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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 1: Soldering alloys

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ABSTRACT

The making of frameworks reinforcing the ceramic part of fixed partial denture involves joining alloys of different natures. Some of the solder joints, made of post-solder alloys, can be in contact with buccal saliva and then possibly suffer corrosion. In this work electrodes were prepared from four soldering alloys classically used after ceramic deposit, and were immersed in three different simple solutions derived from an artificial saliva usually used for such tests of dental materials. Their corrosion behaviours were characterized by the measurement of the open circuit potential and their polarization resistances according to the Stern-Geary method for estimating their corrosion currents. The recorded open circuit potentials are high ($\cong 100$mV/NHE) or very high ($\cong 300$mV/NHE) and they generally depend both on the chemical composition of the studied soldering alloy as well as on the electrolyte (its pH: 6.6 or 7.4 and its NaCl concentration: 9 or 90g/L). The E_{ocp} potentials logically indicate that the noblest elements are in their immunity domains while the others are in their passivation ones (criterion: 1mol/L). Polarization resistances are high (several k$\Omega \times$ cm²) or very high (almost 1 M$\Omega \times$ cm²), and they lead to low or very low corrosion currents (less than 0.1 µA/cm² in several cases). © 2011 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Inside a fixed partial denture, the most visible part of which is the ceramic (called "cosmetic") part, there is generally a metallic framework the role of which is to ensure the resistance of the prosthesis against mechanical solicitations. Such an underlying metallic part needs to be modified/corrected at several steps of the prosthesis fabrication since distortion may occur during the casting process[1], the seating accuracy possibly needs be improved[2], a teeth movement can have appeared before prosthesis cementation[3], ... To take into account these possible phenomena and their necessary corrections, a framework supporting a fixed partial

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denture is thus generally realized by manufacturing individual parts (made on a "parent alloy": noble rich in Au, Pt or Pd, or Cr-rich nickel or cobalt-based alloys) and by joining these ones together first during a primary brazing (operation followed by the covering with ceramic), and second by soldering the extremities of the preceding prosthetic elements during a second brazing. Since this final brazing is achieved after the ceramic deposit on the frameworks parts and is not followed by a new ceramic covering, the post-solder alloy remains uncovered and it is necessarily exposed to the buccal milieu (as well as the extremities of the framework parts of parent alloy, sometimes). This potentially leads to a possible local corrosion by saliva of the metallic frameworks in these post-soldered parts, which can be aggravated by a pH lower than the physiologic one (almost neutral) following acidification due to the possible presence of dental plaque, or by a temporary elevated chloride concentrations due to eat food.

In order to better know the possible damages resulting from such corrosion on long times (which can locally weaken the mechanical resistance of the framework and consecutively of the whole prosthesis, the corrosion behaviours of four post-solder alloys were studied in three simple solutions simulating saliva, the pH and the chloride concentrations of which have different values. This was done by using the Stern-Geary method, which allows estimating, with simple electrochemical measurements (polarisation resistances), the corrosion currents[4,5]).

EXPERIMENTAL

The studied post-solder alloys; preparation of the electrodes

Four post-solder alloys were considered in this study. They are all of them rich in Au (between 56 and 65% in mass) and contain also less noble elements. These alloys, provided by the Ivoclar Vivadent company, are the followings (manufacturer's data):

- **.585** (58.5Au-16.0Ag-18.0Cu-7.2Ga, with possibly Zn, <1%)

- **.615** (61.3Au-13.1Ag-17.4Cu-7.6In, with possibly Zn, <1%)

- **.650** (65.0Au-19.6Cu-13Ag-2.0Ga, with possibly Zn, < 1%)

- **LFWG** (56.1Au-27.4Ag-15.8Zn, with possibly In and Sn, each < 1%)

all contents being in weight percents.

