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## Influence of the pH and of the chloride concentration on the corrosion of metallic alloys for frameworks reinforcing dental prostheses. Part 2: Parent alloys

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### ABSTRACT

This second part of the study deals with eight parent alloys, which are considerably more present in the frameworks reinforcing fixed partial denture, but which also are more preserved from the buccal milieu and then from possible corrosion phenomena than post-solder alloys, because covered by the ceramic part. However, to anticipate what can occur in case of emergence of parent alloy's extremities, the same electrochemical experiments as for the post-solder alloys in the first part were realized in the same three simple solutions (open circuit potential follow-ups, polarization resistance measurements followed by estimation of corrosion currents according to Stern-Geary. Here too the recorded open circuit potentials are high ( $\cong 100\text{mV/NHE}$ ) or very high ( $\cong 450\text{mV/NHE}$ ) for the high noble alloys (but significantly lower for the Pd-based and NiCr-based alloys). Generally, the elements Cu, In, Ga, Sn, Zn, Ni, Cr, ... which are not in their immunity domain as gold, platinum or palladium, are in their passivation domain and the corrosion of the alloys containing them is limited, as proven by the high and even very high values of polarization resistance (at least several  $\text{k}\Omega \times \text{cm}^2$  but often of several hundreds of  $\text{k}\Omega \times \text{cm}^2$ ). Corrosion currents are thus of only  $10\mu\text{A/cm}^2$  to  $10\text{nA/cm}^2$ .

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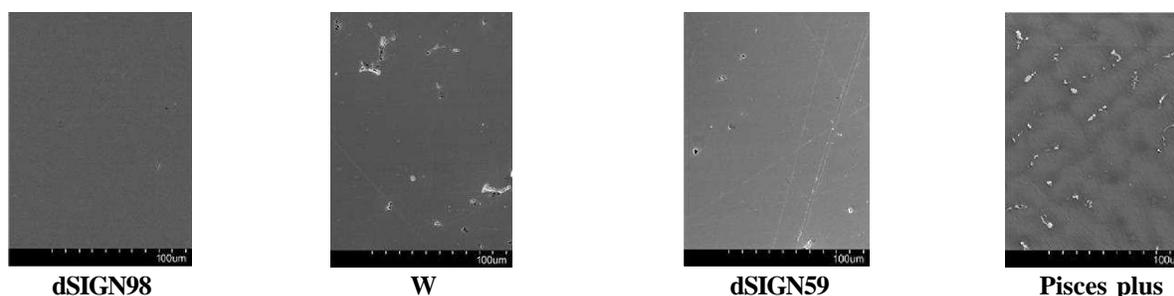
### KEYWORDS

Dental prostheses;  
Parent alloys;  
Corrosion;  
Artificial saliva;  
pH;  
Chloride concentration.

### INTRODUCTION

The frameworks bringing its mechanical resistance to ceramo-metallic fixed partial dentures are mainly constituted of metallic alloys called "parent alloys". They are joined together by primary brazing before being

covered by the ceramic ('cosmetic') part (the artificial teeth), and thereafter by secondary brazing with post-solder alloys which can emerge in the mouth. If the latter alloys are necessarily in contact with the buccal milieu, it is also possible that the extremities of the frameworks of the individual elements (the secondary soldering of



**Figure 1 : Four examples of parent alloys' microstructures, single phased one or double-phased, on the left hand for two High Noble alloys (dSIGN98 and W), on the right hand for a Noble alloy (dSIGN59) and a Predominantly Base alloy (Pisces Plus) (SEM micrographs, taken in SE mode)**

which led to the whole prosthesis), can be them too exposed to saliva. This is the reason why, after the post-solder alloys, the parent alloys needs themselves to be better known concerning their electrochemical behaviour in electrolytes simulating saliva. As for the post-solder alloys<sup>[1]</sup>, experiments of open circuit potential follow-ups (and comparison to E-pH diagrams<sup>[2]</sup> and short linear polarizations around the latter for estimating corrosion currents by applying the Stern-Geary method<sup>[3,4]</sup>, were performed in three solutions derived from a simple {9g/L NaCl – pH=7.4} classically used for the characterization of the corrosion behaviour of such dental alloys<sup>[5-7]</sup>, even by impedance spectroscopy<sup>[8]</sup>.

