June 2010 ISSN : 0974 - 7486 Volume 6 Issue 2

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 6(2), 2010 [132-137]

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

Pascal De March[1,2], **Patrice Berthod**[2]*

[1]Faculte d'Odontologie de Nancy, Département de Protheses, 96 avenue de Lattre de Tassigny,
B.P. 50208, 54000 Nancy, (FRANCE)

[2]Institut Jean Lamour (UMR 7198), Department of Chemistry and Physics of Solids and Surfaces,
Faculty of Sciences and Technologies, B.P. 70239, 54506 Vandoeuvre-les-Nancy, (FRANCE)

E-mail : Patrice.Berthod@lcsm.uhp-nancy.fr

Received: 18th February, 2010 ; Accepted: 28th February, 2010

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 $k\Omega.cm^2$) or very high (more than 1 $M\Omega.cm^2$), and consequently corrosion currents very low (levels: 1 $\mu A/cm^2$ down to 10 $\mu A/cm^2$). 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.

KEYWORDS

Dental prosthesis;
Parent alloy;
Post-solder alloy;
Corrosion;
Neutral artificial saliva.

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

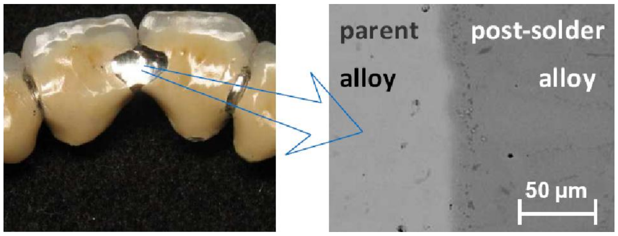

Figure 1 : Post-solder alloy appearing at the junction of two prosthetic elements; SEM/BSE micrograph of the local microstructure (Scanning electrons microscope, back scattered electrons mode)

TABLE 1 : Chemical compositions of the studied alloys (in wt.%; manufacturer's data)

Parent alloys	Post-solder alloys
dSIGN98	.585
85.9Au-12.1Pt-2Zn	58.5Au-16.0Ag-18.0Cu-7.2Ga
(+ possibly: In, Ir, Fe, Mn, Ta each <1)	(+ possibly: Zn <1)
Aquarius Hard	.650
86.1Au-8.5Pt-2.6Pd-1.4In	65.0Au-19.6Cu-13Ag-2.0Ga
(+ possibly: Ru, Fe, Li, Ta each < 1)	(+ possibly : Zn < 1)
dSIGN91	.615
60.0Au-30.6Pd-8.4In-1.0Ga	61.3Au-17.4Cu-13.1Ag-7.6In)
(+possibly: Re, Ru each <1)	(+ possibly: Zn <1)
dSIGN59	.615
59.2Pd-27.9Ag-8.2Sn-2.7In-1.3Zn	61.3Au-17.4Cu-13.1Ag-7.6In)
(+ possibly: Pt, Re, Ru, Li each <1)	(+ possibly: Zn <1)
Lodestar	.615
51.5Au-38.5Pd-8.5In-1.5Ga	61.3Au-17.4Cu-13.1Ag-7.6In)
(+ possibly: Re, Ru each < 1)	(+ possibly: Zn <1)
W	LFWG
54.0Au-26.4Pd-15.5Ag-2.5Sn-1.5In	56.1Au-27.4Ag-15.8Zn
(+ possibly: Re, Ru, Li zach < 1)	(+ possibly: In, Sn each < 1)
Pisces Plus	LFWG
61.5Ni-22.0Cr-11.2W-2.6Si-2.3Al	56.1Au-27.4Ag-15.8Zn
(+ possibly: Mischmetall < 1)	(+ possibly: In, Sn each < 1)
4ALL	LFWG
61.4Ni-25.7Cr-11.0Mo-1.5Si	56.1Au-27.4Ag-15.8Zn
(+ possibly : Al, Mn each < 1)	(+ possibly: In, Sn each < 1)