Metallographic observations made using a Scanning Electron Microscope showed that three of them appear being single-phased (example of .585 presented in figure 1, PhilipsXL30 SEM used in Secondary Electrons mode) while LFWG is obviously double-phased (figure 1 too).
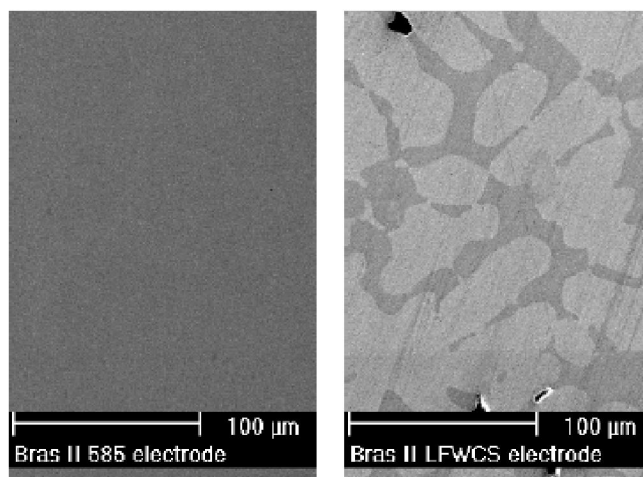
Figure 1 : Two examples of post-solder alloys' micro-structures: A single phased one (.585) on the left hand and a double-phased one (LFWG) on the right hand (SEM micrographs, taken in SE mode)

To prepare for the study the electrodes from these alloys, solder rods were melted in a crucible, heated by a gas-oxygen torch, then solidified. Half ball-like ingots weighing about 1 gram were obtained by this way, and they were heat-treated in order to reproduce what it is done in practice (heat-treatment parameters already detailed in a previous work[6]). The electrodes were realized by tin-soldering a sample per alloy to an electrical wire and by embedding them in a cold resin. The metallic surfaces were polished, until obtaining a mirror-like state, with first SiC papers from 120-grit to 1200-grit, and second 1μm-alumina. The metallic part emerging from resin, as is to say the electrode surface destined to be exposed to the electrolytes, was in each case a disk the surface of which was around 35 mm².

Electrochemical tests and measured properties

The electrochemical experiments were performed

using a potentiostat / galvanostat model 263A (Princeton Applied Research), driven by the software M352 of EGG/Princeton which also allowed the exploitation of the measurements. The electrolytes which were considered were:

- distilled water added with NaCl (9g L⁻¹), with a not-fixed pH (pH measured just before electrochemical experiment ≅ 6.6)
- the same solution as above but with a pH initially fixed to 7.4 (physiologic pH) using either HCl or NaOH diluted solutions
- the same solution (pH rated to 7.4) as above but ten times enriched in NaCl chlorides (90g L⁻¹).

This set of three electrolytes is to be considered as constituted of a simple artificial saliva classically used for for such simulation of dental alloys corrosion (9g L⁻¹, pH=7.4)[7,8] and of two other solutions being either an almost ten times {H⁺}-enriched version or a ten-times {Cl⁻}-enriched version, of this first reference solution.

In all cases the solution temperature was maintained at $37 \pm 1°C$ (with a heating device situated under a special electrochemical cell) and the solutions were supposed to be in equilibrium with the laboratory atmosphere concerning the quantity of dissolved oxygen. The electrode made from the studied alloy was used as Working Electrode while a platinum disk-like electrode played the role of Counter Electrode. The potentials were measured versus the one given by a Saturated Calomel Electrode (SCE electrode: potential = 241.5mV/Normal Hydrogen Electrode).

The electrochemical experiments were successively composed of:

- immersion of the working electrode (the studied alloy) during one hour for continuously measuring the evolution of the open circuit potential (E_{ocp}) versus the SCE electrode,
- linear polarization of the alloy from E_{ocp} - 10mV to E_{ocp} + 10mV at 10mV min⁻¹ for determining the polarization resistance (Rp),
- second following of the E_{ocp} for a second hour,
- and second determination of Rp.

From the two E_{ocp} follow-ups it is possible to know the state in which is each element belonging to the alloy's chemical composition (immunity, corrosion or passivation) with moreover the nature of the eventual oxidized species)[9], while the polarization resistance values allow estimating the density of corrosion current I_{corr} (corrosion rate).

