Acta Odontologica Scandinavica, 2014; 72: 130–138

informa
healthcare

ORIGINAL RESEARCH

Decomposition of Ag-based soldering alloys used in space maintainers after intra-oral exposure. A retrieval analysis study

DESPO SOTERIOU[1], ARGYRO NTASI[2], LISA PAPAGIANNOULIS[1],
THEODORE ELIADES[3] & SPIROS ZINELIS[2]

[1]*Department of Pediatric Dentistry,* [2]*Department of Biomaterials, School of Dentistry, University of Athens, Athens, Greece, and* [3]*Department of Orthodontics and Paediatric Dentistry, Center of Dental Medicine, University of Zurich, Switzerland*

Abstract

Objective. The aim of this study was to evaluate the elemental alterations of Ag soldering alloys used in space maintainers after intra-oral exposure. ***Materials and methods.*** Twenty devices were fabricated by using two different soldering alloys; US (Dentaurum Universal Silver Solder, $n = 10$) and OS (Leone Orthodontic Solder, $n = 10$). All devices were manufactured by the same technician. Surface morphology and elemental quantitative analysis of the soldering alloys before and after intra-oral placement in patients was determined by scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM/EDX). Statistical analysis was performed by *t*-test, Mann Whitney tests and Pearson's correlation. For all tests a 95% confidence level was used ($\alpha = 0.05$). ***Results.*** Both soldering alloys demonstrated substantially increase in surface roughness after intra-oral aging. Statistical analysis illustrated a significant decrease in the Cu and Zn content after treatment. OS demonstrated higher Cu release than US ($p < 0.05$). The remaining relative concentrations of Cu and Zn after the treatment did not show any correlation ($p > 0.05$) with intra-oral exposure time, apart from Zn in OS ($r = 0.840$, $p = 0.04$). ***Conclusions.*** Both soldering alloys demonstrated a significant Cu and Zn reduction after intra-oral exposure that may raise biocompatibility concerns.

Key Words: *Ag-alloys, soldering, space maintainers, SEM/EDX*

Introduction

Space maintainers are orthodontic appliances used in cases of premature tooth loss, (due to trauma, decay or other factors), in order to preserve the space developed until permanent tooth eruption. Fabrication of these devices involves stainless steel (SS) wires, bands and loops that are joined together by means of an Ag-based brazing material. The alloys used are the AISI 303, AISI 304, AISI 305, AISI 316 austenitic type SS and the PH-17-4 martensitic precipitation-hardened SS [1–5]. The silver brazing materials mostly employed are Ag-Cu-Zn low fusing alloys (55–65 wt% Ag, 15–25 wt% Cu and 15–25 wt% Zn), with small amounts (2–5 wt%) of Ni or Sn [6]. The brazing procedure is performed by torch and flux; the latter is provided separately by the alloy manufacturer or it is incorporated into the wire of the brazing alloy as a separate layer [6].

Clinical studies have shown that the main reason of in-service failure of space maintainers is associated with intra-oral degradation of the soldering material at the joint area [7–10]. Although a few *in vitro* studies have documented the ionic release of Ni, Cr, Cu and Zn [2,3,11], which might be implicated in cytotoxic effects, still there is no clinical evidence to verify the experimental findings and the mechanisms involved.

The aim of the present study was to evaluate the elemental alterations induced in modern Ag soldering alloys used in fabrication of space maintainers, after intra-oral exposure. The null hypothesis tested was that the soldering alloys used do not show significant differences in their elemental composition before and after intra-oral exposure.

Correspondence: Spiros Zinelis, Department of Biomaterials, School of Dentistry, University of Athens, Thivon 2, Goudi 11527, Athens, Greece. Tel: +302107461102. Fax: +302107461306. E-mail: szinelis@dent.uoa.gr

(Received 13 February 2013; accepted 30 May 2013)

ISSN 0001-6357 print/ISSN 1502-3850 online
DOI: 10.3109/00016357.2013.812745

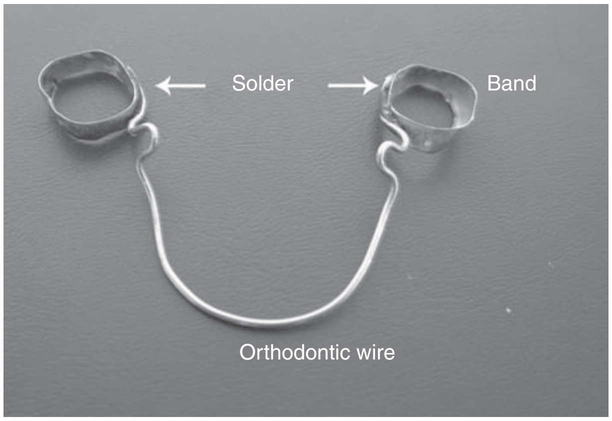

Figure 1. The space maintainer design used in this study: Two bands, one wire and two lingual soldering areas at the wire-band interfaces.

Materials and methods

Subjects and materials

The patients of this study were treated in the Paediatric Dentistry Clinic of the Dental School of the University of Athens. Twenty patients were selected for the present study with the following enrolling criteria; (a) free medical history, (b) 6–8 years old, (c) premature loss of primary molars and (d) need of treatment with space maintainers. The protocol of the study was approved by the Ethics Committee of the Dental School of the University of Athens (Ref 129A/10.06.2009). Signed informed consent was obtained from the parents of all the participating patients.

