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Titanium orthodontic brackets: structure, composition, hardness and ionic release

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Summary *Objectives*: The aim of the present study was to investigate the composition, morphology, bulk structure and ionic release of two brands of titanium orthodontic brackets: Orthos2 (Ormco, USA) and Rematitan (Dentaurum, Germany).

Methods: Five specimens of each group were examined with computerized X-ray microtomography, to reveal the morphology and structure of brackets, whilst resin-embedded and metallographically polished specimens were subjected to SEM/EDS analysis and Vickers microhardness measurements. Brackets were also maintained in 0.9% saline for 2 months and the ionic release in the immersion medium was determined with Inductively Coupled Plasma Atomic Emission Spectroscopy. The results of the hardness and ionic release measurements were statistically analyzed with two-way ANOVA and Tukey's test ($\alpha = 0.05$).

Results: Orthos2 brackets consisted of two parts, the base (commercially pure Ti grade II) and the wing (Ti–6Al–4V alloy), joined together by laser welding, producing large gaps along the base–wing interface. The base was of lower hardness ($H_v = 145$), than the wing ($H_v = 392$) and incorporated a standard foil base-mesh pad. Rematitan brackets consisted of commercially pure Ti grade IV, with a single-piece manufacturing pattern of virtually identical hardness ($p > 0.05$) at the base and wings, featuring a laser-etched base-mesh pad. The hardness of the Rematitan brackets was significantly lower than the hardness of the Orthos2 wings, but double the hardness of the Orthos2 base. Released Ti levels were below the threshold level (1 ng/ml) of analysis for both materials, whilst traces of Al (3 ppm) and V (2 ppm) were found in the immersion media for Ti–6Al–4V alloy.

Significance: The structural and hardness differences found may influence the torque transfer characteristics from activated archwires to the brackets and the crevice corrosion potential at the base–wing interface (Orthos2). The detection of Al and V in the immersion medium (Orthos2) may imply a different biological response from the two types of Ti brackets.

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Introduction

The issue of metal release and associated biological effects of nickel-containing orthodontic alloys has received some attention in the biomedical materials literature.[1-3] Concomitantly, research efforts have focused on the phenomena occurring with Ni alloys in vivo, including cytotoxicity and allergenicity.[4-7] The biocompatibility concerns deriving from use of Ni-containing alloys in the oral cavity of humans for extended periods of time have prompted the study of alternative materials. Thus, non-metallic, nickel-free alloys or steels with reduced nickel content have been tried in orthodontics. Specifically, a 2205 stainless steel alloy that contains half the amount of Ni found in 316L alloy was proposed as one alternative to conventional orthodontic brackets. This alloy has a duplex microstructure consisting of austenitic and delta-ferritic phases, is harder than the 316L alloy and has demonstrated substantially less crevice corrosion in vitro.[6] The search for an alternative to conventional steel has also resulted in the introduction of the precipitation-hardening (PH) 17-4 alloy, which shows higher hardness but lower corrosion resistance relative to its 316L counterpart.[3]

Titanium (Ti) has been recently introduced as an alternative material for the production of metallic orthodontic brackets.[8] The reason underlying the choice of this metal resides in its proven biocompatibility, lack of allergenicity and increased corrosion resistance.[9-11] Moreover, there has been extensive evidence from a wide variety of long-term titanium biomedical applications, such as dental implants, arthroplasty components, and plates/screws used in orthopedic and maxillofacial surgery.[12]

The currently available titanium brackets consist of two products: a commercially pure (cp) Ti and a Ti alloy (Ti-6Al-4V) bracket.[13] The bulk material properties and the potential for ionic release from these appliances remain unknown. The latter may be of interest for the second titanium alloy product, which contains vanadium and aluminum. Recent studies indicate that, under certain conditions, these elements are linked with various undesirable effects.[14-18]

The hypothesis tested in this study is that the different manufacturing methods and composition of the cp Ti brackets and Ti alloy brackets result in significantly different physical, mechanical and bulk material properties and variations in ionic release. Therefore, the purpose of this study was: to investigate the surface and bulk morphology, structure and hardness of the brackets, and qualitatively and quantitatively assess the metal ions released in vitro from a cp Ti and a Ti-6Al-4V alloy product.