More precisely, the values of the corrosion current I_{corr} were deduced, according to the Stern-Geary method, by exploiting the four following equations:

$$\mathbf{I_{corr} = B / Rp} \qquad\qquad (1)$$
$$\mathbf{B = (\beta_a \times \beta_c) / (2{,}303 \times (\beta_a + \beta_c))} \qquad (2)$$
$$\mathbf{\beta a = 2{,}303 \times R \times T / (0{,}5 \times n_a \times F)} \qquad (3)$$
$$\mathbf{\beta_c = 2{,}303 \times R \times T / (0{,}5 \times n_c \times F)} \qquad (4)$$

in which: Rp is the measured polarization resistance, B is calculated from the Tafel coefficients β_a and β_c (Eq. 3 and 4), F is the Faraday's number (96500C/Mol), T=310K (for 37°C), n_a = 2 or 3 and n_c = 2.

The values of the anodic (β_a) and cathodic (β_c) Tafel coefficients were deduced from the positions of the measured values of E_{ocp} in the Pourbaix's diagrams[9], which allowed considering that the oxidation reactions were either $M \rightarrow M^{II} + 2.e$ or $M \rightarrow M^{III} + 3.e$ ($n_a = 2$ or 3) and the reduction reaction was $\frac{1}{2} O_2 + H_2O + 2.e \rightarrow 2.OH^-$ ($n_c = 2$).