## EXPERIMENTAL

### The studied parent alloys; preparation of the electrodes

In this second part of the study eight parent alloys were considered. They are the parent alloys for which the post-solder alloys studied in the first part<sup>[1]</sup> are proposed by the manufacturer (Ivoclar Vivadent). Among them there are five High Noble alloys displaying a total weight content of Au, Pt and Pd together higher than 60%, a Noble alloy (Au+Pt+Pd comprised between 25 and 60%) and two Predominantly Base alloys, free of noble elements and based on nickel and chromium. Their chemical compositions are given below:

- **dSIGN98** (85.9Au-12.1Pt-2.0Zn, with possibly In, Ir, Fe, Mn and Ta, each < 1%), to be joined using the .585 post-solder alloy
- **Aquarius hard** (86.1Au-8.5Pt-2.6Pd-1.4In, with possibly Ru, Fe, Li and Ta, each < 1%), to be joined

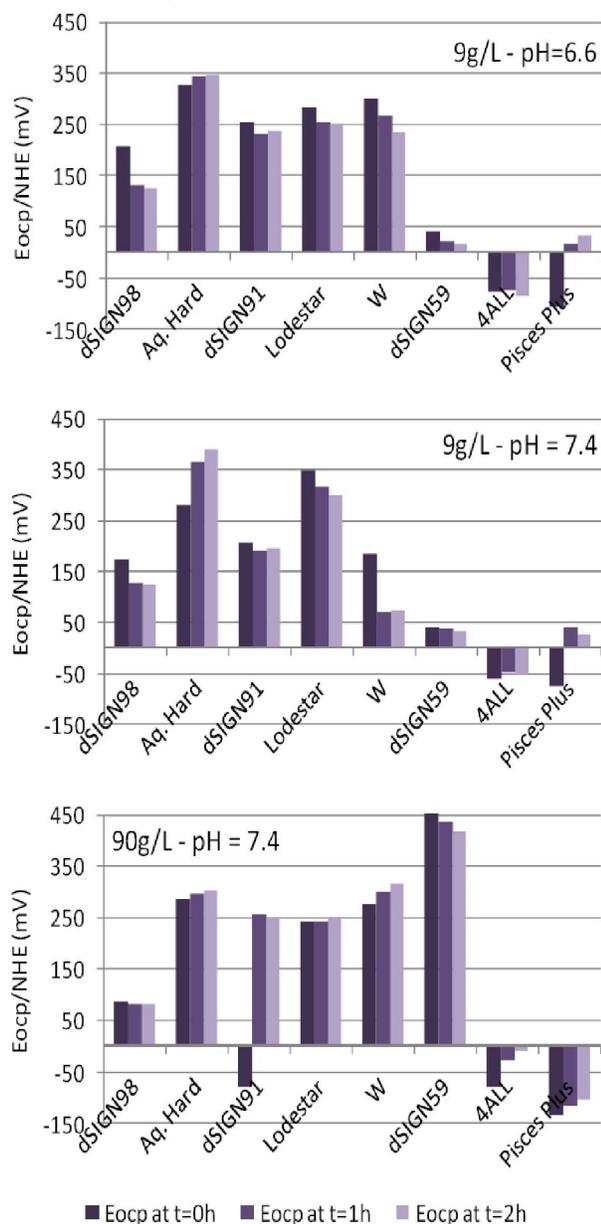
using the .650 post-solder alloy

- **dSIGN91** (60.0Au-30.6Pd-1.0Ga-8.4In, with possibly Re and Ru, each < 1%), to be joined using the .615 post-solder alloy
- **Lodestar** (51.5Au-38.5Pd-1.5Ga-8.5In, with possibly Re and Ru, each < 1%), to be joined using the .615 post-solder alloy
- **W** (54.0Au-26.4Pd-15.5Ag-1.5In-2.5Sn, with possibly Re, Ru and Li, each < 1%), to be joined using the LFWG post-solder alloy
- **dSIGN59** (59.2Pd-8.2Sn-2.7In-1.3Zn, with possibly Pt, Re, Ru and Li, each < 1%), to be joined using the .615 post-solder alloy
- **4ALL** (61.4Ni-25.7Cr-11.0Mo-15Si, with possibly Al and Mn, each < 1%), to be joined using the LFWG post-solder alloy
- **Pisces plus** (61.5Ni-22.0Cr-11.2W-2.6Si-2.3Al, with possibly Mischmetal < 1%), to be joined using the LFWG post-solder alloy

As for the post-solder alloys studied in the first part of the study, when observed using a Scanning Electron Microscope some of these alloys appear single-phased and the others double-phased, as illustrated by selected micrographs presented in figure 1 (taken using a Hitachi S4800 SEM-FEG used in Secondary Electrons mode).