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[1,2]). 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[3-6] 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 ($10 \times 10 \times 1 mm^3$) were cut in order to obtain four parts, the dimensions of which were $5 \times 5 \times 1 mm^3$. 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 embedding in a cold resin. The metallic surfaces were then polished with SiC papers from 120-grit to 1200-grit, and finished by polishing with 1μm-alumina. The metallic part of the electrode's head (emerging alloy), which will be exposed to the artificial saliva, was a square of about $25 mm^2$ in the case of a parent alloy and a disk of around $35 mm^2$ for a post-solder alloy.

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

TABLE 2 : Composition of the used saliva (Afnor norm[2])

Product	Concentration (g/L)
Na_2HPO_4	0.26
NaCl	6.76
KSCN	0.33
KH_2PO_4	0.20
$NaHCO_3$	1.50
KCl	1.20

TABLE 3 : Pourbaix's domains corresponding to the E_{ocp} values

Parent alloys	Post-solder alloys
dSIGN98	.585
Au°-Pt°-$Zn(OH)_2$	Au°-Ag°-$Cu(OH)_2$ / Cu_2O- Ga_2O_3
Aquarius hard	.650
Au°-Pt°-Pd°-In_2O_3	Au° -$Cu(OH)_2$ / Cu_2O-Ag°- Ga_2O_3
dSIGN91	.615
Au°-Pd°-In_2O_3-Ga_2O_3	Au° -$Cu(OH)_2$ / Cu_2O-Ag°- In_2O_3
dSIGN59	.615
Pd°-Ag°-$Sn(OH)_4$-In_2O_3-$Zn(OH)_2$	Au° -$Cu(OH)_2$ / Cu_2O-Ag°- In_2O_3
Lodestar	.615
Au°-Pd°-In_2O_3-Ga_2O_3	Au° -$Cu(OH)_2$ / Cu_2O-Ag°- In_2O_3
W	LFWG
Au°-Pd°-Ag°-$Sn(OH)_4$-In_2O_3	Au°-Ag°-$Zn(OH)_2$
Pisces plus	LFWG
$Ni(OH)_2$-$Cr(OH)_3$-WO_3	Au°-Ag°-$Zn(OH)_2$
4 ALL	LFWG
$Ni(OH)_2$-$Cr(OH)_3$-MoO_4^{2-}	Au°-Ag°-$Zn(OH)_2$

was a platinum disk-like electrode. The reference potential was given by a Saturated Calomel Electrode (241.5mV/Normal Hydrogen Electrode).

Each electrochemical experiment, repeated two times in order to examine the reproducibility of the results, was composed of the followings:

1 Immersion of the alloy (working electrode) during one hour with continuous measurement of the open circuit potential (E_{ocp}) versus the SCE electrode.
2 Polarization of the alloy between E_{ocp}-10mV and E_{ocp}-10mV at 10mV/min for the measurement of the polarization resistance (Rp).
3 Repetition of 1.
4 Repetition of 2.

The two follow-up of E_{ocp} (i.e. E_{corr}(t)) allow to know in which state is each element of the alloy's chemical composition: immunity, corrosion or passivation (with identification of the oxidized species)[9] while the values of the polarization resistance allow to estimate the density of corrosion current I_{corr} (i.e. the corrosion rate) according to (Eq. (1)) where Rp is the measured polarization resistance and B is given by (Eq. (2)) in which the Tafel coefficients appear. These coefficients can be estimated using the equations (Eq. (3)) and (Eq. (4)) in which F is the Faraday's number (96500C/Mol), T=310K (for 37°C), n_a = 2 or 3 and n_c = 2. These values of the anodic and cathodic Tafel coefficients resulted from the positions of the measured values of E_{ocp} in the Pourbaix's diagrams, which allowed considering that the oxidation reactions were either $M \rightarrow M^{II} + 2.e$ or $M \rightarrow M^{III} + 3.e$ (anions or oxides/hydroxides) and the reduction reaction was $\frac{1}{2} O_2 + H_2O + 2.e \rightarrow 2.OH$.

