Galvanic coupling and mechanical properties of low Ni orthodontic brackets with representative types of orthodontic wires

Géraldine Kummer,^{*} Georgios Polychronis,[†] Spiros Zinelis[†] and Theodore Eliades^{*} Clinic of Orthodontics and Paediatric Dentistry, Centre of Dental Medicine, University of Zurich, Zurich, Switzerland^{*} and Department of Biomaterials, School of Dentistry, National and Kapodistrian University of Athens, Greece[†]

Aim: To characterise the mechanical properties and galvanic coupling of Ni-free orthodontic brackets with stainless steel (SS) and Nickel-Titanium (NiTi) orthodontic wires.

Methods: Three Ni-free bracket types (Topic [TOP], Equilibrium [EQU] and Orthos [ORT] made of Ni-free alloys), one conventional (Mini 2000 [MIN]) made of SS alloy and an SS and a NiTi wire were examined in the present study. All brackets and wires were embedded in epoxy resin and, after metallographic grinding and polishing, the Martens hardness (HM), the indentation modulus (E_{π}), and the elastic index (η_{π}) were recorded, employing Instrumented Indentation Testing (IIT) by monitoring force over indentation depth curves during a loading-unloading cycle. The galvanic coupling of all bracket-wire combinations was tested in 0.1M NaCl-0.1M lactic acid and 0.3% (wt.) NaF solutions by noting the potential differences over 48 hours. The mechanical properties were statistically analysed by one-way ANOVA and Tukey multiple comparison tests at alpha = 0.05. Results: Significant differences were identified in the mechanical properties of the materials tested. The TOP (2372 ± 182 N/ mm²), ORT (wing) (2418 ± 164) and SS wire (2302 ± 85) showed significantly higher HM compared with all other materials tested. The MIN (base) (1115 \pm 81) and ORT (base) (1237 \pm 101) showed the lowest HM while MIN (wing) (1520 \pm 138), EQU (1620 \pm 139) and NiTi wire (1526 \pm 42) demonstrated intermediate HM values. The ORT (wing) (101 \pm 6 GPa) displayed the highest E_{π} while NiTi wire (24 ± 5) showed the lowest. The latter had the highest elastic index (59 ± 5%) with MIN (base)(15 ± 3) possessing the lowest. The potential difference for all bracket wire combinations was found below the threshold for the initiation of galvanic corrosion (200 mV) apart from MIN coupled with NiTi wire in the NaF solution. Conclusions: The mechanical properties of Ni-free brackets are significantly different compared with the SS bracket assessed. Galvanic testing revealed that conventional and Ni-free brackets are compatible with both SS and NiTi wires in media containing chloride and fluoride ions.

(Aust Orthod J 2019; 35: 53-60)

Received for publication: October 2018 Accepted: March 2019

Géraldine Kummer geraldine.kummer@bluewin.ch; Georgios Polychronis: gpolisg@yahoo.gr; Spiros Zinelis: szinelis@dent.uoa.gr; Theodore Eliades: Theodore.Eliades@zzm.uzh.ch

Introduction

The extensive usage of Nickel (Ni)-containing stainless steel (SS) orthodontic brackets in clinical practice and related biocompatibility issues are well documented and a highly investigated area of concern.¹⁻³ Manufacturers have attempted to overcome nickel reactivity by developing Ni-free fixed appliances based on Cobalt-Chrome (CoCr) and Titanium (Ti) alloys. Although these seem to be promising alternatives, clinical efficacy requires a combination of desired material properties that must be fulfilled.

The replacement of conventional SS brackets with Ti and CoCr base metal alloys invariably has clinical implications associated with the differences in metal mechanical properties, especially hardness, which is associated with sliding and wear after wire placement. A significant increase in bracket hardness may have deleterious effects on orthodontic arch wires, increasing roughness and friction^{4,5} and therefore reducing sliding efficacy. In the case of brackets made of softer alloys than SS, there is increased vulnerability to wear effects induced by harder wires, with adverse consequences on sliding and biocompatibility from the release of metallic particles.^{6,7}