RESULTS AND DISCUSSION

Evolution of the open circuit potential over two hours

E_{ocp} was recorded at the beginning of the experiment just in the first minutes after immersion ("t=0h"), after one hour of immersion (just before the measurement of the first polarization resistance, "t=1h") and one hour later (just before the second Rp measurement, "t=2h"). The measured values are presented in a histogram in figure 2. In the {9g/L – pH=7.4} solution all the soldering alloys are at a high potential (more than +250mV/NHE), and no significant evolution can be observed over the two hours of immersion. In the {9g/L – pH=6.6} solution the potentials tend to be less regular over the two hours (except for the Au-richest of the alloys: .650) as well as a little lower in average for the three other soldering alloys in this more acid solution. When the quantity of NaCl dissolved in the electrolyte is multiplied by ten for a pH initially also equal to 7.4, the potential are seemingly more regular again but they stay at a level significantly lower than for the {9g/L – pH=7.4} solution.
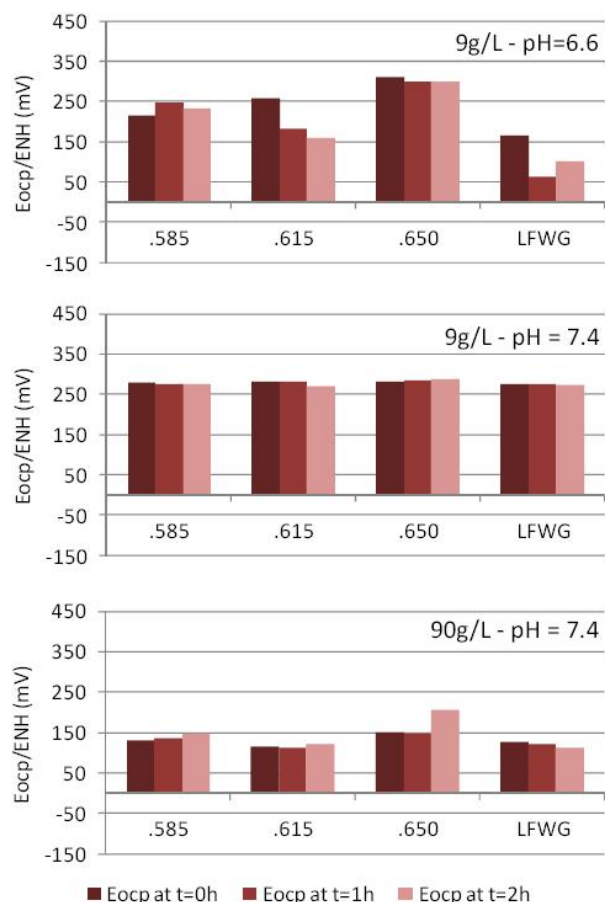
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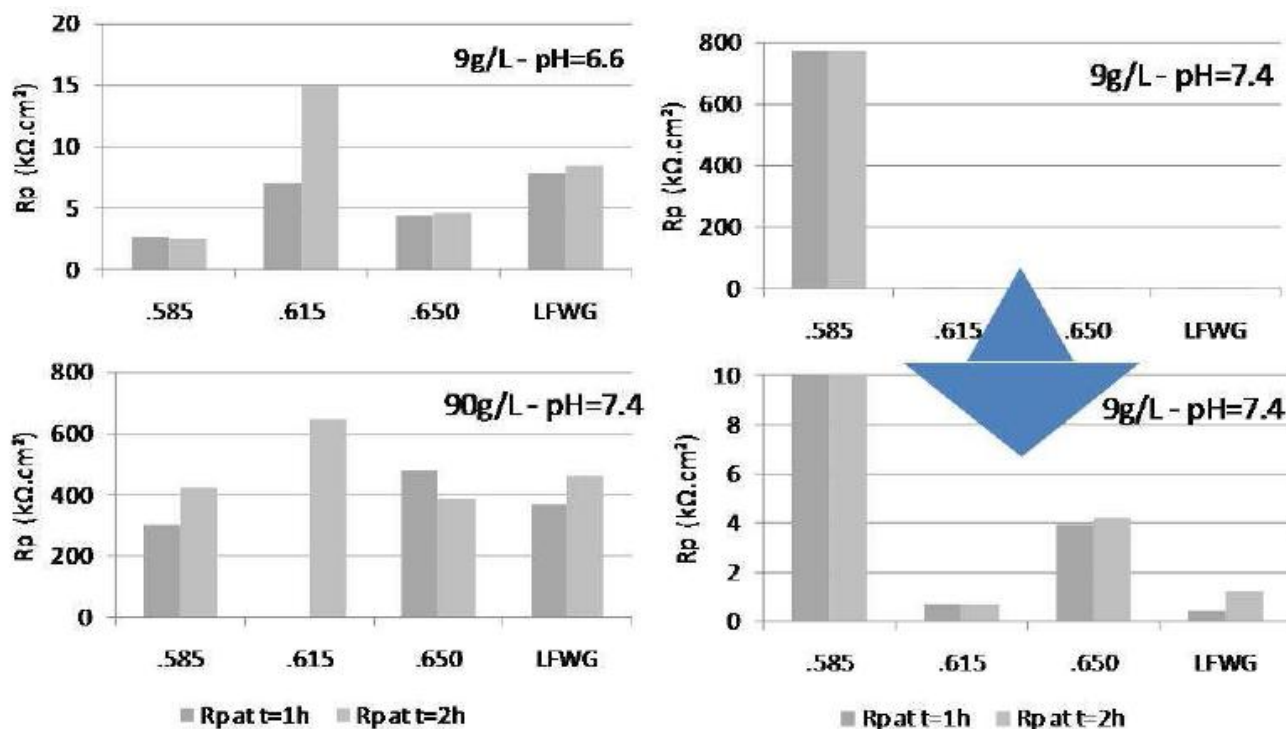**Figure 2 : Evolution of the open circuit potential over 2 hours**

In all cases these potentials correspond to the immunity domain of both gold and silver, major elements present in the chemical compositions of the four alloys. Inversely the potentials are high enough to lead copper to be oxidized at the degree I or II, indium and gallium to be also oxidized at the degree III, and zinc at the degree II. If the criterion of corrosion is considered to be 1Mol/L of dissolved ions, these species are either oxides (Cu_2O, In_2O_3, Ga_2O_3) or hydroxydes ($Cu(OH)_2$, $Zn(OH)_2$).

Polarization resistance over two hours and calculated corrosion currents

The polarization resistances at t=1h and at t=2h, deduced from the polarization curves around E_{ocp} (inverse values of the slopes at $E=E_{ocp}$), are graphically presented as histograms in figure 3. In the two solutions containing 9g/L of NaCl the polarization resistances displayed by the four alloys are high: several $k\Omega \times cm^2$, and even almost $1M\Omega \times cm^2$ for the .585 alloy in the pH=7.4 solution (figure 3). By considering the previous values of E_{ocp} potentials and the corresponding valences of the ions, oxides or hydroxides of Cu, In, Ga and Zn (n_a = 2, 3 or between 2 and 3), one can assess, accordingly to the Stern-Geary method, the values of

Figure 3 : Evolution of the polarization resistance over 2 hours for all the soldering alloys (+ vertical enlargement of the histogram in the case of the {9g/L – pH=7.4})

β_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_{corr} using the measured Rp.