Ten patients per group were assigned to the treatment group in an alternative fashion. All the fixed appliances ($n = 20$) were fabricated by the same dental technician using prefabricated molar bands (Snap fit, GAC Int, Islandia, NY, USA) and SS wires (R.51408000 Dentaurum, Ispringen, Germany). Each appliance consisted of two bands and one wire with two soldering points (Figure 1). For half the number of the devices the Orthodontic Solder R022-00 (Leone Spa, Sesto Fiorentino, Firenze, Italy; OS) was used, whereas for the other half the

Table I. Type of soldering alloy used and treatment duration per patient.

Patient	Soldering alloy	Treatment duration (months)
1	OS	12.0
2	US	13.3
3	OS	12.6
4	US	13.3
5	OS	11.6
6	US	—
7	OS	12.0
8	US	16.3
9	OS	12.0
10	US	15.0
11	OS	12.0
12	US	11.0
13	OS	16.0
14	US	13.0
15	OS	—
16	US	12.0
17	OS	12.5
18	US	—
19	OS	12.5
20	US	13.0

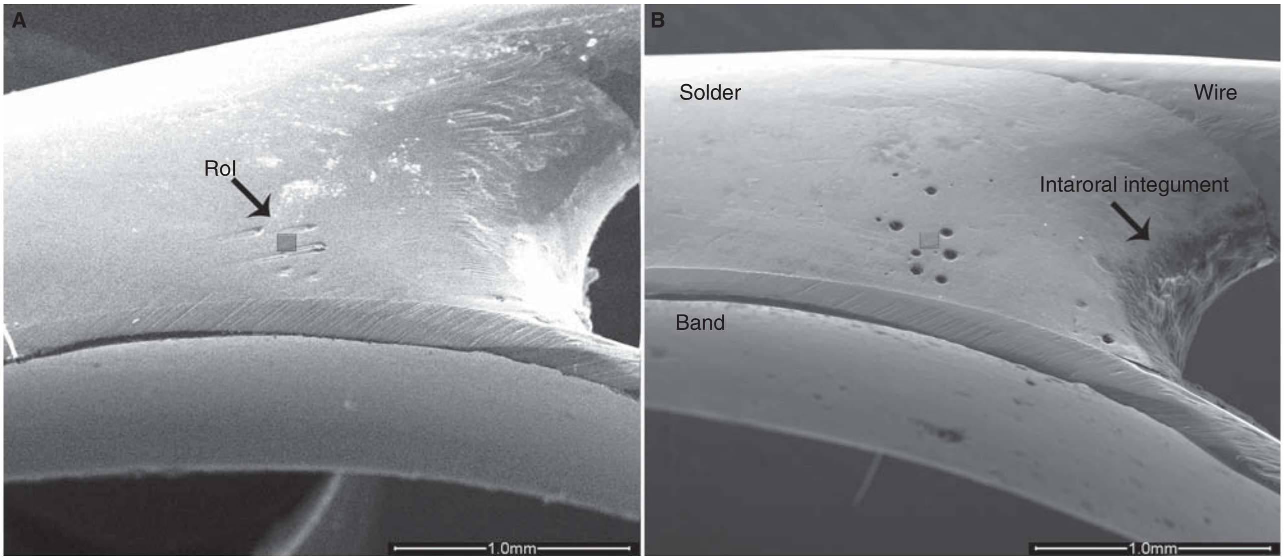

Figure 2. Secondary electron images showing the identification method of the regions of interest (RoI) before (A) and after treatment (B). A region with intra-oral integument (pointed by the arrow) along with band, solder and wire are presented in (B). The surface porosity pattern (outlined by the gray rectangle) was used to locate the same region before and after treatment for EDX analysis. Original magnification 50×, bar: 1 mm.