Materials and methods

The study included two types of titanium brackets: Orthos2 (Ormco, Glendora, CA, USA) and Rematitan (Dentaurum, Ispringen, Germany).

Structure

Five specimens of each type were subjected to high resolution computerized X-ray microtomography (Skyscan 1072, Aartselaar, Belgium) under the following conditions: W Kα source, 100 kV accelerating voltage, 98 μA beam current, 4.75 μm pixel size and 4.5 μm cross-section pixel size at 1024×1024 pixels resolution. Two-dimensional and three-dimensional reconstructed images were obtained to study the bulk and surface structure of the brackets employing the cone-beam reconstruction and 3D-creator software (Skyscan).

Elemental composition

Five slot size-matched and prescription-matched brackets from each brand were embedded in epoxy resin in a direction perpendicular to their longitudinal axis. The specimens were ground with 220–2000 grit size SiC papers under water cooling, polished up to 0.05 μm with alumina suspensions (Bueler, Lake Bluff, IL, USA) in a grinding/polishing machine (Ecomet III, Bueler), and cleaned in an ultrasonic water bath for 5 min.

The polished specimens were coated with a 20 nm layer of carbon in a sputter-coater unit (SCD 004 unit with CEA 035 attachment, Bal-Tec, Balzers, Liechtenstein) and the elemental composition of the bracket base and wing components was determined by SEM/EDS analysis. An SEM (Quanta 200, FEI, Hilsboro, OR, USA) coupled to an energy dispersive spectrometry unit (Sapphire CDU, EDAX, Mahwah, NJ, USA) equipped with a super-ultrathin Be window was used in the study. Spectra were obtained at three randomly selected regions of the base and wing under the following conditions: 5.1×10^{-6} Pa vacuum, 25 kV accelerating voltage, 100 μA beam current, $500\times$ original magnification with a 0.26×0.26 mm sampling window, 100 s acquisition time and 30–40% dead time. The quantitative analysis of the percent weight concentration of the probed elements was performed by non-standard analysis and ZAF (Z, atomic number;

A, absorption; F, fluorescence) matrix correction employing the Genesis 3.5 software (EDAX).

Vickers hardness

The Vickers hardness (H_v) of the base and wing components of the sectioned brackets was assessed by using a microhardness instrument (HMV-2000, Shimadzu, Tokyo, Japan) under 200 g load and 15 s testing time. Four measurements were performed on three randomly selected regions on the base and wing of five brackets per material.

Ionic release

Three sets of 20 brackets of each group, which corresponds to a typical clinical case, were immersed in sterile plastic tubes containing 50 ml of 0.9% w/v normal saline and maintained at 37 °C temperature for 2 months. During the immersion period, the solutions were agitated twice daily. At the end of the immersion period 40 ml of eluent were removed from each solution using a syringe with a plastic tip.

The ionic release of the bracket components in the saline solutions was studied by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). A 15 ml sample of the solution was added to a 50 ml plastic vessel and dried under heating with infrared radiation. A 3 ml volume of aqua regia [conc. HCl(25%)/conc. HNO_3(75%)] was added to the dried product, which was dissolved under heating with infrared radiation. The homogenous solutions obtained were diluted with distilled water up to 20 ml in a volumetric flask and the metal content of the sample solutions was determined using an ICP-AES unit (OPTIMA 3000, Perkin Elmer Corp., Norwalk, CT, USA). Saline blanks were used as negative controls. Calibration standards were made from standard solutions of Ti, Al, and V (Merck, Darmstadt, Germany) and formulated to be matrix-matched to the saline-contained samples. Under these conditions, the detection threshold of the technique was estimated to 1 ng/ml.[19] The spectroscopic analysis was performed in triplicate for each of the two groups of materials and the results were averaged.