These parent alloys were elaborated by investment casting, which led to parallelepipedic ingots (dimensions: 1010×1 mm<sup>3</sup>), which were cut in order to obtain four parts with dimensions: 5×5×1 mm<sup>3</sup>. As for the post-solder alloys, these parent alloys were heat-treated in order to reproduce what it is done in practice (heat-treatment parameters already given in a previous work<sup>[9]</sup>). For each alloy the electrode was realized by tin-soldering a part to an electrical wire, and by embedding in a cold resin. The metallic surfaces were pol-

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**Figure 2 : Evolution of the open Circuit Potential over 2 hours**

ished with SiC papers from 120-grit to 1200-grit, and finished by polishing with 1 $\mu$ m-alumina. The emerging metallic part of the electrode, which will be exposed to the corrosion, was thus a square of about 25 mm<sup>2</sup>.

### Electrochemical tests and measured properties

The electrochemical experiments were the same as for the post-solder alloys characterized in the first part of the study<sup>[1]</sup>. They were performed using the same apparatus (three electrodes cell, potentiostat model 263A of Princeton Applied Research, software M352 of EGG/Princeton) and the electrolytes were also the same ones:

- Distilled water added with NaCl (9g L<sup>-1</sup>), with a not-fixed pH (pH measured just before electrochemical experiment  $\cong$  6.6)
- The same solution as above but with a pH initially fixed to 7.4
- The same solution (pH rated to 7.4) but with 90g L<sup>-1</sup> NaCl

The solution temperature was also maintained at  $37 \pm 1^\circ\text{C}$  and the solutions were supposed to be in equilibrium with the laboratory air concerning the dissolved O<sub>2</sub> concentration. The working electrode, the auxiliary electrode and the potential reference electrode were here too respectively the electrode made from the studied alloy, a platinum disk-like electrode and a Saturated Calomel Electrode ( $E = 241.5\text{mV/NHE}$ ).

For these parent alloys the electrochemical experiments were here too composed of:

- Immersion of the working electrode for one hour with measurement of the evolution of the open circuit potential  $E_{\text{ocp}}$  versus the SCE electrode
- Linear polarization from  $E_{\text{ocp}} - 10\text{mV}$  to  $E_{\text{ocp}} + 10\text{mV}$  at  $10\text{mV min}^{-1}$  and determination of the polarization resistance  $R_p$
- Following of the  $E_{\text{ocp}}$  for a second hour
- Second determination of  $R_p$ .