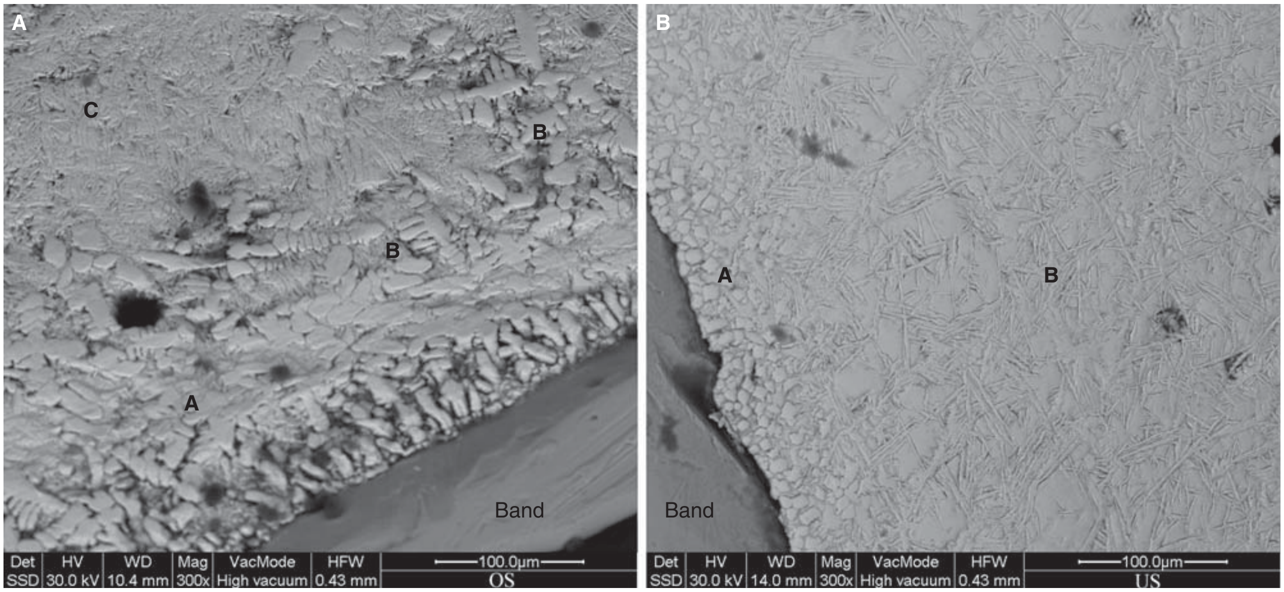

Figure 3. Representative BEI from the joint of both alloys to metallic band. (A) OS alloy surface illustrate a region with coarse grains (A), dendritic structures (B) and acicular grains. (B) OS depicts a narrow zone (A) with rectangular grains followed by a diffused distribution of acicular grains (B). Nominal magnification 300×, Bar 100 µm.

Dentaurum Universal Silver Solder (Ref.380-604-50, Dentaurum; US) was employed (Table I). Depending on the patients' treatment plan, intra-oral exposure ranged from 11–16 months (Table I).

Surface investigation and elemental analysis

The surface structure and elemental composition of both alloys before and after retrieval from the oral cavity was investigated employing a SEM unit (Quanta 200, FEI, Hillsboro, OR) equipped with an EDX spectrometer (Sapphire CDU, EDAX Int, Mahwah, NJ) with a liquid N_2-cooled Si(Li) detector and a super-ultrathin Be window (SUTW+). Backscattered electron images (BEI) were recorded from the surface of both alloys using 30 kV accelerating voltage and 110 µA beam current under high vacuum chamber conditions at 300× and 4000× nominal magnifications. Spectra were collected employing the area scan mode (200 µm × 200 µm sampling area), 300 s acquisition time and 25–35% detector dead time. Soldering alloys, orthodontic wire and band were also analyzed in the as received condition. Quantitative analysis was performed by Genesis software (v 5.2, EDAX Int.) under a non-standard mode, using ZAF correction methods. The elemental composition of the Ag solder areas of each space maintainer was analyzed before and after intra-oral exposure. Despite the fact that, due to specimen geometry and inclination, it is impossible to analyze the same area, the regions of interest were identified in each specimen by using characteristic morphological features as markings (Figure 2).

For the evaluation of the net differences in the elemental content before and after intra-oral exposure, elemental quantification (wt%) was performed after excluding the contribution of elements assigned to intra-oral integuments (C, O, P and S). In addition, the percentage reduction in elemental content after intra-oral exposure relative to the native reference before exposure (RC%) was calculated according the equation: $RC\% = [1 - (C_b - C_a/C_b)] \times 100$, where C_b and C_a the content of the same element before and after intra-oral exposure, respectively.

Statistical analysis

Statistical analysis was performed by *t*-tests or Mann-Whitney Sum Rank tests in cases of not normal distributions. The correlation between RC% and treatment duration was assessed by Pearson coefficient. In all cases a 95% confidence level was used ($\alpha = 0.05$). Statistical analysis was performed by SigmaPlot (v12) software (Systat Software Inc. San Jose, CA).

Results

The type of the soldering alloy used per patient and the intra-oral exposure period are summarized in Table I. From the total number of 20 patients, three did not finish the treatment (one in OS and two in US groups) and, thus, were excluded from the study. The mean treatment duration was 12.6 ± 1.3 and 13.4 ± 1.6 months for OS and US groups, respectively. No statistically significant difference was found in the treatment duration between the two groups ($p = 0.13$).

Figure 3 shows the representative BEI form the joint between band and soldering alloys. Both alloys show a completely different microstructure close to