The replacement of SS brackets by other alloys has overlooked the effect of galvanic corrosion as a contributing factor to intraoral metal deterioration and ion release. This is a biological concern related to all heavy metals used in orthodontics including brackets, wires and soldering alloys.⁸⁻¹¹ Galvanic coupling is generally associated with a pair of dissimilar metallic materials capable of acting as an electron source when a current flows from one material to the other through an electrolytic medium. During this electrochemical process, it is possible for one metal to preferentially corrode, which simultaneously increases the corrosion resistance of the other. The galvanic coupling between two metallic materials establishes an electrochemical gradient but a low millivoltage (mV) is unlikely to initiate galvanic corrosion. However, if the electrical potential is over 200 mV, galvanic corrosion could result.¹² During orthodontic treatment, brackets are coupled to orthodontic arch wires made of SS and NiTi alloys and recent laboratory electrochemical studies have recorded high galvanic values when dissimilar alloy brackets and arch wires are in contact.¹³⁻¹⁵ This indicates an active process, leading to metal ion loss. The corrosive environment as well as the corrosive resistance and stability of an orthodontic alloy play a major role.16-18

The aim of the present study was to compare the mechanical properties of SS and Ni-free orthodontic brackets along with the measurement of potential differences as a result of galvanic coupling with representative orthodontic arch wires under electrolyte media. The null hypothesis states that Ni-free appliances will not demonstrate significant differences in mechanical and galvanic coupling performance compared with conventional SS materials.

Materials and methods

Materials tested

Three Ni-free bracket types and one conventional SS bracket type were examined in the present study. These were Topic (TOP) (Dentaurum, Ispringen, Germany, Lot: 476025), which is a single piece bracket made of CoCr alloy using Metal Injection moulding technology, and Equilibrium (EQU) (Dentaurum, Lot: 353284) as a single unit bracket made by pure Ti. Orthos (ORT) (Ormco, CA, USA, Lot: 011696323) is a two piece structure made of Ti and Ti6Al4V alloy,⁷ and Mini 2000 (MIN) (Ormco, Lot: 00209522) also as a two piece bracket made from SS alloys. In addition, one rectangular 0.016 × 0.022" SS orthodontic arch wire (Dentaline, Birkenfeld, Germany, Lot: 92706622) and a NiTi wire of similar dimension (Neo Sentalloy, DENTSPLY GAC, New York, USA, Lot: 135229) were also included in this study.

Instrumented indentation testing

Five brackets from each manufacturer were embedded in epoxy resin (Epofix, Struers, Belarup, Denmark). The central segment (about 20 mm in length) of five wires of each type were also embedded in epoxy resin along their longitudinal axis. All specimens were ground with water-cooled SiC papers from 220 to 4000 grit and polished with 3 and 1 µm diamond pastes (DM Paste, Struers) in a grinding/polishing machine (Dap-V, Struers). Subsequently, the specimens were ultrasonically cleaned for 10 minutes and left to air dry. Instrument Indentation Testing (IIT) measurements were conducted by employing a universal hardness testing machine ZHU0.2/Z2.5 (Zwick Roell, Ulm, Germany). Force indentation depth curves were generated by applying a force of 4.9 N with a 2 second dwell time delivered by a Vickers indenter. Five readings were recorded for each wire, bracket base and wing region and the mean value was used as representative of the specimen. All force-indentation depth curves were recorded and the Martens hardness (HM) Indentation modulus (E_{rr}) and elastic index (η_{TT}) were calculated according to ISO 14577-1 specifications.¹⁹

Galvanic coupling testing

The mesh surfaces of the orthodontic bracket bases were laser welded (R102915, LaserStar Technologies, RI, USA) to SS metallic rods. The base area of each bracket that clinically is in contact with tooth was insulated by non-conducting epoxy resin. Only 20 mm of each wire was exposed to the solution while the remainder was insulated by an elastic rubber. The electrochemical apparatus consisted of an electrolyte glass container with a plexiglass lid, which permitted the delivery of a galvanic couple while preventing electrolyte evaporation, a voltmeter (P903, Consort, Turnhout, Belgium) and a personal computer. The construction of the electrochemical cell and the measurement procedure for galvanic potential difference complied with the ASTM G71-81²⁰ standard. The electrolyte volume followed the recommended ratio of 40 ml per cm² metal surface area (≈ 50 ml). Prior to electrolyte immersion, the exposed metal surfaces were cleaned of organic impurities by immersion in acetone. The bracket-arch wire distance was kept constant at 1 cm. The voltameter's positive pole remained connected to the orthodontic bracket for comparative reasons. The potential difference measurements were recorded at room temperature (25°C), three times for each galvanic couple and after 48 hours since pilot studies showed that a plateau phase was reached during the first seven to eight hours. The recorded data were measured using Consort nv software (Consort) and graphically represented after smoothing.