Statistical analyses

Hardness data were analyzed with two-way ANOVA with bracket group and bracket component (base, wings) as discriminating variables. Released ions values were also analyzed with two-way ANOVA with the source of the eluent (bracket group), and the individual elements serving as discriminating variables. Further group differences were investigated with Tukey's multiple comparison test at $\alpha = 0.05$ level of significance.

Results

Fig. 1a illustrates a representative 3D-reconstructed X-ray microtomographic image of an Orthos2 bracket indicating defects at the outer margin of the base–wing laser joint. This process results in large gaps at the base–wing interface located at the central part and periphery of the brackets (Fig. 1b). A 3D-reconstructed image of the entire volume of the empty space between the base and wing components is depicted in Fig. 1c. The highest empty volumes are located at the top and bottom margins of the interface. This empty space, in several specimens, was found to extend up to the external surface of the bracket. Orthos2 brackets incorporate a base-mesh pad as retentive element (Fig. 1d).

The corresponding X-ray microtomography image of the wing–base transition for the Rematitan brackets is shown in Fig. 2a and b. No intermediate phase is identified because this bracket is a single-piece appliance. In Fig. 2c the bracket base-mesh pad is illustrated, where evidence of laser-etching is identified as the mesh impregnates the base surface.

In Fig. 3a and b EDS spectra of the base and wing components of the Orthos2 bracket are illustrated. The base is composed of Ti, whereas the wings are Ti–6Al–4V alloy. The elemental line scan of Ti, Al and V at the base–wing interface of an Orthos2 bracket clearly shows the distribution of Al and V at the wing site (Fig. 4), suggesting the presence of a Ti–6Al–4V alloy. The EDS spectrum of Rematitan brackets confirmed the absence of elements other than Ti.

The results of the microhardness testing are presented in Fig. 4. Because Rematitan brackets are single-piece appliances, identical hardness values were found for the base and wing components. On the contrary, Orthos2 brackets, demonstrated higher hardness values for the wing component. These results are in agreement with previous studies.[13]

Table 1 shows the results of the ionic release assay. Titanium was not identified in either bracket immersion media, whereas traces of Al and V were found for the Ti alloy bracket group.