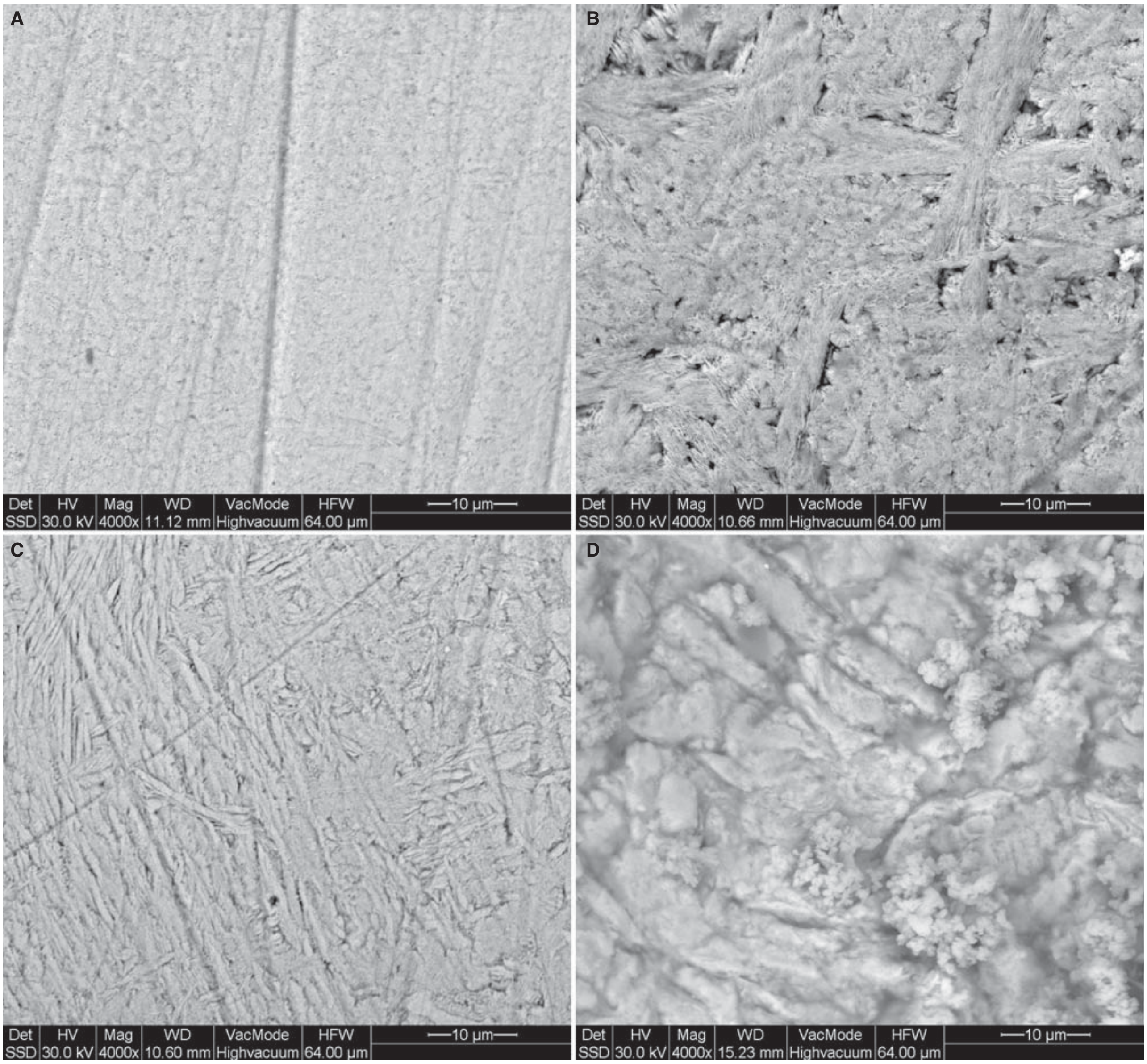

Figure 4. Representative backscattered electron images (BEI) from the surface of both alloys tested. (A) OS before placement in the oral cavity. (B) OS after *in vivo* aging. (C) US before and (D) after retrieval from the oral cavity. Surface scratches in (A) and (C) are attributed to surface grinding and polishing, while both alloys demonstrate increased roughness after *in vivo* aging (B and D). Original magnification 4000×, bar 10 µm.

the joint with band (region A). OS shows a zone with coarse grain (region A, Figure 3A) followed by a zone with dendritic structure (B), while region C is dominated by acicular grains. US depicts a narrow zone with almost rectangular grains (region A, Figure 3B) followed by a matrix of acicular grains. To avoid any bias, the region of interest was solely located on C areas for both alloys. Figure 4 illustrates representative BEI from both alloy surfaces before and after intra-oral aging. Both alloys illustrate surface scratches (Figures 4A and C) which are readily attributed to the surface grinding and polishing procedure. However, these scratches have been vanished after intra-oral aging, while both alloy surfaces demonstrate a deterioration of their surface quality by an increase in surface roughness (Figures 4B and D).

Table II presents the elemental composition of the materials used for the fabrication of the space maintainers. Figure 2 demonstrates representative EDX spectra of the same solder region before and after intra-oral exposure. A decrease in the linear intensity of Cu and Zn peaks is clearly observed after intra-oral exposure for both the Ag soldering alloys (Figure 5). The quantitative results are given in Table III. A statistically significant reduction in Cu ($p < 0.001$ for OS and US) and Zn ($p = 0.006$ for OS and $p = 0.002$ for US) were identified.

The results of the decrease in Cu and Zn content after intra-oral exposure for each soldering alloy are shown in Table IV. OS demonstrated a significantly greater Cu decrease than US ($p < 0.001$). Figure 3 illustrates the RC% as a function of time.

