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Multitechnique characterization of conventional and experimental Ag-based brazing alloys for orthodontic applications

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Objectives. To characterize the microstructure, mechanical properties, ionic release and tarnish resistance of conventional and experimental Ag-based soldering alloys for orthodontic applications.

Methods. Disk shaped specimens were prepared from four commercial Ag based soldering alloys [Dentaurum Universal Silver Solder (DEN), Orthodontic Solders (LEO), Ortho Dental Universal Solder (NOB), and Silver Solder (ORT)] and four experimental alloys Ag12Ga, Ag10Ga5Sn, Ag20In and Ag7Sn. The elemental composition and microstructure was determined by SEM/EDX and XRD analysis, while the mechanical properties were determined by Instrumented Indentation Testing. Ionic release of Ag, Cu, Zn, Ga, In and Sn was determined by ICP-EAS in 0.9% NaCl and Ringer's solutions after 28, 49 and 70 days. Tarnish resistance was also tested and colorimetry was applied to quantify the differences in color (DE) before and after immersion in testing media. DSC was used to determine the melting range of the experimental alloys. Mechanical properties, ionic release and DE were statistically compared by ANOVA and Holm-Sidak multiple comparison test ($a = 0.05$).

Results. All commercially alloys belong to the Ag–Zn–Cu ternary system and consist a Ag rich face centered cubic (FCC) and Cu (FCC) phase. The former is the predominant phase also in experimental alloys. Conventional alloys demonstrated higherhardness, less ductility and lower melting rangers compared to experimental alloys. Immersion testing revealed the release of Cu and Zn ions from the commercially alloys and Ga ions from AgGa and AgGaSn while no ionic release was identified for AgIn and AgSn. All alloys failed tarnish testing according to ISO 10271 showing DE values much higher than the clinical acceptable limit (3.7).

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Significance. The conventional Ag based soldering alloys showed substantial differences in their microstructure, mechanical properties and ionic release, and thus different clinical performance is anticipated. Ga, Sn and In might be employed as alloying addition to modify the properties of Ag brazing alloys.

1. Introduction

Brazing of dissimilar stainless steel (SS) alloys (i.e orthodontic wires and bands) is mandatory in the manufacturing of orthodontic appliances such as headgears, space maintainers, brackets, hyrax appliances and others [1–3]. Despite their extensive use in these orthodontics devices, the release of metallic toxic ions from them due to corrosion or wear mechanisms [4] is a constant concern of modern dental literature [5,6].

All contemporary Ag based brazing alloys belong to the Ag–Cu–Zn ternary system [7] and many in vitro studies have found out that this ternary system is vulnerable to Cu and Zn release [8–12] and coupling with SS alloys may trigger galvanic action [13]. Indeed a previous study reported that the potential difference between SS and Ag brazing alloys is almost double the threshold for galvanic corrosion [9]. Experimental findings were recently confirmed by two different studies based on clinical data. Measuring the concentration of metallic ions in human saliva up to 60 days after the placement of Hyrax appliances, Freitas et al. [1], reported the release of Cu, Zn and Cd from Ag brazing alloys. In an other study, the intraoral decomposition of two commercially available Ag brazing alloys were proven by comparing their elemental composition before and after intraoral aging [3].

The clinical implications of these findings are twofold. The decomposition of Ag brazing alloys has been associated with the mechanical degradation of the joint itself and thus with the early failure of orthodontic devices, especially of space maintainers [14–19]. In this scenario the failed appliance is replaced by a new one, increasing the uptake of released elements [3]. The uptake of Cu and Zn by the human body is associated with different biological consequences. The intake of Cu beyond the acceptable oral limit [20] is associated with liver and gastrointestinal complications [21] and atherogenesis [22], while it may trigger oxidative damage and carcinogenesis and neurodegenerating processes [21,23–26] through a mechanism forming reactive oxygen species (ROS). The excess intake of Zn has been proven to be cytotoxic for fibroblasts [27] and it has also been implicated in reduced HDL cholesterol and immunological response [28]. In addition beyond the adverse effect of diffusion of Cu and Zn in the body the accumulation of these elements at the adjacent tissues has been associated with allergic reaction [29] and oral lesions [30]. In any case the decomposition of a biomaterial in the oral cavity is far beyond the ideal.

In order to overcome the aforementioned limitations new formulations of Ag brazing alloys without Cu and Zn should be developed and thus the aim of this study was the comparative analysis of conventional and experimental alloys. The null hypothesis was that experimental alloys will show better properties than conventional ones.

2. Materials and methods

2.1. *Specimen preparation*

Four commercially available Ag brazing alloys for the manufacturing of space maintainers and four experimental alloys were tested. The four experimental alloys were prepared in an induction melting machine (Ducatron S3, UGIN' Dentaire, Seyssins, France) by melting pre-weighted quantities in a silicate crucible (UGIN' Dentaire) appropriate for melting precious metal alloys. The pre-weighted quantities were inductively melted and left to cool to ambient temperature in the silicate crucible. For the preparation of the alloys the following pure elements were used: Ag 99.99 wt% (AG006105/4, Goodfellow, Huntingdon, England), Ga 99.99 wt% (S97020, Johnson Matthey GmbH, Karlsruhe, Germany), Sn 99.995 wt% (SN006102/4, Goodfellow) and In 99.99 wt% (9300, Johnson Matthey GmbH). Table 1 shows the elemental composition, the melting range of the commercial alloys according to their manufacturers and the code used for them in this study. Also shown the experimental alloy compositions.

All commercial alloys are provided as wires to facilitate the brazing procedure. A small quantity of each commercial alloy was melted in a reducing flame and left to solidify in a circular mould. Eighteen disk shaped samples (approximately 6 mm in diameter and 2 mm in height) were prepared from each experimental alloy. The wires of NOB and DEN contain the requested flux as a separated layer in the wire structure, while for LEO and ORT the corresponding fluxes from their manufacturers were used (Leone fluoride flux paste (Leone S.p.a, Italy), and Ortho Technology TruFlow Orthodontic Flux (Ortho Technology) respectively). One sample from each group was kept as cast and the rest were embedded in an epoxy resin (Caldofix, Struers, Ballerup, Denmark). Afterwards the specimens of all groups were ground through 4000 grit silicon carbide paper under water cooling and polished with 1 μm diamond suspension (DiaPro suspension solution, Struers) in a grinding/polishing machine (Dap-V, Struers). Finally the samples were cleaned in an ultra sonic bath with ethanol for 3 min and then rinsed with water and dried.

2.2. *Differential scanning calorimetry (DSC)*

The melting temperature range of the experimental alloys was determined by DSC analysis using a differential photo calorimeter analyzer (STA 449C, NETZSCH, Selb, Germany) equipped with a UV 5000 lamp. The measurements were pre-