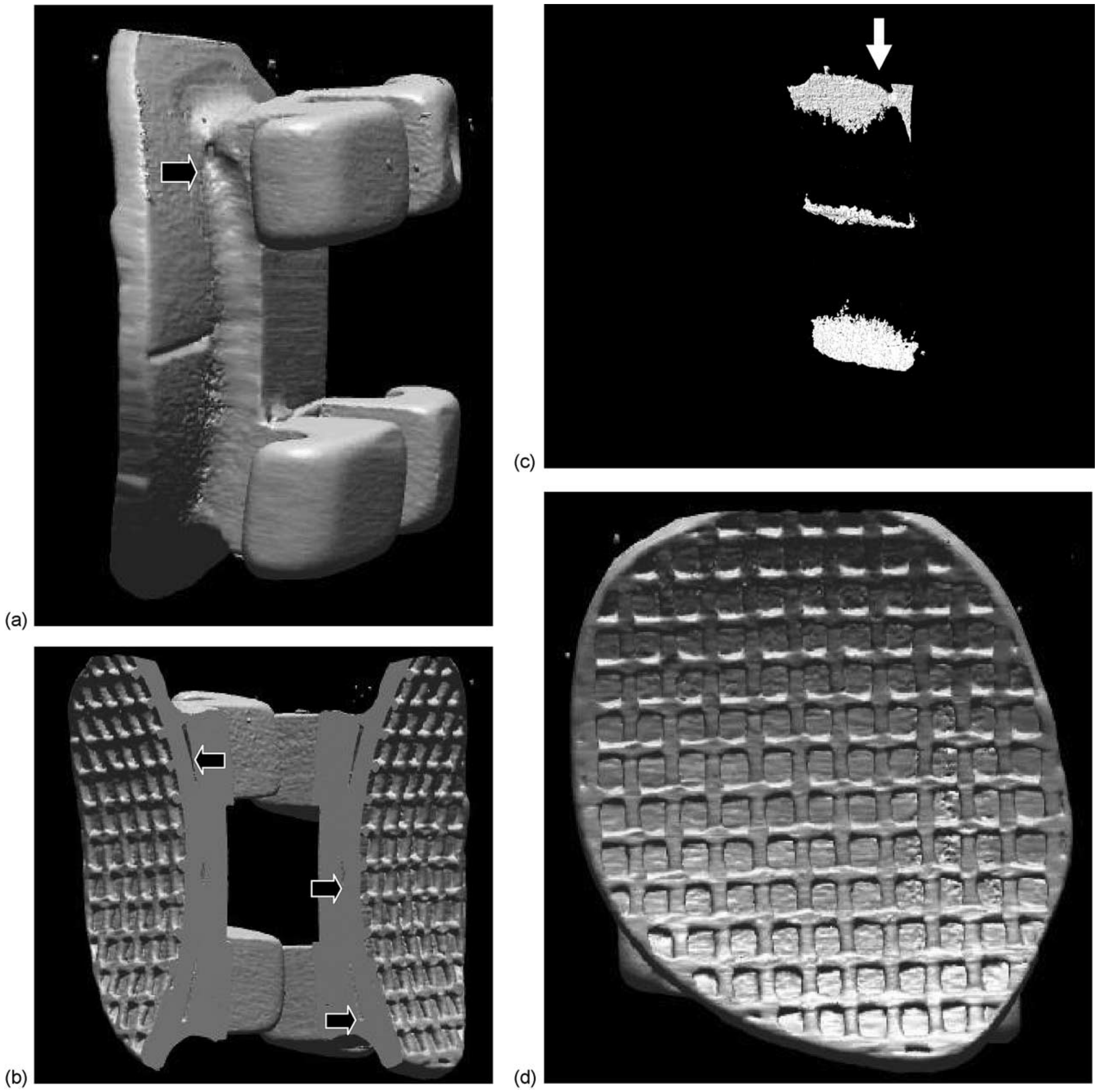


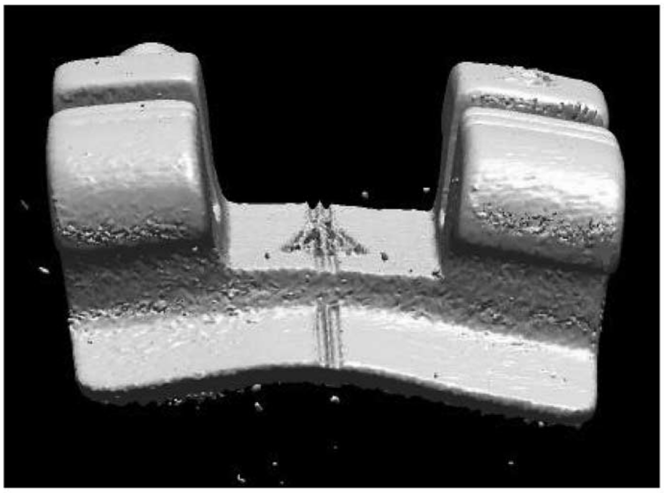
Figure 1 3D X-ray microtomographic image of an Orthos2 bracket. (a) View of the outer base–wing transition demonstrating the presence of pores at the laser welding sites connecting the base and wing components (arrow). (b) Detail of a tomographic section at the base–wing interface, showing the presence of gaps (arrows). (c) Reconstructed image of the empty spaces arranged by the gaps. The empty interfacial space extents to the external bracket surface (arrow). (d) View of the base of the bracket indicating a welded base-mesh pad.