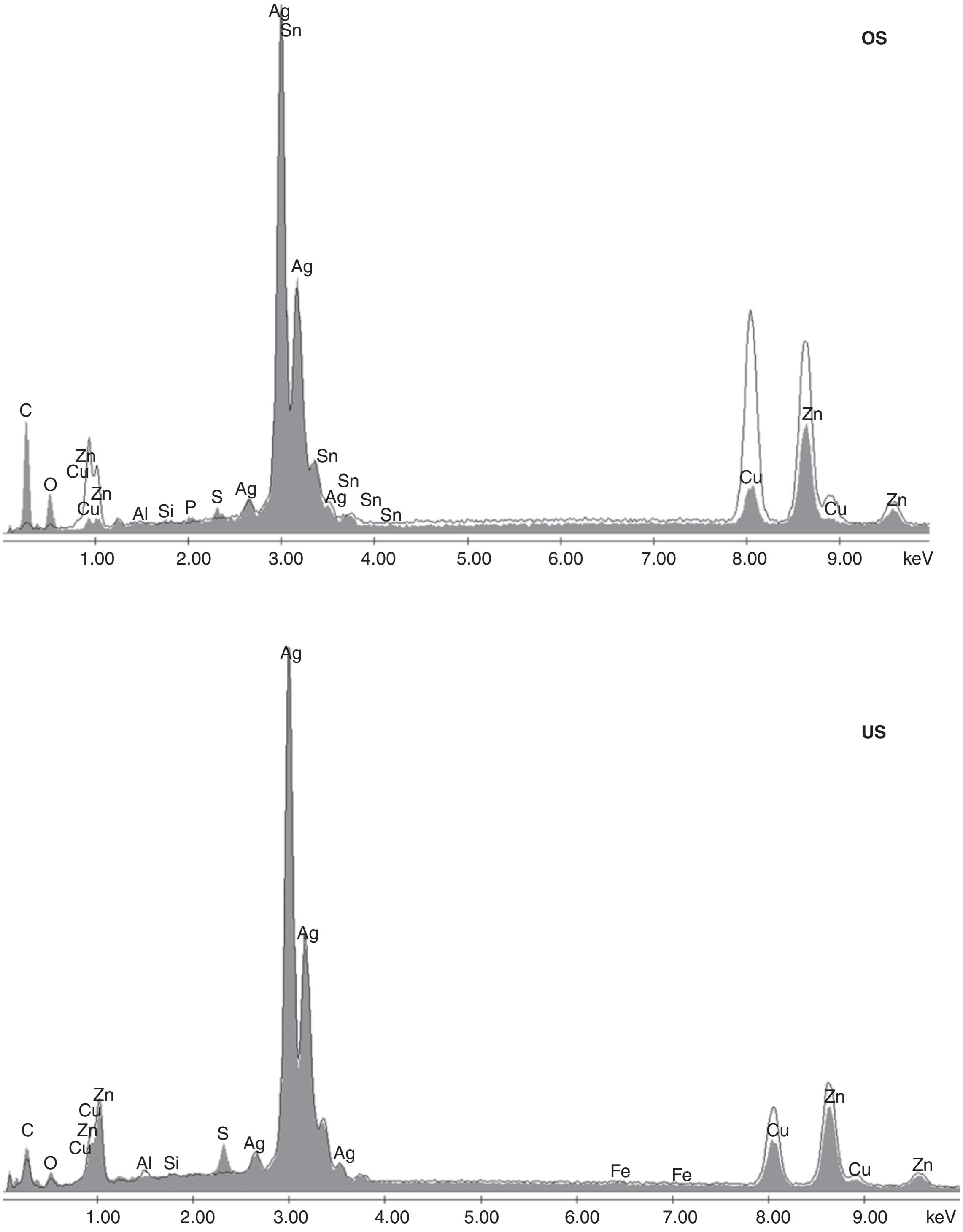

Figure 5. Representative EDX spectra of OS (A) and US (B) soldering alloys before (black line) and after intra-oral exposure (grey area). Note reduction in Cu and Zn peaks after intra-oral exposure in both the Ag soldering alloys.

No correlation was identified between treatment duration and the RC% ($p > 0.05$) apart from Zn in the OS group ($p = 0.004$, Figure 3B).

Discussion

The SS of the bands used in the present study had a composition matching that of PH 17-4 SS (also known as S 17400) precipitation-hardened alloy, which has a nominal composition of (wt%): 0.07 C, 0.7 Mn, 1.0 Si, 15.0–17.5 Cr, 3.0–5.0 Ni, 3.0–5.0 Cu and traces of P, S, Ta and Nb [12]. The composition of the wires used matched with AISI 303 SS, with a nominal elemental composition of (wt%): 17.0–19.0 Cr, 8.0–10.0 Ni, max 2.0 Mn, max 1.0 Si and 0.6 Mo [13]. The two Ag soldering alloys, US and

Table II. Elemental composition (wt%) of the bands, the wires and the two Ag-soldering alloys (OS, US) used for the preparation of the space maintainers.

	Ag	Cu	Zn	Cr	Ni	Fe	Mn	Al	Sn	Si	Mo
Band	—	2.3	—	18.0	6.4	71.1	1.3	—	—	0.9	—
Wire	—	—	—	17.7	7.7	71.6	1.4	—	—	1.3	0.4
OS	46.9	23.9	26.7	—	—	—	—	—	2.5	—	—
US	65.7	13.3	20.5	—	—	—	—	0.5	—	—	—

OS, are classified as the materials with the highest and lowest Ag content among the Ag soldering alloys currently available [6]. This research should not be considered as a typical clinical trial study as neither the materials used nor the treatment plan has been modified in any point and, thus, the experimental protocol better fits to retrieval analysis protocols. Another point of interest is that the aim of this study was not to compare the differences between the two soldering alloys tested but to assure that the materials used did not undergo significant elemental alterations during intra-oral aging which is a main demand for each material in a biological environment. Therefore, randomization is of lesser importance. Despite the limited number of patients included in this study for each group ($n = 10$) the p-values are very small due to big differences in Cu ($p < 0.001$ for OS and US) and Zn ($p = 0.006$ for OS and $p = 0.002$ for US) contents and pair testing before and after intra-oral aging.

