Corrosion in a neutral artificial saliva of metallic alloys used for frameworks strengthening fixed partial dentures

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ABSTRACT
The frameworks supporting the ceramic part of a fixed dental prosthesis are composed of the assemblage of alloys of different natures for soldering reasons. Post-solder joints, and eventually the extremities of parent alloy parts, are exposed to the buccal milieu and can suffer individual or galvanic corrosion. Eight types of parent alloys and four types of solder alloys were immersed in a pH=7.4 artificial saliva (Afnor norm) and their corrosion behaviours were characterized by the measurement of their potential and linear polarization according to the Stern-Geary method. Open circuit potentials are high (±0mV/NHE) to very high (+300mV/NHE) due to the immunity of the noblest elements or to the passivation of the others. Polarization resistances are high (several tens kΩ·cm²) or very high (more than 1 MΩ·cm²), and consequently corrosion currents very low (levels: 1μA/cm² down to 10μA/cm²). Galvanic currents are not attended between parent and post-solder alloys in most cases since the E_ocp are close to one another. However there are three assemblages which can potentially lead to low galvanic currents.

INTRODUCTION
A fixed partial denture can be composed by a ceramic or “cosmetic” part (which can be seen) and a not visible metallic framework which allows the prosthesis to resist compressive stresses. These frameworks are manufactured first by joining “parent alloys” together using a primary brazing alloy, which leads to prosthesis elements after having been covered by ceramic and undergone specific heat treatment. Elements are thereafter joined again together by soldering the frameworks extremities using another brazing alloy, a “post-solder alloy”, and then one obtains the final framework supporting the prosthesis (Figure 1). When the prosthesis is positioned in mouth some parts of the frameworks can appear and then can be exposed to the buccal milieu. Notably the post-solder joint is usually not covered by ceramic and it can be in contact with saliva. In addition, this is sometimes also true for the extremities of the parts of parent alloy. The electrochemical behaviours of the two types of alloys, parent alloy and post-solder alloy can be different and their assemblage may lead to galvanic corrosion for one of them, with as possible result a weakening of the
framework after a sufficiently long time.

In this study we will characterize the separated electrochemical behaviours of the parent alloy and its usually post-solder alloy (from a same usual couple of alloy in practice), by applying the Stern-Geary method (measurement of polarisation resistances and calculation of corrosion currents\(^1\)). This will permit to know their own resistances against possible corrosion and to qualitatively classify them on an increasing nobility scale to anticipate the possibility of galvanic corrosion\(^2\) between the two and the order in such case.

**EXPERIMENTAL**

**The studied alloys**

The alloys were already metallographically characterized in a previous work\(^7\). There are eight parent alloys and four post-solder alloys. Among the parent alloys five are especially rich in noble elements (Au, Pt, Pd), one alloy is based also on a noble metal (Pd) but with a not very high content in this element and two alloys based on both Ni and Cr. The four post-solder alloys are themselves based on gold. All chemical compositions are displayed in TABLE 1, with indication of the parent-alloys ↔ post-solder alloys associations.

The parent alloys were elaborated by investment casting. The obtained parallelepipedic ingots (10×10×1 mm\(^3\)) were cut in order to obtain four parts, the dimensions of which were 5×5×1 mm\(^3\). Solder rods were melted in a crucible, heated by a gas-oxygen torch, solidified in order to obtain half-ball-like ingots weighing about 1 gram. All the alloys were heat-treated in order to reproduce what it is done in practice (heat-treatment parameters already given in a previous work\(^7\)). The electrodes were realized by tin-soldering a sample per alloy to an electrical wire, and by embed-

<table>
<thead>
<tr>
<th>TABLE 1 : Chemical compositions of the studied alloys (in wt.%; manufacturer’s data)</th>
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<tr>
<td><strong>Parent alloys</strong></td>
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<tr>
<td>Sign</td>
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<tr>
<td>dSIGN98</td>
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<tr>
<td>Aquarius</td>
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<td>dSIGN91</td>
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<tr>
<td>Lodestar</td>
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<tr>
<td>Pisces Plus</td>
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<td>4ALL</td>
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**Figure 1 : Post-solder alloy appearing at the junction of two prosthetic elements; SEM/BSE micrograph of the local microstructure (Scanning electrons microscope, back scattered electrons mode)**

**Electrochemical experiments**

The used apparatus was composed of a potentiostat / galvanostat model 263A (Princeton Applied Research), driven by the software M352 of EGG/Princeton. The electrolyte chosen to simulate saliva was an Afnor artificial saliva\(^8\) (composition given in TABLE 2). Its pH was equal to 7.4 and its temperature maintained at 37 ± 1°C thanks to a Julabo F32 device and a special electrochemical cell.