Two water electrolyte solutions were tested. The first was a neutral (pH = 6.5) water-based solution of 0.3% NaF corresponding to 1394 ppm F⁻. The second was an acidic (pH = 2.3) solution of 0.1 M lactic acid and 0.1 M NaCl according to ISO 10271.²¹ In total, eight combinations of orthodontic wires and brackets (four brackets × two wires) were assessed for each electrolyte.

Statistical analysis

The mechanical properties tested were statistically compared by employing one-way ANOVA and Tukey multiple comparison test at alpha = 0.05.

Results

Instrumented indentation testing

Figure 1 demonstrates representative force indentation curves for all materials tested. Different force– indentation depth curves were recorded for MIN (Figure 1A) and ORT (Figure 1D) for base and wing regions, while similar curves were acquired for TOP (Figure 1B), EQU (Figure 1C) and the orthodontic wires (Figure 1E and 1F). The results of the tested mechanical properties are presented in Table I. The TOP, ORT (wing) and SS wire showed significantly higher HM compared with all other materials tested. MIN (base) and ORT (base) showed the lowest HM

Table	I.	Mean	values	and	stan	dard	deviati	ons	of Mar	tens	Hardne	SS
(HM),	Ind	dentatio	on Moo	dulus	(E _{IT})	and	elastic i	inde	$\times (\eta_{IT}).$			

Materials	HM (N/mm²)	E _{IT} (GPa)	η _{ι⊺} (%)
Mini2000 (Base)	1155(81) ¹	62(5) ¹	15(3) ¹
Mini2000 (Wing)	1520(138) ²	82(7) ²	22(7) ²
Торіс	2372(182) ³	83(3) ²	22(3) ²
Orthos (Base)	1237(101) ¹	62(6)1	26(2) ²
Orthos (Wing)	2418(164) ³	101(6) ³	35(8) ³
Equilibrium	1620(139) ²	73(8) ²	23(3) ²
SS wire	2302(85) ³	40(2)4	49(2)4
NiTi wire	1526(42) ²	24(5) ²	59(5) ⁵

Same superscripts denote mean values without statistically significant differences.

while MIN (wing), EQU and NiTi wire demonstrated intermediate HM values. The ORT (wing) illustrated the highest $E_{_{TT}}$ and NiTi wire the lowest. The latter showed the highest $\eta_{_{TT}}$ while MIN (base) presented the lowest.

Galvanic testing

Figure 2 demonstrates representative curves (potential over time) for all tested bracket-wire combinations. All curves reached a plateau phase during the first four to five hours except for the combination of bracket-NiTi arch wires in neutral NaF electrolyte, which required an additional time of several hours.

In Figure 3, the mean potential differences, in descending order, for all bracket-wire combinations are presented for both solutions. The MIN showed the highest mean values (-108 mV, -34 mV) in absolute scale in NaCl/lactic acid when combined with NiTi and SS arch wires, respectively. The Nifree brackets were characterised by very low potential differences (<17 mV). In the NaF solution, the SS brackets presented the highest difference (278 mV) when coupled with the NiTi arch wire, followed by the Ni-free wires with similar results ranging from 78 to 88 mV. EQU coupled to SS arch wires revealed the greatest negative value of -41 mV.

Discussion

Based on the results of the present study, the null hypothesis must be rejected, as Ni-free brackets showed significant differences in mechanical properties and galvanic coupling with orthodontic wires.



Figure 1. Representative force indentation curves from all materials tested. MIN (1A) and ORT (1D) demonstrate big difference in relative curve position for base and wing regions while TOP (1B) and EQU (1C) provide almost identical curves from both regions. The curves of SS (1E) and NiTi wire (1F) are also presented.