$$I_{corr} = B / Rp \qquad (1)$$

$$B = (\beta_a \beta_c) / (2,303 \times (\beta_a + \beta_c)) \qquad (2)$$

$$\beta a = 2,303 \times R \times T / (0,5 \times n_a \times F) \qquad (3)$$

$$\beta_c = 2,303 \times R \times T / (0,5 \times n_c \times F) \qquad (4)$$

RESULTS AND DISCUSSION

Open circuit potential over two hours

The E_{ocp} 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_{ocp} measurements that the reproducibility is the worst. This lack of reproducibility for these noble alloys was maximal here for dSIGN98 (+257 and +293mV/NHE for the two tests) but, in contrast, very small for Aquarius Hard (+293 and +295mV/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 dSIGN59 and of the not noble Pisces Plus, for the three successive values of E_{ocp}, 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_{ocp} is initially high but seems decreasing, the open circuit potential is very high

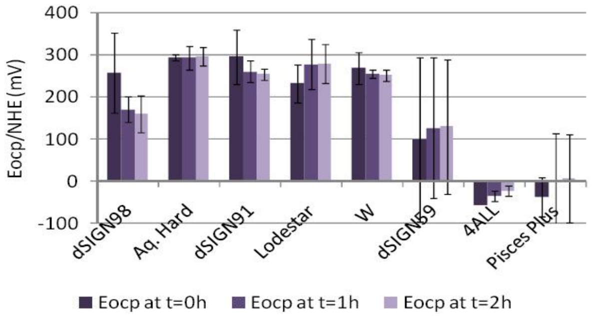

Figure 2 : Evolution of the open circuit potential over 2 hours, in the case of the parent alloys (two sets of measurement)

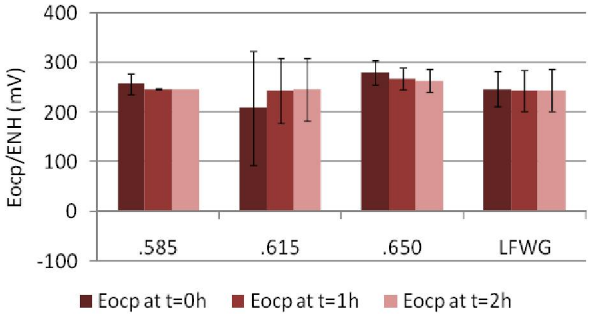

Figure 3 : Evolution of the open circuit potential over 2 hours, in the case of the post-solder alloys (two sets of measurement)

(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 reproducibility (which was generally confirmed by comparing the two numerical values of each Rp for a same parent alloy). With 1 MΩ 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 50kΩ 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 450kΩcm^{-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 cm². 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 1μA cm^{-2}.

The corrosion rates for the four post-solder alloys are also low, with I_{corr} values positioned around the micro-ampere per cm².

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

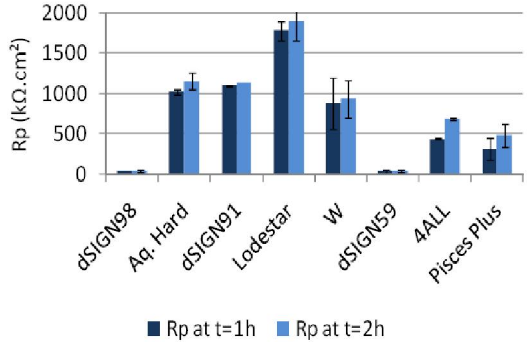

Figure 4 : Evolution of the polarization resistances over 2 hours, in the case of the parent alloys (two sets of measurement)

