are sorted in decreasing order. Only the mean values are presented above each bar.

from the wing alloy, but not the base, and NiTi archwires did not undergo any elemental alteration after *in vivo* aging.<sup>4,9</sup>

Although this data can be representative of single-unit MIM brackets, this is not quite true for conven-

tional brackets consisting of three different alloys (wing, solder, and base). Unfortunately, complex configurations using many materials are extremely difficult to model.<sup>14</sup> However, it is estimated that the wing alloy (PH 17-4) is most prone to corrosion because of the presence of copper in its composition. Although the addition of Cu increases hardness through a precipitation mechanism, it has an adverse effect on corrosion resistance. This specific alloy is less noble than the 316 SS commonly used for the manufacturing of the base and, of course, the Au-based soldering alloy.<sup>15</sup> These remarks are in full accordance with the aforementioned results from retrieved devices, wherein ionic release was found only from the wing alloy in a conventional bracket with a Au-based brazing alloy.<sup>9</sup>

The results of this study showed that CuNiTi archwires produce lower potential differences than NiTi archwires with OptiMESH and MiniTwin brackets and thus are less susceptible to galvanic corrosion. Although those combinations demonstrate lower susceptibility to galvanic corrosion, this does not necessarily predict their clinical behavior. Couples that may

not undergo galvanic corrosion under clinical conditions may be more prone to other corrosion processes (ie, crevice, pitting, uniform, etc), and thus show unfavorable clinical results. Although the MiniTwin bracket exhibited comparable galvanic potential to the OptiMESH bracket, extensive clinical and laboratory research is required to characterize the safety and efficacy of these recently introduced orthodontic devices.

## CONCLUSIONS

- MiniTwin (MIM) brackets produce similar potential differences to OptiMESH (conventionally manufactured) brackets with both types of NiTi archwires.
- Based on galvanic potential findings of the present study, it seems that both brackets are more compatible with CuNiTi archwires regarding the decrease in the consequences of galvanic susceptibility.

## ACKNOWLEDGMENT

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## REFERENCES

1. Kim H, Johnson J. Corrosion of stainless steel, nickel-titanium, coated nickel-titanium, and titanium orthodontic wires. *Angle Orthod.* 1999;69:39–44.
2. Pereira MC, Pereira ML, Sousa JP. Histological effects of iron accumulation on mice liver and spleen after administration of a metallic solution. *Biomaterials.* 1999;20:2193–2198.
3. Eliades T, Zinelis S, Papadopoulos M, Eliades G, Athanasios A. Nickel content of as-received and retrieved NiTi and stainless steel archwires: assessing the nickel release hypothesis. *Angle Orthod.* 2004;74:151–154.
4. Eliades T, Athanasios A. In vivo aging of orthodontic alloys: implications for corrosion potential, nickel release, and biocompatibility. *Angle Orthod.* 2002;72:222–237.
5. Zinelis S, Annousaki O, Eliades T, Makou M. Elemental composition of brazing alloys in metallic orthodontic brackets. *Angle Orthod.* 2004;74:394–399.
6. Eliades T, Zinelis S, Eliades G, Athanasios A. Characterization of as-received, retrieved, and recycled stainless steel brackets. *J Orofac Orthop.* 2003;64:80–87.
7. Fontana MG. *Corrosion Engineering.* New York, NY: McGraw Hill; 1986.
8. Von Fraunhofer J. Corrosion of orthodontic devices. *Semin Orthod.* 1997;3:198–205.
9. Eliades T, Zinelis S, Eliades G, Athanasios A. Nickel content of as-received, retrieved, and recycled stainless steel brackets. *Am J Orthod Dentofacial Orthop.* 2002;122:217–220.
10. Matasa C. Characterization of used orthodontic brackets. In: Eliades G, Eliades T, Brantley WA, Watts DC, eds. *Dental Materials In Vivo: Aging and Related Phenomena.* New York, NY: Quintessence; 2003:141–156.
11. Zinelis S, Annousaki O, Makou M, Eliades T. Metallurgical characterization of orthodontic brackets produced by metal injection molding (MIM). *Angle Orthod.* 2005;75:811–818.
12. Schoefer EA. Properties of cast stainless steels. In: Benjamin D, ed. *Stainless Steels, Tool Materials, and Special Purpose Metals.* ASM Handbook, Vol. 3. Metals Park, Ohio: ASM International; 1985:107–108.
13. ASTM G71-81. Standard guide for conducting and evaluating galvanic corrosion tests in electrolytes. West Conshohocken, Pa: ASTM International; 1998.
14. Hack P, Taylor D. Evaluation of galvanic corrosion. In: Korb LJ, Olson DL, eds. *Corrosion.* ASM Handbook, Vol. 13. Materials Park, Ohio: ASM International; 1987:234–238.
15. Redmond JD. Corrosion resistant materials. In: Boyer H, Gall T, editors. *Metals Handbook.* Metals Park, Ohio: American Society for Metals; 1985:15.1–15.7.