Figure 2. Representative curves from all bracket wire combinations tested showing the potential difference over time for both solutions. A and B depict the curves of bracket-SS wire combinations for 0.1 M NaCl -0.1 M lactic acid solution and 0.3% NaF respectively. C and D show the curves for bracket-NiTi wire combinations.



Figure 3. Mean potential differences for all bracket-wire combinations in descending order from left to right in both solutions tested. In all cases the standard deviations were found to be less than 23 mV and they are not presented for the sake of clarity. Positive mean values denote wire oxidation while negative depict bracket oxidation as shown by the arrows.

IIT is considered a more accurate technique in the determination of material hardness compared with traditional techniques (i.e., Vickers, Knoop etc.) as it is fully automated and the final outcome is not influenced by an operator's perception and change in diagonal length due to elastic recovery after load removal.^{22,23} IIT confers additional mechanical properties such as indentation modulus, elastic index and indentation creep, and other mechanical properties described by ISO 14577-1 specifications.¹⁹ In the present study, the indentation modulus and elastic index were included; the former is the elastic modulus derived by the unloading curve and the elastic index is indicative of the relative ductility of the alloy tested.

Although the HM of SS and NiTi wires was found to be supportive of recently-published data,²³ there is no data for the Ni-free and SS brackets tested. Twopiece brackets were found to differ in their mechanical properties in their base and wing regions of MIN and ORT. The harder wing in both cases (Table I) is in accordance with contemporary orthodontic technology in which the wing is made from a harder alloy to withstand wear effects.^{7,24} TOP wings made from the Ti6Al4V alloy⁷ and TOP made from a CoCr alloy share the same HM with SS wire and therefore may be considered compatible from the standpoint of mutual wear at the contact interface. A significant mismatch in HM values heralds the wear of a softer material with adverse consequences in biocompatibility due to release of wear particles and clogging of the wire in the slot.²⁴ However, until now, there was no specific guideline of biomechanical concern in orthodontic therapy. The HM values of EQU made of Ti and the MIN wing made by an SS alloy are compatible with the HM of NiTi wire. However, during orthodontic therapy both types of orthodontic wires may be used and therefore the selection of appropriate brackets to eliminate an HM mismatch and mitigate wear must be considered.^{6,25} Apart from the modulus of elasticity for the ORT (wing) (101 GPa), all other values were lower than the nominal values of the alloys tested, in a finding which is associated with the inherent limitation of IIT to determine the elastic modulus in non-stress-free samples.²⁶ It is known that orthodontic wires are delivered in the market after cold drawing (a process that develops residual stresses) but the manufacturing process and thermal treatment of orthodontic brackets are proprietary information and

remain undisclosed to the dental community. Twopiece brackets are manufactured by casting the wing and base separately and then brazing the two parts using a soldering alloy, in a method that might induce residual stresses.²⁴ In addition, brackets made by metal injection moulding (MIM) need final thermal treatment to relieve manufacturing stresses.²⁷

The major criteria for electrolytic solution selection were the presence of chlorides and fluorides to simulate intraoral conditions and assess their effect on the Cr and Ti oxides passivation layers, respectively. In general, Ti is considered more resistant to Cl ions compared with SS but more vulnerable to F ions as the latter destroys the TiO, oxide protective film.^{28,29} The first electrolyte followed the ISO 10271 standard and contained Cl ions in acidic conditions. The second solution had a concentration of 0.3% NaF which corresponds to 1394 ppm F ions. Since the effect of F ions is concentration related, it was deliberately used at a level below the upper limit of 1450 ppm recommended as the concentration for children's toothpaste.³⁰ The exposed surfaces were in accordance with common clinical practice involving the anterior bracket surface and 8 mm of arch wire length.^{16,17} The potential difference in measurements was recorded over 48 hours, since a pilot study showed that a plateau phase was reached during the first seven to eight hours.