Discussion

This study identified substantial morphological and structural differences between the Ti brackets, both at the base and wing components, probably attributable to the different methods of fabrication, involving metal injection molding or laser welding processes,[20] so the hypothesis was confirmed. The latter type has shown the presence of large gaps along the base–wing interface, a fact which may have clinical complications arising from the mechanical strength of the welding, with undesirable effects such as wing breakage during archwire activation or during bracket removal at the end of the treatment. The interfacial gaps extending to the bracket surface may increase plaque accumulation between the base and wing components, thus establishing an environment prone to crevice corrosion.

The variation found between the brackets tested with respect to base-mesh morphology may be attributed to the different manufacturing processes

(a)



(b)

(c)

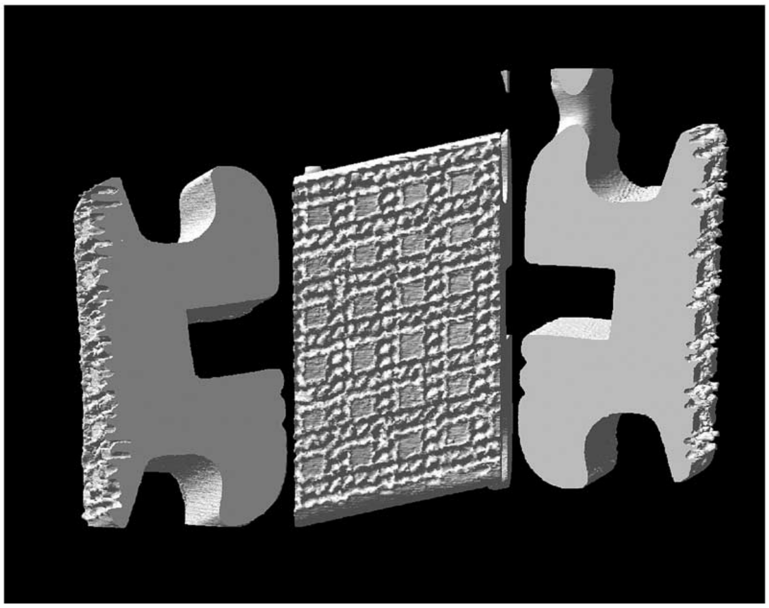


Figure 2 3D X-ray microtomographic image of a Rematitan bracket. (a) Detail of the outer base–wing region showing a smooth transitional zone. (b) View of the base mesh at an angle depicting the laser-etched base and the smooth base–wing transitional zone. (c) Face view of the base mesh demonstrating the non-welded base-mesh pattern and tomographic sections revealing a continuous base–wing interface.

employed for the production of the two appliances: Orthos2 has a standard system with a simple foil mesh pad, whilst for Rematitan, a laser treatment of the base is employed to create the base pads.[21] This results in the melting and evaporation of the metal forming retentive features on the base, which may lead to higher bond strength.[22]

The EDS analysis indicates that the base of the Orthos2 bracket consists of Ti, with a Vickers value within the range reported for cp Ti grade II.[23] The elemental composition of the alloy used in the wing component of Orthos2 is in accordance with the range specified for commercial Ti–6Al–4V alloys used in surgical implants.[24] Rematitan brackets were produced by machined forged and rolled profiles in a single-piece unit.[15] The EDS analysis identified Ti as the only element of these appliances with a Vickers hardness close to that reported for the cp Ti grade IV.[23]

The difference in Vickers hardness between the brackets tested may have significant effects upon the wear phenomena encountered when an activated archwire is engaged into a pre-adjusted bracket slot. NiTi archwires possess a hardness ranging from 300 to 430 VHN,[6] which is close to that of Orthos2 wing hardness, whereas stainless steel