The level of the recorded  $E_{\text{ocp}}$  follow-ups allows thereafter knowing the state in which are all elements belonging to the alloy's chemical composition (immunity, corrosion or passivation), while the measured  $R_p$  values permit to estimate the corrosion rate by calculation of the corrosion current  $I_{\text{corr}}$  by using the following relationships (Stern-Geary method):

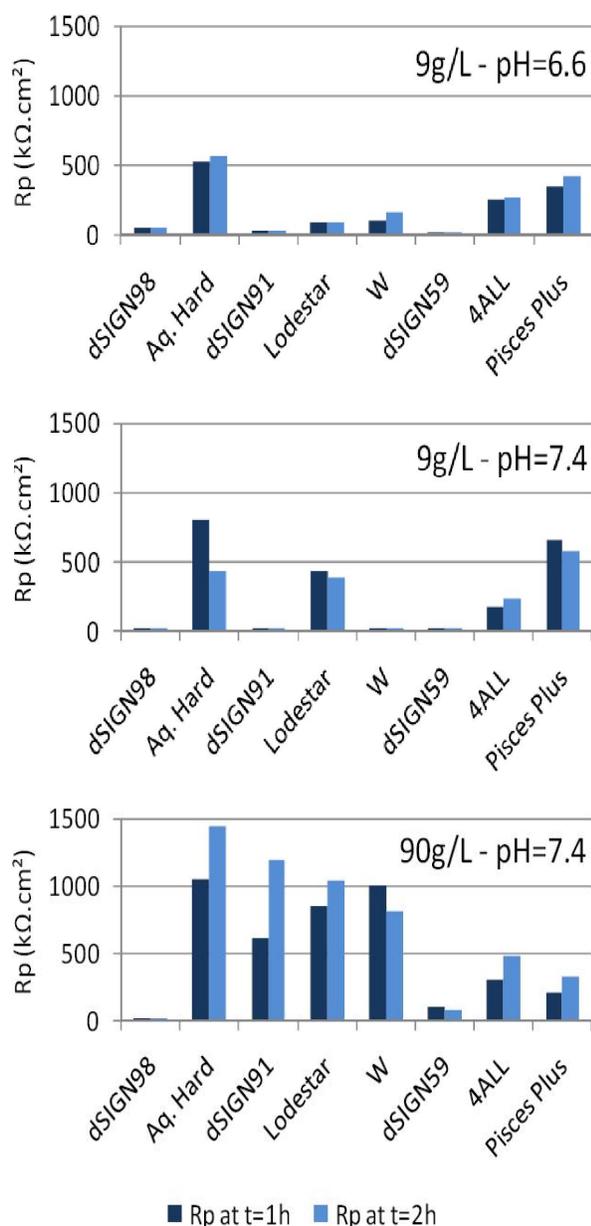
$$I_{\text{corr}} = B / R_p \text{ with } B = (\beta_a \times \beta_c) / (2,303 \times (\beta_a + \beta_c))$$

in which  $\beta_a = 2,303 \times R \times T / (0,5 \times n_a \times F)$  and  $\beta_c = 2,303 \times R \times T / (0,5 \times n_c \times F)$  ( $R_p$ : measured polarization resistance,  $B$ : calculated from the Tafel coefficients  $\beta_a$  and  $\beta_c$ ,  $F$ : Faraday's number = 96500C/Mol,  $T=310\text{K}$  ( $37^\circ\text{C}$ ),  $n_a = 2$  or  $3$  and  $n_c = 2$ ).