The electrode made from the studied alloy played the role of Working Electrode and the Counter Electrode
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A platinum disk-like electrode. The reference potential was given by a Saturated Calomel Electrode (241.5 mV/NHE). The open circuit potential (E<sub>ocp</sub>) was measured with continuous measurement of the open circuit potential (E<sub>ocp</sub>) versus the SCE electrode. Polarization of the alloy between E<sub>ocp</sub> - 10 mV and E<sub>ocp</sub> + 10 mV at 10 mV/min for the measurement of the polarization resistance (R<sub>p</sub>). Repetition of 1.

RESULTS AND DISCUSSION

Open circuit potential over two hours

The E<sub>ocp</sub> was recorded at the beginning of the experiment, just in the first minutes after immersion, after one hour of immersion (just before the measurement of the first polarization resistance) and one hour after again (just before the second Rp measurement). The results are presented with the form of a histogram in figure 2. In the case of the noblest alloys (from dSIGN98 to W), between the two sets of measurement, it is for the initial E<sub>ocp</sub> measurements that the reproducibility is the worst. This lack of reproducibility for these noble alloys was maximal here for dSIGN98 (+257 and +293 mV/NHE for the two tests) but, in contrast, very small for Aquarius Hard (+293 and +295 mV/NHE). Thereafter (at t = 1 hour and t = 2 hours) the reproducibility is much better. However, the error bars (calculated from only two values it is true) do not allow seeing any evolution over these two hours, neither increase nor decrease. The reproducibility is especially bad in the cases of the dSIGN98 and of the not noble Pisces Plus, for the three successive values of E<sub>ocp</sub>, while this is much better for the other not noble alloy, 4ALL, for which one can distinguish a constant increase in potential over the two hours of immersion.

Except dSIGN98 for which E<sub>ocp</sub> is initially high but seems decreasing, the open circuit potential is very high...
(just under +300mV/NHE) for the noblest alloys, by comparison with the less noble dSIGN59 (fluctuations around +100mV/NHE) and the two nickel/chromium-based alloys (just under 0 mV/NHE).

Concerning the post-solder alloys, the reproducibility, which is rather good (except for the .615 alloy), allow seeing that the potential is almost constant over the two hours of immersion (Figure 3). As for the noblest parent alloys, the open circuit potentials for these gold-rich post-solder alloys are all initially very high and they remain at this level during the whole 2 hours-period.

Polarization resistance over two hours

The Rp were also measured along the 2 hours-immersion, but only two times: at t = 1 hour and t = 2 hours. Indeed, at t = 0 the whole electrochemical cell with its three electrodes is not yet at equilibrium. For each of the two instants two values are available, and they led, as for the \( E_{ocp} \) potentials, to the calculation of an average value and a standard deviation. This one is not really significant because resulting from only two values. However, for the parent alloys, the error bars are rather small, which seems showing a tendency for a good reproduciblity (which was generally confirmed by comparing the two numerical values of each Rp for a same parent alloy). With 1 M\( \Omega \) cm\(^2\) and more, the values of the polarization resistances are very high for four out of the five noblest alloys (Aquarius Hard, dSIGN91, Lodestar and W) while, in contrast, the Rp values for dSIGN98 are ‘only’ 30 to 50k\( \Omega \) cm\(^2\) (Figure 4). The Rp values recorded for the less noble dSIGN59 alloy are also low (the same levels as dSIGN98) while, curiously, the two not noble alloys, 4ALL and Pisces Plus gave higher values of Rp: between 200 and 450k\( \Omega \)cm\(^2\). The Rp values of the four post-solder alloys are also rather low (Figure 5), since they are at the same level as dSIGN98 and dSIGN59.

Corrosion currents

Corrosion currents, more precisely current densities of corrosion \( I_{corr} \), were estimated from these values of polarization resistances. The results are displayed in figure 6 for the parent alloys and in figure 7 for the post-solder alloys. Since the values obtained for \( I_{corr} \) were extremely variables among all the twelve alloys, it was chosen to consider the decimal logarithm of these values, and in order to have the bars in the upper part of the histograms, to consider the absolute value of these logarithms. Thus, the histograms must be red as follows: the higher the bar, the lower the corrosion rate.