In acidic conditions the SS brackets exhibited undesirable electrochemical behaviour. The negative potential difference values indicated oxidation of the bracket alloy, which was exacerbated when coupled with NiTi arch wires. This is not a clinically advantageous effect, since the brackets remain bonded throughout orthodontic treatment in contrast to the arch wires. However, the galvanic potential difference was below the 200 mV threshold required for galvanic corrosion, irrespective of the arch wire combination. However, Ni-free brackets were largely unaffected as they recorded minimal potential difference values.

In the presence of a neutral NaF electrolyte, MIN showed positive potential difference values of over 200 mV when coupled with NiTi arch wires, in a finding that supports previously published data.¹⁶ This is associated with arch wire oxidation, which may lead to undesirable ion release. Similarly, Ni-free brackets were characterised by cathodic behaviour when coupled with NiTi arch wires. However, the potential difference values did not indicate intense

galvanic effects as the concentration of F ions used in this electrolyte solution was much lower than clinically applicable. It is therefore suggested that the temporary removal of the NiTi arch wire is appropriate when preventive measures involving fluoride gel therapy (12,000 ppm F ions or more²⁸) are taking place. The Cr-containing brackets (MIN and TOP) did not show significant potential electrical difference values when coupled with SS arch wires. Beyond the clinical implications of the present study, it is worthwhile to note that the experimental results are considered indicative and not conclusive of the clinical performance of materials tested, as intraoral conditions are different and much more complicated compared with the charged laboratory interface between metallic surfaces and aqueous reagents. However, in vitro testing is the only way to assess galvanic compatibility between dissimilar orthodontic materials. Finally, the combination of experimental findings with in vivo ion release could reveal additional information related to the electrochemical degradation mechanism of orthodontic materials under clinical conditions.

Conclusions

- Ni-free brackets possess significantly different mechanical properties compared with SS brackets.
- SS and Ni-free brackets are galvanically compatible with SS and NiTi arch wires in media containing chlorine or fluoride ions.
- Fluoride treatment should be seriously considered in relation to galvanic effects when NiTi wires are coupled with SS brackets.

Corresponding author

Theodore Eliades Clinic of Orthodontics and Pediatric Dentistry Center of Dental Medicine University of Zurich Plattenstrasse 11 Zurich 8032 Switzerland