## RESULTS AND DISCUSSION

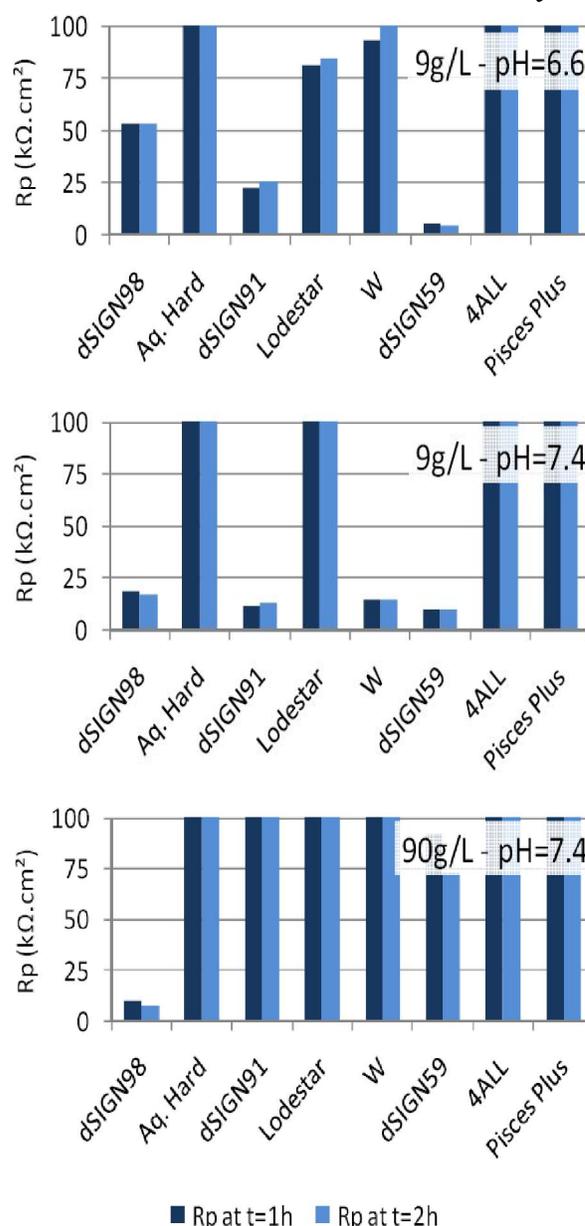
### Evolution of the open circuit potential over two hours

Here too  $E_{\text{ocp}}$  was recorded at the experiment start ("t=0h"), then after one hour of immersion (just before



**Figure 3a : Evolution of the polarization resistance over 2 hours for all the parent alloys**

the measurement of the first polarization resistance, “t=1h”) and finally one hour later (just before the second Rp measurement, “t=2h”). The measured values, presented as histograms in figure 2, first show that the  $E_{ocp}$  can be high (dSIGN98) and even very high (the other High Noble alloys), but also significantly lower (the Noble dSIGN59) and even negative (the two Predominantly Base 4ALL and Pisces Plus). Among the alloys rich in noble elements, Aquarius Hard, dSIGN91 and Lodestar constantly display a high open circuit potential while dSIGN98 is characterized by a  $E_{ocp}$  systematically lower (but positive) and W can show



**Figure 3b : Enlargement of the graphs in the low Rp domain**

also rather low potential. The less Noble palladium-based dSIGN59 also remains at a low open circuit potential, except in the especially NaCl-rich electrolyte which led for it to the highest values of  $E_{ocp}$ . It can be noticed that, by comparison with the {9g/L-pH=7.4} solution, the high NaCl concentration of the third electrolyte tends to stabilize the  $E_{ocp}$  potentials of the High Noble (except dSIGN98) and Noble alloys at very high values.

Compared to the Pourbaix’s diagrams of the different elements, all the { $E_{ocp}$ ; pH} couples indicate,; for the {1 Mol/L of dissolved ions} criterion, that the

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noblest elements (Au, Pt, Pd, Ag) are in their immunity domains while indium, gallium, zinc and tin would be in their passivation domains ( $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Sn}(\text{OH})_2$  or  $\text{Sn}(\text{OH})_4$ , and  $\text{Zn}(\text{OH})_2$ ). Concerning the Predominantly Base alloys, nickel and chromium would be also in their passivation domains ( $\text{Ni}(\text{OH})_2$  and  $\text{Cr}(\text{OH})_3$ ), as well as tungsten in the case of Pisces Plus ( $\text{WO}_3$ ). Only molybdenum is in an active state ( $\text{MoO}_4^{2-}$ ), which can explain that its  $E_{\text{ocp}}$  potential remains at a very low level whatever the solution, while Pisces Plus succeeds to passivate (increase in potential to positive values after less one hour), except in the NaCl-richest solution (in which pitting corrosion due to chlorides probably disturbs the establishment of the passivation layer).