The obtained results are displayed in figure 4, as histograms too. Following the high values seen for the polarization resistances, all corrosion currents are low (lower than 0.1 mA/cm²), or very low (lower than 0.01mA/cm²). In several cases (.585 in the {9g/L – pH=7.4} solution and all soldering alloys in the NaCl-enriched {90g/L – pH=7.4} solution), the corrosion current is even lower than 0.1μA/cm². The latter cases logically correspond to the very high values obtained for the polarization resistances (several hundreds of thousands $\Omega \times$ cm²).

can be noticed between the alloys, for example concerning the high values of polarization resistances which can be spread over a wide interval (1 to 1000kΩ × cm²), with consequently also an extended interval of corrosion currents.

If the studied alloys are based on noble metals (notably Au, but also Ag) which are obviously staying in their respective immunity domains as shown by the comparison between the {E_{ocp}; solution's pH} couples and the Pourbaix's diagrams corresponding to these elements, it is true that the state of the other elements (Cu, Zn, In, Ga, ...) is an oxidized state, characterized by oxides or hydroxides if the corrosion criterion is 1 Mol/L of dissolved ionic species. If the criterion is more severe (the more usual 10^{-6} Mol/L value), some of these E_{ocp}; pH} couples can lead to the corrosion domains for several of the less noble elements. The differences between high Rp values and very high Rp values may be due to a more or less great exposition of these not noble element to corrosion, the latter one partly depending on the total
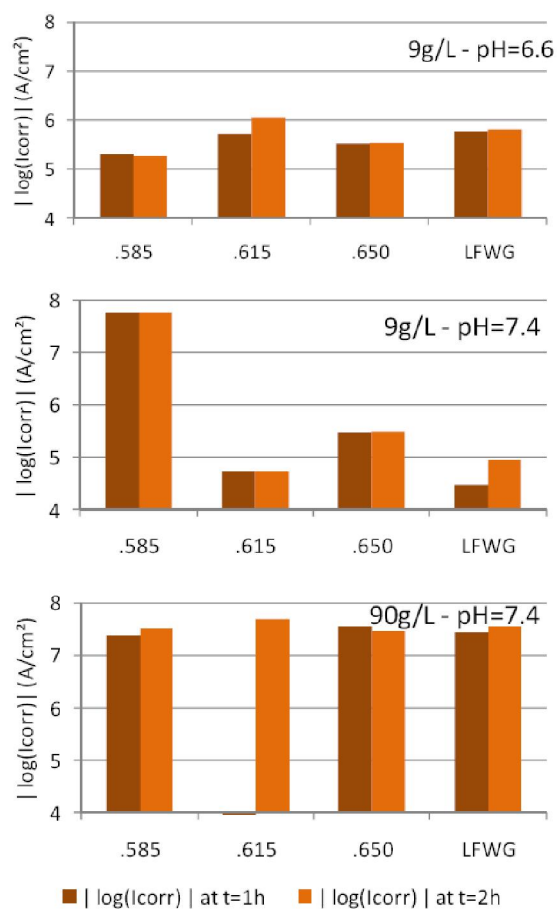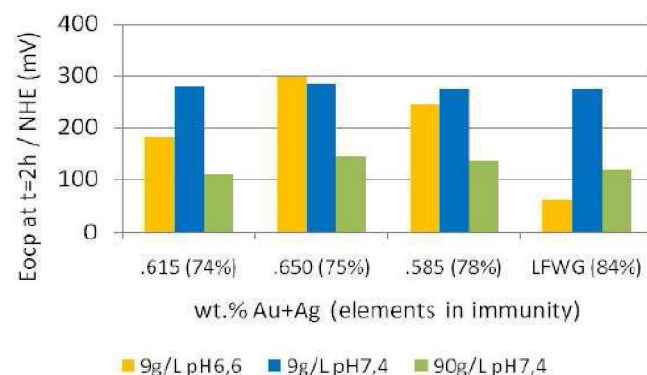