According to the results of Table III, the null hypothesis of this study must be rejected, since both the Ag soldering alloys tested showed significant differences in their elemental composition, before and after intra-oral exposure. In both alloys, the percentage Ag content was significantly increased after treatment. However, since there is no source of Ag uptake (i.e. diet, etc.), this increase should be rather attributed to the balance of the reduced Cu and Zn content. The results of this study regarding the leaching of Cu and Zn are in accordance with the experimental [3,14–16] and clinical data [17] for the Ag-based soldering alloys used in orthodontic soldering. In all the retrieved specimens, other elements (S, O, P and C) were also identified (Figure 5), which are mainly assigned to biofilm formation. The content of these elements was not taken into account in the assessment of the changes in the elemental content of the soldering alloys, to avoid over-estimation of the rest elements.

Although Ag-based soldering alloys have a substantial record of publications in dental literature, the knowledge regarding their metallurgical microstructure has been based only to one study where an Ag-based soldering alloy with different composition (56Ag-22Cu-17Zn-5Sn) has been tested [2]. However, the grain coarsen at the adjacent zone of Ag-based solder with stainless steel is a typical finding in dental and non-dental applications [2,18], which is attributed to the thermal gradient during solidification. Previous data have correlated the microstructural features of this adjacent zone with brazing temperatures and time [18]. According to the results of this study both alloys illustrate acicular grain microstructures which differentiate from previously mentioned microstructures of other Ag-based alloys with similar compositions where the eutectic Ag-Cu region composed of alternate Ag-rich and Cu-rich stripes [18] along with Cu-rich primary dendrites [2] and scattered granules [19,20] have been identified. These formations, being in disagreement with the phases predicted from the binary phase diagrams, can be attributed to the fabrication procedure of the systems studied and the limited time available for alloy solidification. However, the full microstructural characterization of the

Table III. Mean values and standard deviations for the elemental content (wt%) of the Ag-soldering alloys, before and after intra-oral exposure, according to the EDX analysis.

	OS		US	
Element	Before	After	Before	After
Ag	52.9 ± 6.6^{a}	71.4 ± 1.9^{b}	63.1 ± 2.5^{a}	73.4 ± 3.5^{b}
Cu	21.9 ± 3.7^{a}	7.4 ± 3.9^{b}	15.1 ± 1.3^{a}	9.4 ± 2.2^{b}
Zn	22.6 ± 3.1^{a}	16.6 ± 2.0^{b}	20.8 ± 1.4^{a}	16.6 ± 2.0^{b}
Sn	3.9 ± 1.1^{a}	3.8 ± 3.4^{a}	—	—
Al	0.3 ± 0.2^{a}	0.4 ± 0.2^{a}	0.4 ± 0.3^{a}	0.1 ± 0.1^{a}
Fe	0.3 ± 0.2^{a}	0.3 ± 0.2^{a}	0.4 ± 0.2^{a}	0.4 ± 0.2^{a}
Si	0.1 ± 0.1^{a}	0.1 ± 0.1^{a}	0.8 ± 0.6^{a}	0.2 ± 0.1^{a}

Different superscripts define statistically different means before and after treatment, per Ag-soldering alloy ($p < 0.05$).

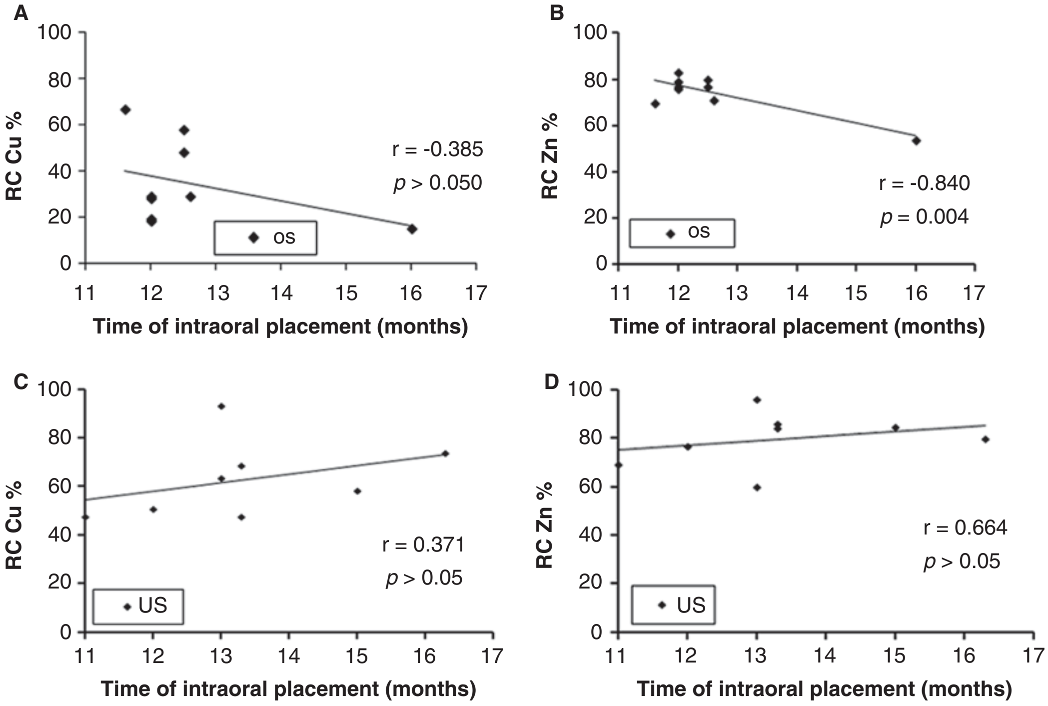

Figure 6. Graphical representation of the relative remaining concentrations (RC%) of Cu and Zn for OS (A, B) and US (C, D) after the intra-oral exposure (for $t = 0$, RC% = 100%).

alloys used in this study requires further analysis on metallographic prepared specimens. This analysis will provide essential data for the estimation of *in vivo* decomposition mechanism.