### Polarization resistance over two hours and calculated corrosion currents

The  $R_p$  values measured at  $t=1\text{h}$  and at  $t=2\text{h}$ , deduced from the polarization curves around  $E_{\text{ocp}}$  are graphically presented as histograms in figure 3a (full scale) and figure 3b (vertical enlargement for better seeing the low values). In the two {9g/L NaCl} – containing solutions very different values of polarization resistances are shown by the alloys, especially among the noblest ones: if the Aquarius Hard (and maybe also Lodestar)  $R_p$  are constantly at a high level, the other high noble alloys display significantly lower values of  $R_p$  (but which are however of several  $\text{k}\Omega \times \text{cm}^2$  or several tens of  $\text{k}\Omega \times \text{cm}^2$ ). Except for dSIGN98, the situation is greatly improved when the chlorides concentration is multiplied by ten since several hundreds of  $\text{k}\Omega \times \text{cm}^2$  are reached in this electrolyte. The  $R_p$  of dSIGN59 is also significantly improved in this third solution. Paradoxically the polarisation resistances of the two nickel-based alloys, 4ALL and Pisces Plus, are good whatever the considered studied solution, with systematically several hundreds of  $\text{k}\Omega \times \text{cm}^2$ .

By considering the previous values of  $E_{\text{ocp}}$  potentials and the corresponding average valences of the ions, oxides or hydroxides of the not noble elements ( $n_a = 2, 3$  or  $4$ ), one can assess, accordingly to the Stern-Geary method, the values of  $\beta_a$ , and then, supposing that  $n_c = 2$  (reduction of the dissolved oxygen considered as the main oxidant), the values of  $B$  and finally  $I_{\text{corr}}$  using the measured  $R_p$ . The obtained results are displayed as histograms in figure 4. Despite the differences of  $R_p$

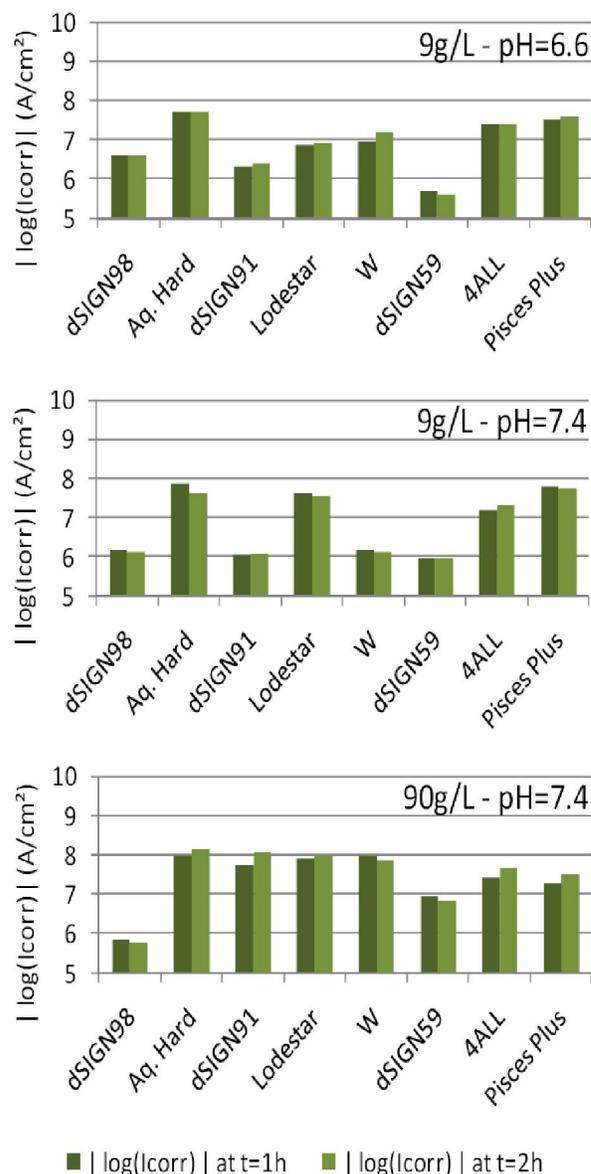


Figure 4 : Evolution of the corrosion current over 2 hours for all the parent alloys