Figure 4 : Evolution of the corrosion current over 2 hours for all the soldering alloys

General commentaries

When immersed in the solutions of this study the four studied soldering alloys display good behaviours since the open circuit potentials are high as well as the polarization resistance. However significant differences

Figure 5 : Evolution of the E_{ocp} after 2h of immersion versus the whole weight content in elements in their immunity state (Au + Ag)
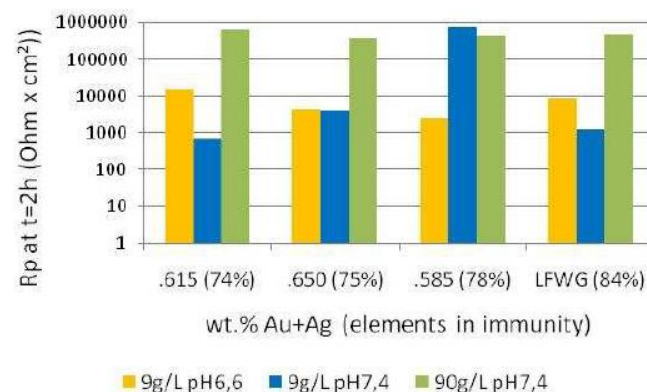

Figure 6 : Evolution of the R_p after 2h of immersion versus the whole weight content in elements in their immunity state (Au + Ag)

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weight content of these oxidizable elements in the chemical composition in the four different soldering alloys. Hence it can be interesting to plot the values of E_{ocp}, Rp or Icorr versus this total content of these elements easy to oxidize or inversely versus the complementary content in noble elements. This was done in figure 5 for the value of open circuit potential recorded after 2 hours of immersion and in figure 6 for the polarization resistance resulting from the Stern-Geary run at the same time (in logarithmic scale for distinguishing the values of both the high Rp and the less high ones).

Concerning the open circuit potential one can notice again the variability already observed for {9g/L ; pH=6.6} but no new clear dependence versus the alloy's nobility (except maybe the fact that the lowest E_{ocp} is obtained for the noblest alloy LFWG which also contains in great quantity – 16wt% - a very oxidizable element: Zn), the great and stable level of E_{ocp} for {9g/ L ; pH=7.4}, and the low but also stable level of E_{ocp} for {90g/L ; pH=7.4}.

Concerning the polarization resistance, the plot versus the Au+Ag weight content seems revealing a clearer dependence of Rp versus the chemical composition since the polarization resistance at t=2h regularly increases with this content in noble elements among the three first soldering alloys (.585 → .615 → .650) while it falls again for the alloy LFWG which is the richest in Au but also which contains a great quantity of Zn. The polarization resistance of the alloys is independent on the chemical composition when pH is 6.6. This is also observed for the chlorides-richest pH=7.4 solution in which the Rp values are exceptionally high despite chlorides are generally considered as detrimental for the corrosion resistance of alloys. It is true that it is pitting corrosion affecting the passivation layer which is often evocated in their cases while no such passivation scale is really expected here since the base element (Au) cannot be oxidized in such solution in normal conditions. On the contrary the especially high [Cl⁻] concentrations maybe led to precipitation of compounds involving metallic cations from the alloys and chlorides ions, which may lower corrosion rate.

CONCLUSIONS

The four soldering dental alloys studied here showed a good, and even in some cases a very good, resistance against corrosion when immersed in each of the three simple solutions displaying two different pH and two different chrlorides concentrations. Open circuit potentials were high and the polarization resistances situated between $1k\Omega \times cm^2$ and $1M\Omega \times cm^2$ led to low or very low corrosion currents obtained by applying the Stern-Geary method. However the differences observed between two alloys in the same electrolyte or between two solutions for the same alloys, are not always easy to interpret. This first article will be followed by a second one[10] which, by characterizing the corrosion behaviour of parent alloys according to the Stern-Geary method too, will complete this study.

ACKNOWLEDGEMENTS

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