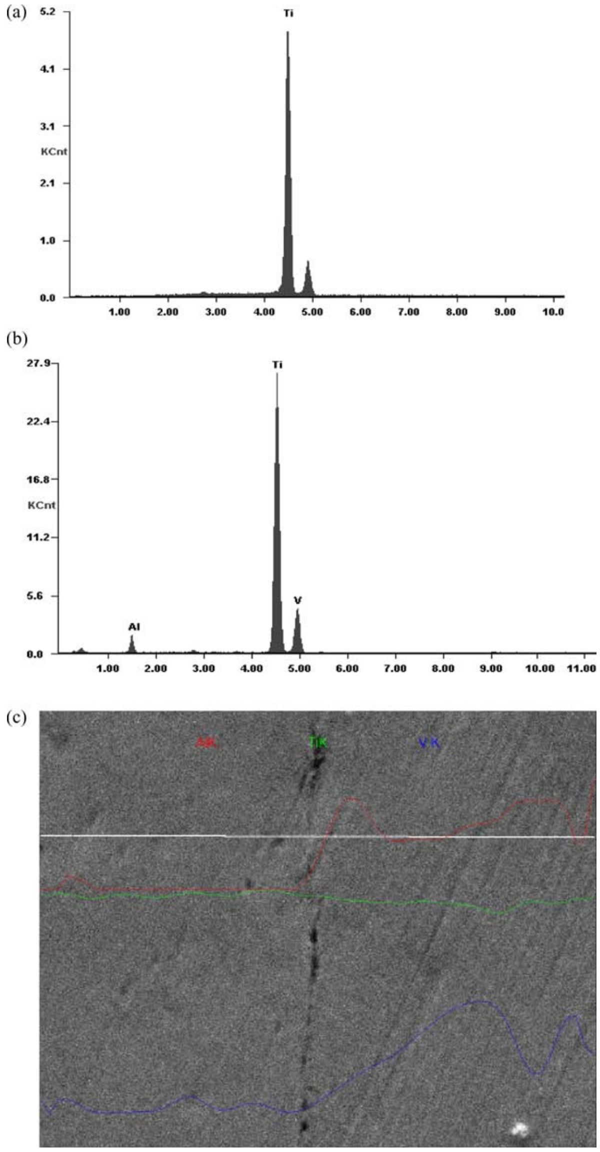


Figure 3 X-ray EDS spectra of the brackets. (a) Orthos2 bracket base showing that the bracket is composed of Ti. Similar to the spectrum of Rematitan. (b) Orthos2 bracket wing showing the presence of Ti, Al and V. (c) X-ray line scan images of the elemental distribution of Ti, Al and V at the base–wing interface revealing increased Al and V concentration at the wing component. Note the interfacial porosity.

(SS) archwires have a hardness of 600 VHN. Since Rematitan brackets present Vickers hardness values much lower than NiTi and SS archwires, an increased wear rate of the bracket slot walls is anticipated during orthodontic treatment. This effect arises from the generally poor wear resistance of Ti alloys, which require surface treatments before being employed in tribological applications.[11] The use of Ti–6Al–4V alloy with a friction coefficient of 0.28 for the production of the Orthos2 wing may result in different static and kinetic

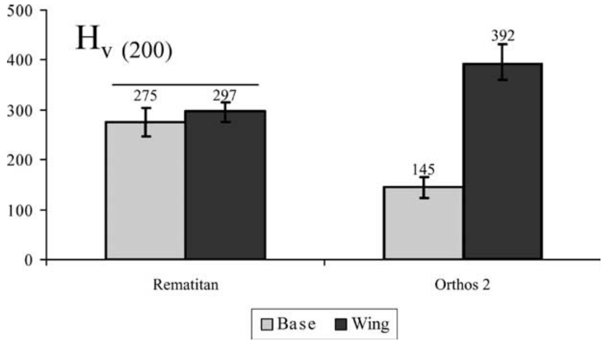


Figure 4 Vickers microhardness (HV_{200}) for the base and wing components of the two bracket types tested. Bar indicates values of no statistical difference ($p > 0.05$).