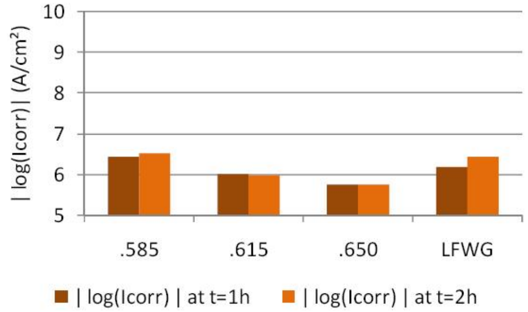

Figure 7 : Evolution of the absolute value of log(I_{corr}) deduced from the Rp values, over 2 hours in the case of the post-solder alloys (two sets of measurement)

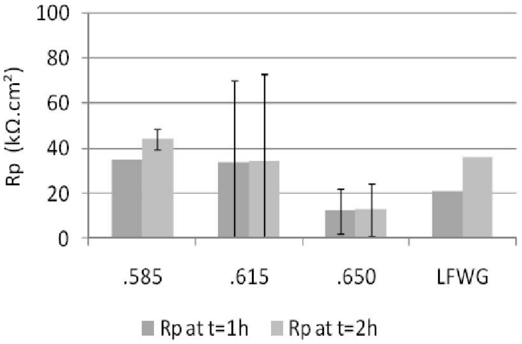

Figure 5 : Evolution of the polarization resistances over 2 hours, in the case of the post-solder alloys (two sets of measurement)

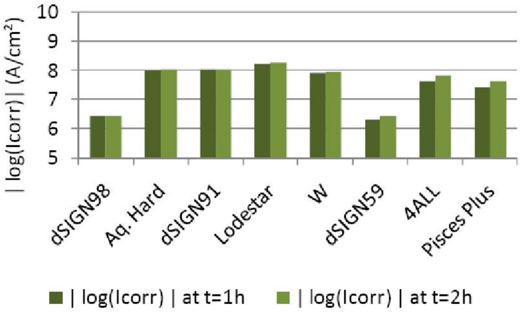

Figure 6 : Evolution of the absolute value of log(I_{corr}) deduced from the Rp values, over 2 hours in the case of the parent alloys (two sets of measurement)

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°, Pt°, Pd°, and Ag° 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_2O_3, In_2O_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°) or in their passivation domains (Ga_2O_3, In_2O_3, Cu_2O 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.

ACKNOWLEDGEMENTS

The authors gratefully thank Ivoclar-Vivadent who provided them all alloys and solders they needed.

REFERENCES

[1] C.Rochaix; ‘Electrochimie, Thermodynamique-Cinétique’, Nathan, **(1996)**.

[2] P.Steinmetz, C.Rapin; ‘La Corrosion Des Alliages Dentaires: Phenoménologie et Exemples’, In : Cahiers De Biomatériaux Dentaires 1, Materiaux mineraux, Masson, Paris, **(1992)**.

[3] Y.Fovey, J.Pourreyron, Y.Gal; Dental Materials, **16**, 364 **(2000)**.

[4] J.Karov, I.Hindberg; Journal of Oral Rehabilitation, **28**, 212 **(2001)**.

[5] E.J.Sutow, W.A.Maillet, J.C.Taylor, G.C.Hall; Dental Materials, **20**, 823 **(2004)**.

[6] A.Ciszewski, M.Baraniak, M.Urbanek-Brychczynska; Dental Materials, **23**, 1256 **(2007)**.

[7] P.De March, P.Berthod; Materials Science: An Indian Journal, **4(4)**, 297 **(2008)**.

[8] AFNOR Norm NF S90-701, Medico-Surgical Equipment, Biocompatibility of Materials and Medical Devices, Methods for Extraction.

[9] M.J.Pourbaix; ‘Atlas of Electrochimica Equilibra in Aqueous Solution’, Pergamon Press, Oxford, **(1966)**.