The lack of correlation between the RC% (apart from Zn in OS) (Figure 6) and the treatment duration has a 2-fold explanation. First, the decomposition procedure is dominated by factors that have not been controlled in this study (i.e. dietary habits, microstructural differences of the alloys, etc.) and, second, the Cu- and Zn-rich regions prone to corrosion have already been dissolved and, thus, the phenomenon slows down or stops after a certain period of time in each appliance. The last approach fits well to recently published data showing that the concentration of Cu and Zn in patients' saliva has a decreasing trend over time [17]. Definitely, this is not the case for Zn in OS, where a continuous decrease in Zn concentration over the time was detected, implying a slower kinetic in Zn degradation compared to Cu. In the present study, it was not possible to measure the elemental content at intermediate periods, mainly due to ethical reasons (need of multiple removals and replacements of the appliances) and, thus, no conclusions on the kinetics of this phenomenon can be drawn.

Corrosion of the silver joint may cause mechanical decay and failure of the assembly. According to the results of the present study, no failures were found during treatment, resulting in a survival rate of more than 12 months. This finding is in accordance with previous studies where survival rates of 14 and 18 months have been documented for space maintainers of similar design [21]. However, Tulunoglu et al. [7] and Quideimat et al. [22] have reported shorter survival rates of 6 and 7 months, respectively, implying the need for replacement of space maintainers and, thus, the patient is exposed to additional uptake of released elements.

Since no statistical differences existed in the mean values of intra-oral exposure time between space maintainers fabricated with different soldering alloys, direct comparison of elemental alterations between the two Ag soldering alloys is feasible. According to Table IV the decrease of Cu content was higher after the intra-oral exposure of OS, a finding that may be attributed to the lower initial Ag content of OS compared to US and/or microstructural differences. Despite the fact that there was no statistical difference between the Ag soldering alloys in the wt% of Zn reduction, there

Table IV. Mean values and standard deviations of the decrease in the content of Cu and Zn (wt%) after intra-oral exposure in the Ag soldering alloys tested.

	OS	US
Cu	14.5 ± 5.4^{a}	5.7 ± 2.6^{b}
Zn	6.0 ± 2.9^{a}	4.3 ± 2.5^{a}

Different superscripts are used for defining statistical differences per Ag soldering alloy ($p < 0.05$).

is a correlation between the RC% of Zn and the duration of treatment in OS. Comparing the decrease in the content of Cu and Zn, it may be assumed that Zn disintegrates at a lower rate than Cu in OS, which may be appended to a variety of microstructural properties such as phase volume, micro- and macro-segregation, etc.

As the exact amount of Cu and Zn reduction is not feasible based on the data of the current study, no assumptions can be made for the daily intake of Cu and Zn from the degradation of the solder in space maintainers. Consequently, the potential toxicity of these assemblies must be studied in more detail. The clinical implication of this study is related to the fact that the majority of failures in space maintainers occur at the area of the joint [7,8,22] and, consequently, the intra-oral degradation of these materials may be considered as one of the contributing factors to these failures. In any case the replacement of a failed device before the end of the treatment exposes the patient to additional uptake of released elements. The adverse effects of excess intake of Cu is associated with gastrointestinal irritation, liver damage and neurodegenerative processes [23], while excess intake of Zn limits Fe absorption, causes some functional impairment in the immunological response and reduces the HDL cholesterol [23]. Contrary to the aforementioned concerns, other authors [24] do not share the some anxiety for the release of Cu and Zn from soldering alloys, claiming that both elements are needed for bodily functions. Indeed both elements belong to nutritionally essential metals with Recommended Dietary Allowance (RDA) stands for the intake at which the risk of inadequacy is small (2 ~ 3%) 0.44 mg/day and 4 mg/day [23] for Cu and Zn, respectively. In contrast, the tolerable upper intake level UL above which the risk for adverse effects increases has been estimated to be 3 mg/day for Cu and 12 mg for Zn. All the aforementioned values are referred for children between 4–8 years old and the values are much lower compared to those for adults. However, the above limits are associated only with the acute toxicity overlooking the ability of metal ions to cause long-term damage associated with sub-clinical or chronic damage [17]. However, beyond the effect of diffusion of these elements in the body their accumulation at the adjacent tissues has been associated with allergic reaction [25] and oral lesions [26].

The results of this study verified the initial concerns based on experimental data [3] for the inferior electrochemical properties of Ag-based alloys and the possibility for their intra-oral decomposition. Definitely the application of these alloys for this purpose is far from ideal and new materials or new joining techniques should be implemented to overcome this complication and eliminate any possible biological consequences.