frictional coefficients from the values available in literature. This is because the latter have been calculated from the cp Ti friction coefficient (0.34); this alloy is used in the manufacturing of Rematitan brackets.[25]

The clinical significance of the hardness findings may arise from the fact that a low-hardness wing component may reduce the transfer of torque from an activated archwire to bracket. The wear of the bracket slot and/or wire surfaces arising from the low hardness of the alloys may preclude a full engagement of the wire with the slot walls, and possibly result in plastic deformation of the wing.[26]

From a corrosion perspective, Orthos2 may be more susceptible to galvanic corrosion relative to Rematitan since the former is composed of two different alloys. The wear process developed during sliding of archwires into the bracket slot walls may exacerbate the corrosion potential for these appliances. However, validation of this hypothesis requires further evidence.

Although this study suggested minimum Al and V release, long-term release may be higher than that occurring within the first weeks, and therefore, studies employing time intervals within the 1 month range for the investigation of ionic release suggest a low margin for safety.[27] In general, in vitro protocols involving the study of ionic leaching in

Table 1 Metal content in the immersion media of the two groups of titanium brackets used in the study.

Eluent source	Element released (ng/ml)		
	Ti, mean (SD)	Al, mean (SD)	V, mean (SD)
cp Ti (1 case—20 brackets)	[a]	[a]	[a]
Ti alloy (1 case—20 brackets)	[a]	3 (0.2)	2 (0.3)

[a] Concentration below the detection limit of the analysis (1 ng/ml).

solutions suffer from the limited release capacity induced by the saturation of the immersion medium.[28] Nonetheless, all other alternatives present much higher degrees of uncertainty and methodological difficulties, which render their use inappropriate.

The series of methods employed by other workers to study the release of ions from metallic appliances include the analysis of biological fluids such as saliva. This presents fundamental difficulties related to the momentary sampling of the saliva, the various secretion rates among individuals participating, and the inability to study the additive effect of ionic release over an extended period of time.[28]

On the other hand, the investigation of levels of metals in blood is complicated by the permeability and excretory ratios for metallic ions.[29] The former represents the ratio of concentration of an element in urine relative to plasma and is both species- and element-specific, whereas the excretory ratio is defined as the relative efficiency for excretion of a substance and it is highly variable.[30]

The inability of in vitro protocols to simulate clinical conditions has given rise to retrieval analysis, which furnishes critical information on the service history and alterations of materials.[31] Nonetheless, this type of study precludes the clarification of mechanisms underlying the phenomena occurring during service, since the study of specimens is that of a post hoc type.[28]

The presence of constituent elements with potential biologically hazardous action, especially Vanadium, has led the broader orthopedic biomaterials research interest in adopting V-alternatives. Thus, a new generation of Ti orthopedic alloys has been developed, comprising of Ti–6Al–7Nb, employing Nb as a beta stabilizer.[32] Nonetheless, in contrast to the long-term biomedical applications of Ti alloys in orthopedics, the orthodontic use of Ti brackets has a limited service life and exposes the material to substantially decreased load magnitudes. Thus, the minute levels of V release may not constitute an alarming situation. Further studies should examine the release of V during use by comparing the V levels in as-received and retrieved orthodontic brackets following the completion of treatment.

Care should be taken in extrapolating the clinical behavior of orthodontic alloys from in vitro tests. This may arise from the complex phenomena associated with intraoral application of brackets and the engagement of archwires with either elastomeric or stainless steel ligatures. The loads developed during sliding of a metallic wire on the slot of the bracket with the underlying mechanism involving the cold welding at the interfaces under pressure may result in rupturing of the contact points (wear–oxidation).[3] In addition, enzymatic activity and microbial attack on materials surfaces may complicate further the interfacial properties of the wire-bracket system.

Lastly, in clinical conditions, orthodontic alloys are in contact with a variety of substances, a fact imposing potent effects on its reactive status and surface integrity. These include saliva containing acids arising from degradation and decomposition of food, as well as oral flora and its by-products.

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