Considering the parent alloys, the \( I_{corr} \) values are extremely low for Aquarius Hard, dSIGN91, Lodestar and W, with about 10\(^{-8}\)Acm\(^{-2}\), as is to say only several nano-amperes per cm\(^2\). Corrosion rates are also extremely low for the two nickel/chromium-based alloys, for which the values of \( I_{corr} \) are of the same level. For the two more or less noble alloys, dSIGN98 and dSIGN59, for which the Rp values were significantly lower than for the preceding other noble parent alloys, the corrosion rate is nevertheless very low too, with only less than 1\( \mu \)A cm\(^{-2}\).

The corrosion rates for the four post-solder alloys are also low, with \( I_{corr} \) values positioned around the micro-ampere per cm\(^2\).

General commentaries

When immersed in the Afnor saliva the alloys are all at a high or very high value of \( E_{ocp} \) and they remain at these potentials at least during several hours. This is true for the alloys, parent or post-solder, which are especially rich in noble elements as gold, platinum or
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Figure 4: Evolution of the polarization resistances over 2 hours, in the case of the parent alloys (two sets of measurement)

Figure 5: Evolution of the polarization resistances over 2 hours, in the case of the post-solder alloys (two sets of measurement)

Figure 6: Evolution of the absolute value of log(I_{corr}) deduced from the Rp values, over 2 hours in the case of the post-solder alloys (two sets of measurement)

Figure 7: Evolution of the absolute value of log(I_{corr}) deduced from the Rp values, over 2 hours in the case of the parent alloys (two sets of measurement)

palladium, but with nevertheless two noticeable exceptions: dSIGN98 and dSIGN59. The two not noble alloys, 4ALL and Pisces Plus are at potentials significantly lower than the preceding values, but their E_{ocp} are not very low since close to 0mV/NHE to which their potentials progressively increase along the 2 hours-immersion.

It can be interesting to compare these values of potential to the Pourbaix’s diagrams of each main element present in the chemical composition of the alloys. The domains to which belong the different points (E_{ocp}; pH=7.4) are given in TABLE 3. One can see in this table that the noblest elements are always in their immunity domains (Au\(^\circ\), Pt\(^\circ\), Pd\(^\circ\), and Ag\(^\circ\) too), even for the two alloys dSIGN98 and dSIGN59 the potentials of which are not so high. The other main elements belonging to the noble parent alloys are in a passive state: Ga\(^2+\), In\(^3+\), Sn(OH)\(_4\) and Zn(OH)\(_2\). This is also true for the not noble alloys, despite their lower E_{ocp}: Ni(OH)\(_2\) and Cr(OH)\(_3\). If the third main element of Pisces Plus is also passivated in these conditions (WO\(_3\)) the molybdenum present in 4ALL should be in an active state and dissolved in the electrolyte in the anionic MoO\(_4^{2-}\) specie. However, since this element is partly included in solid solution in the Ni-Cr matrix and only a part of Mo is more available in the grain boundaries, one can reasonably think that after a very short time of oxidation, either it has disappeared from the surface or it has been more probably covered by the Cr(OH)\(_3\) passivation scale. This can explain why the polarization resistances of all these alloys were high (dSIGN98 and dSIGN59, probably due to Zn) or very high (the other noble alloys and the nickel/chromium alloys), revealing very low or extremely low corrosion currents.

Concerning the post-solder alloys, thanks to very high open circuit potentials their constitutive elements are either in their immunity domains (Au, Ag\(^\circ\)) or in their passivation domains (Ga\(_2\)O\(_3\), In\(_2\)O\(_3\), Cu\(_2\)O or Cu(OH)\(_2\), Zn(OH)\(_2\)). In contrast their Rp are not very high and I_{corr} values not extremely low, probably due to the corrosion of Cu and Zn (as dSIGN98 and dSIGN59) not so slow.

CONCLUSIONS

The dental alloys studied here are very resistant against corrosion by the Afnor artificial saliva at human
body temperature. This is due to the high contents in noble elements but also to the passivation of the other elements present in their chemical compositions. In the case of the two nickel-chromium alloys, the passivation of the base elements (probably more Cr than Ni, as in austenitic stainless steels) allows them to reach interesting levels of corrosion resistance which are as high as the ones of the noblest alloys. However the latter can be perhaps potentially more threatened by a possible rupture of the passive film. The open circuit potential levels are generally high and of a same level for most of the alloys, which let think that no serious galvanic corrosion can appear. Nevertheless, such a problem remains possible for the assemblages dSIGN59 0.615 or nickel-chromium alloys ↔ LFWG but with probably extremely low galvanic currents.

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