Conclusions

- The Ag-based alloys used for the manufacturing of space maintainers demonstrated increased roughness and significantly decrease of Cu and Zn contents after intra-oral exposure.
- OS demonstrated a higher decrease in Cu content compared to US.
- The decomposition of Cu and Zn did not show any correlation with the duration of treatment (apart from Zn in OS).

***Declaration of interest*:** The authors alone are responsible for the content and writing of the paper.

References

[1] Zinelis S, Annousaki O, Eliades T, Makou M. Elemental composition of brazing alloys in metallic orthodontic brackets. Angle Orthod 2004;74:394–9.

[2] Vahed A, Lachman N, Knutsen RD. Failure investigation of soldered stainless steel orthodontic appliances exposed to artificial saliva. Dent Mater 2007;23:855–61.

[3] Berge M, Gjerdet NR, Erichsen ES. Corrosion of silver soldered orthodontic wires. Acta Odontol Scand 1982;40: 75–9.

[4] Matassa C. Characterization of used orthodontic brackets. In Eliades T, Brantley WA, Watts DC, editors. Dental materials in vivo: aging and related phenomena. New York: Quintessence; 2003. p 141–56.

[5] Eliades T. Orthodontic brackets. In Brantley WA, Eliades T, editors. Orthodontic materials. Stuttgart: Thieme; 2001. p 146–7.

[6] Zinelis S, Soteriou D, Ntasi A, Papagianoulis L, G. E. Elemental characterization of contemporary Ag-based soldering alloys. 23rd Congress of the International Association of Paediatric Dentistry; Athens; 2011.

[7] Tulunoglu O, Ulusu T, Genc Y. An evaluation of survival of space maintainers: a six year follow up study. J Contemp Dent Pract 2005;6:1–8.

[8] Rajab LD. Clinical performance and survival of space maintainers: evaluation over a period of 5 Years. J Dent Child 2002; 69:156–60.

[9] Baroni C, Franchini A, Rimondini L. Survival of different types of space maintainers. Pediatr Dent 1994;16:360–1.

[10] Qudeimat MA, Fayle SA. The Longevity of space maintainters: a retrospective study. Pediatr Dent 1998; 20:267–72.

[11] Mueller HJ, Greener EH, Marker BC. Corrosion by external polarization of soldered orthodontic wires in cleanser solutions. Am J Orthod 1979;76:555–64.

[12] Eliades T, Zinelis S, Eliades G, Athanasiou AE. Characterization of as-received, retrieved, and recycled stainless steel brackets. J Orofac Orthop 2003;64:80–7.

[13] Darabara M, Bourithis L, Zinelis S, Papadimitriou GD. Assessment of elemental composition, microstructure, and hardness of stainless steel endodontic files and reamers. J Endod 2004;30:523–6.

[14] Heidemann J, Witt E, Feeg M, Werz R, Pieger K. Orthodontic soldering techniques: aspects of quality assurance in the dental laboratory. J Orofac Orthop 2002;63:325–38.

[15] Staffolani N, Damiani F, Lilli C, Guerra M, Staffolani NJ, Belcastro S, et al. Ion release from orthodontic appliances. J Dent 1999;27:449–54.

[16] Kuhta M, Pavlin D, Slaj M, Varga S, Lapter-Varga M, Slaj M. Type of archwire and level of acidity: effects on the release of

metal ions from orthodontic appliances. Angle Orthod 2009; 79:102–10.

[17] Freitas MP, Oshima HM, Menezes LM. Release of toxic ions from silver solder used in orthodontics: an *in-situ* evaluation. Am J Orthod Dentof Orthop 2011;140:177–81.

[18] Feng J, Zhang L. Interface structure and mechanical properties of the brazed join of TiC cermet and steel. J Eur Ceram Soc 2006;26:1287–92.

[19] Warinsiriruk E, Phung-on I. Microstructure of Induction Brazed Interface between Cobalt-based Alloy and Martensitic Stainless Steel using Ag-Cu-Zn filler metal. Asian Intern J Sci Techn Prod Manuf Eng 2010;3:41–4.

[20] Ardashnikova EI, Eliseev AA, Sokolov VI, Chekmareva PP. Effect of microstructure on the mechanical properties of cast silver solders. Khimicheskoe i Neftyanoe Mashinostroenie 1978;8:29–30.

[21] Baroni C, Franchini A, Rimondini L. Survival of different types of space maintainers. J Pediatr Dent 1994;16:360–1.

[22] Qudeimat MA, Fayle SA. The longevity of space maintainers: a restrospective study. Pediatr Dent 1998;20:267–72.

[23] Food and Nutrition Board. Dietary reference intakes for vitamin A, vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium and Zinc. DRI. Washington, DC: National Academic Press; 2000. p 224–52; 442–89.

[24] Zahrowski JJ. Silver solder toxicity? Show me the evidence. Am J Orthod Dentof Orthop 2012;140:756–7; author reply 7–8.

[25] Schuster G, Reichle R, Bauer RR, Schopf PM. Allergies induced by orthodontic alloys: incidence and impact on treatment. Results of a survey in private orthodontic offices in the Federal State of Hesse, Germany. J Orofac Orthop 2004;65:48–59.

[26] Bishara SE. Oral lesions caused by an orthodontic retainer: a case report. Am J Orthod Dentof Orthop 1995;108: 115–17.