values previously seen (but which are all at least of several  $\text{k}\Omega \times \text{cm}^2$ ), the corrosion currents are all low (lower than  $10 \mu\text{A}/\text{cm}^2$ ), or very low (until  $10\text{nA}/\text{cm}^2$ ), accordingly of course with the repartition of the high and very high values of polarization resistances.

### General commentaries

The commentaries which can be done about the electrochemical results obtained for the parent alloys are globally similar to the ones already done in the first part of the study. Indeed the eight parent alloys studied here display good behaviours, shown by high to very high open circuit potentials and values of polarization

resistance. Here too significant differences were be noticed between the alloys, with notably polarization resistances spread over a wide interval, from 5 to almost  $1500\text{k}\Omega \times \text{cm}^2$ , with consequently too an extended interval of corrosion currents.

When one compares the parent alloys to one another it appears difficult to correlate the  $E_{\text{ocp}}$  levels and  $R_p$  values with the total amount of noble elements. Indeed, on the one hand the richest alloy in noble element (dSIGN98) is among the less resistant alloys and on the other hand the not noble parent alloys (Pisces Plus notably) display polarization significantly high. For the latter, despite open circuit potentials a little low by comparison to the noble alloys, the development of a passivation layer probably constituted of  $\text{Cr}(\text{OH})_3$  or chromia allows them to very correctly resist corrosion. Indeed the increase in  $E_{\text{ocp}}$  potential of Pisces Plus (when chlorides anions are not too present, i.e. for the two first solutions) clearly shows that this alloy is being covered by a passivation layer during the first hour of immersion. In contrast, in the electrolyte containing 90g/L of NaCl, pitting corrosion obviously delays the establishment of this protection and the free potential does not increase so much. In the case of the other not noble alloy, the possibility of oxidation of molybdenum (present in its chemical composition in rather great quantity) into anions  $\text{MoO}_4^{2-}$ , seems preventing a so efficient protection in the two 9g/L NaCl solutions.

The corrosion behaviours of the High Noble and Noble alloys containing Zn are apparently disabled by the oxidation of this very oxidizable element (dSIGN98: 2wt.% Zn, dSIGN59: 1.3wt.%). The same remark can be done concerning the alloys containing tin (W, dSIGN59 again). In contrast the relatively low  $E_{\text{ocp}}$  and  $R_p$  displayed by dSIGN91 in the two solutions containing 9g/L of NaCl are more difficult to explain.

To finish, it can be noticed that the same effect of a tenfold chlorides concentrations leads here too, as for the post-solder alloys<sup>[1]</sup>, to a curious apparent improvement of the corrosion behaviour of the alloys (better  $R_p$ ), except the ones the good corrosion resistance of which is due to the development of a passivation scale of chromium oxide or hydroxide (the two PB alloys). Inversely, a high chlorides concentration led here to increase  $E_{\text{ocp}}$  while it lowered these potentials for the post-solder alloys.

## CONCLUSIONS

Globally, results similar to the ones obtained in the first part of this study about the post-solder alloys have been obviously found here for this selection of parent alloys. In general, with high to very high free potentials and polarization resistances, all the parent alloys, as all the post-solder alloys, are very resistant - and some of them extremely resistant - against corrosion, even for varying pH and chlorides concentrations. This is particularly important for the post-solder alloys, necessarily exposed to the buccal milieu (in contrast it is not systematically the case for the parent alloys) since a too severe corrosion may aggravate the metallurgical health of the secondary brazed joint which is already the weakest part of the framework<sup>[10,11]</sup>.

## ACKNOWLEDGEMENTS

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