Email: theodore.eliades@zzm.uzh.ch

References

- Mikulewicz M, Chojnacka K, Zielińska A, Michalak I. Exposure to metals from orthodontic appliances by hair mineral analysis. Environ Toxicol Pharmacol 2011;32:10-6.
- Mikulewicz M, Chojnacka K. Release of metal ions from orthodontic appliances by in vitro studies: a systematic literature review. Biol Trace Elem Res 2011;139:241-56.
- 3. Eliades T, Athanasiou AE. In vivo aging of orthodontic alloys: implications for corrosion potential, nickel release, and biocompatibility. Angle Orthod 2002;72:222-37.
- 4. Eliades T, Bourauel C. Intraoral aging of orthodontic materials: the picture we miss and its clinical relevance. Am J Orthod Dentofacial Orthop 2005;127:403-12.
- Rongo R, Ametrano G, Gloria A, Spagnuolo G, Galeotti A, Paduano S et al. Effects of intraoral aging on surface properties of coated nickel-titanium archwires. Angle Orthod 2014;84:665-72.
- Regis S Jr, Soares P, Camargo ES, Guariza Filho O, Tanaka O, Maruo H. Biodegradation of orthodontic metallic brackets and associated implications for friction. Am J Orthod Dentofacial Orthop 2011;140:501-9.
- Zinelis S, Annousaki O, Eliades T, Makou M. Metallographic structure and hardness of titanium orthodontic brackets. J Orofac Orthop 2003;64:426-33.
- Hersche S, Sifakakis I, Zinelis S, Eliades T. Elemental, microstructural, and mechanical characterization of high gold orthodontic brackets after intraoral aging. Biomed Tech (Berl) 2017;62:97-102.
- Zinelis S, Pandis N, Al Jabbari YS, Eliades G, Eliades T. Does longterm intraoral service affect the mechanical properties and elemental composition of multistranded wires of lingual fixed retainers? Eur J Orthod 2018;40:126-31.
- Freitas MP, Oshima HM, Menezes LM. Release of toxic ions from silver solder used in orthodontics: an in-situ evaluation. Am J Orthod Dentofacial Orthop 2011;140:177-81.
- 11. Soteriou D, Ntasi A, Papagiannoulis L, Eliades T, Zinelis S. Decomposition of Ag-based soldering alloys used in space maintainers after intra-oral exposure. A retrieval analysis study. Acta Odontol Scand 2014;72:130-8.
- Pryor MJ, Staehle RW. Metal-liquid reactions: Corrosion. In: Hannay N, ed. Treatise on Solid State Chemistry: Volume 4 Reactivity of Solids. Vol 4. New York: Plenum Press, 1976;486.
- Iijima M, Endo K, Yuasa T, Ohno H, Hayashi K, Kakizaki M et al. Galvanic corrosion behavior of orthodontic archwire alloys coupled to bracket alloys. Angle Orthod 2006;76:705-11.
- Darabara MS, Bourithis LI, Zinelis S, Papadimitriou GD. Metallurgical characterization, galvanic corrosion and ionic release of orthodontic brackets coupled with Ni-Ti archwires. J Biomed Mater Res B Appl Biomater 2007;81B:126-34.
- Tahmasbi S, Ghorbani M, Masudrad M. Galvanic corrosion of and ion release from various orthodontic brackets and wires in a fluoridecontaining mouthwash. J Dent Res Dent Clin Dent Prospects 2015;9:159-65.
- Polychronis G, Al Jabbari YS, Eliades T, Zinelis S. Galvanic coupling of steel and gold alloy lingual brackets with orthodontic wires. Angle Orthod 2018;88:450-7.
- Bakhtari A, Bradley TG, Lobb WK, Berzins DW. Galvanic corrosion between various combinations of orthodontic brackets and archwires. Am J Orthod Dentofacial Orthop 2011;140:25-31.
- Schiff N, Boinet M, Morgon L, Lissac M, Dalard F, Grosgogeat B. Galvanic corrosion between orthodontic wires and brackets in fluoride mouthwashes. Eur J Orthod 2006;28:298-304.
- ISO, 14577-1. Metallic materials: Instrumented indentation test for hardness and materials parameters: International Organization for Standardization Geneva; 2002.
- 20. ASTM:G71-81. Standard guide for conducting and evaluating

galvanic corrosion tests in electrolytes. West Conshohocken, PA: ASTM International; 2014.

- ISO:10271. Dentistry -- Corrosion test methods for metallic materials. Switzerland: Geneva 2011: International Organization for Standardization; 2011.
- 22. Shahdad SA, McCabe JF, Bull S, Rusby S, Wassell RW. Hardness measured with traditional Vickers and Martens hardness methods. Dent Mater 2007;23:1079-85.
- Zinelis S, Al Jabbari YS, Gaintantzopoulou M, Eliades G, Eliades T. Mechanical properties of orthodontic wires derived by instrumented indentation testing (IIT) according to ISO 14577. Prog Orthod 2015;16:19.
- Eliades T, Zinelis S, Bourauel C, Eliades G. Manufacturing of orthodontic brackets: A review of metallurgical perspectives and applications. Rec Pat Mater Sci 2008;1:135-9.
- 25. Holst AI, Holst S, Hirschfelder U, Seckendorff VV. Retrieval analysis of different orthodontic brackets: the applicability of electron

microprobe techniques for determining material heterogeneities and corrosive potential. J Appl Oral Sci 2012;20:478-85.

- Suresh S, Giannakopoulos AE. A new method for estimating residual stresses by instrumented sharp indentation. Acta Metal 1998;46:5575-767.
- Zinelis S, Annousaki O, Makou M, Eliades T. Metallurgical characterization of orthodontic brackets produced by Metal Injection Molding (MIM). Angle Orthod 2005;75:1024-31.
- Nakagawa M, Matsuya S, Udoh K. Corrosion behavior of pure titanium and titanium alloys in fluoride-containing solutions. Dent Mater J 2001;20:305-14.
- Li X, Wang J, Han EH, Ke W. Influence of fluoride and chloride on corrosion behavior of NiTi orthodontic wires. Acta Biomater 2007;3:807-15.
- Spencer AJ. The use of fluorides in Australia: guidelines. Aust Dent J 2006;51:195-9.