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Corrosion of dental alloys for fixed partial denture when exposed to high anodic potentials

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ABSTRACT

The metallic alloys used to mechanically strengthen ceramic-metallic dental prosthesis may partly emerge in contact with the saliva present in the buccal milieu. They are then subjected to a possible corrosion by the more or less aerated saliva. Specific electrochemical runs were here performed to measure the corrosion rates of several selected dental alloys used in frameworks reinforcing some fixed partial dentures when they are maintained at a high anodic potential in an acidified Fusayama saliva, in order to better know the behaviour of these alloys in a saliva which may contain a lot of dissolved oxygen. The initial cyclic polarization runs performed over a large anodic range of potentials allowed choosing, in the E-increasing part of the obtained curves, values of high potential at which alloys were permanently exposed during 3 days. After each experiment the electrolyte was analyzed by ICP measurements to detect the eventual presence of the more or less noble metallic elements initially belonging to the alloys.

KEYWORDS

Dental alloys;
Corrosion;
Artificial saliva;
High anodic potentials.

INTRODUCTION

Many dental alloys used for dental prostheses contain noble elements (e.g. Au, Pt, Pd...) while other alloys, based on less noble metals (Ni, Co, Cr...) may show also a very good resistance against corrosion in the buccal milieu, thanks to their easiness to reach a passivation state. However, they can lead to significant anodic currents when exposed to high potentials (in a three-electrodes cell for example), as shown by the end of the anodic parts of some polarization runs performed in artificial saliva. In real cases high electrochemical potentials can be sometimes encountered, for instance when saliva is intensively aerated. Thus, it may appear important to know the corrosion behaviour of the alloys in some extreme situations.

Such metallic alloys can be present in dental prostheses in which they constitute the internal frameworks which mechanically support the cosmetic ceramic (the artificial teeth). This framework can be effectively concerned by corrosion since a small part of it can be let outside the ceramic and then exposed to the buccal milieu. Such a framework for fixed partial denture results of the assemblage of several main parts made of a "parent alloy", joined together by brazing (using a "presolder alloy"). The obtained assemblages are thereafter them too joined to one another by brazing (this time using a "post-solder alloy") to finally obtain the prosthesis. If the pre-solder alloy is not in contact with the buccal milieu thanks to the cosmetic ceramic deposed after joining, it is not the case for the post-solder alloy which cannot be covered and necessarily emerges outside. The extremities of the two joined pieces of parent alloy sometimes partly appear too, when the ceramic does not always cover them entirely. Thus, post-solder joints, and sometimes a part of parent alloy, are exposed to a possible corrosion by saliva more or less rich in dissolved oxygen[1].

This is why electrochemical runs are often performed to evaluate the corrosion behaviour of post-solder alloys and of parent alloys in different electrolytes simulating saliva which can be of different types, such as simple neutral NaCl-containing aqueous solutions[2-4], Afnor saliva[5,6] or Fusayama saliva[7], for example.

In this work several parent alloys and post-solder alloy were chosen among families of various nobilities, to be studied in a complex artificial saliva (Fusayama-type) acidified down to pH=2.3. The investigations were done first by performing cyclic polarizations, and second by applying constant anodic potentials (selected from the potential increasing parts of the cyclic polarization curves previously obtained) during three days. These latter runs were followed by the ICP analyses of the electrolyte, and by the characterization of the surface states of the electrodes.

EXPERIMENTAL DETAILS

Eight parent alloys and four post-solder alloys, supplied by Ivoclar Vivadent®, were studied. Five out of these parent alloys are very rich in noble elements (dSIGN98, Aquarius Hard, dSIGN91, Lodestar, W: TABLE 1), one is less noble (dSIGN59: TABLE 2) and two are simple (Ni, Cr)-based alloys (4ALL, Pisces Plus: TABLE 3), while the four post-solder alloys are all rich in gold (TABLE 4). The parent alloys were obtained, by investment casting, as parallelepipedic samples of average dimensions 10 mm × 10 mm × 1 mm. Fusion implied a gas-oxygen torch and the filing a centrifugal arm. Each sample was cut into four parallelepipedic pieces (5 mm × 5 mm × 1 mm) using a Isomet 5000 precision saw (Buehler). They were thereafter blasted with alumina 50 µm - powder. A heat treatment was applied to the alloys in a Programat X1 ceramic oven (Ivoclar Vivadent), with realization parameters conform to the manufacturer's preconisation for ceramic (IPS dSIGN ceramic, Ivoclar Vivadent®).

TABLE 1 : Chemical compositions of the five high noble parent alloys studied here (all contents in wt.%; manufacturer's data).

COMMERCIAL NAME	Au	Pt	Pd	Ga	In	Others
dSIGN98	86	12	/	/	/	2.0 Zn
Aquarius Hard	86	8.5	2.6	/	1.4	/
dSIGN91	60	/	31	1.0	8.4	/
Lodestar	52	/	39	1.5	8.5	/
W	54	/	26	/	1.5	16 Ag - 2.5 Sn

TABLE 2 : Chemical composition of the single noble parent alloy studied here (all contents in wt.%; manufacturer's data).

COMMERCIAL NAME	Pd	Ag	Sn	In	Zn	Others
dSIGN59	59	28	8.2	2.7	1.3	/

TABLE 3 : Chemical compositions of the two predominantly base parent alloys studied here (all contents in wt.%; manufacturer's data).

COMMERCIAL NAME	Ni	Cr	Mo	W	Si	Others
4ALL	61	26	11	/	1.5	/
Pisces Plus	62	22	/	11	2.6	2.3 Al

TABLE 4 : Chemical compositions of the four post-solder alloys studied here (all contents in wt.%; manufacturer's data).

COMMERCIAL NAME	Au	Ag	Cu	Ga	Others	To use with:
.650	65	13	20	2		dSIGN98
.615	61	13	17	/	7.6 In	d91, d59, Lodestar
.585	59	16	18	7	/	Aquarius Hard
LFWG	56	27	/	/	16 Zn	W,Pisces Plus, 4ALL

The post-solder alloys were melted in a borax-vitrified crucible using a butane-oxygen blowtorch, then solidified as half ball-like ingots weighing about 1 gram. These ones were also sand-blasted, then steam-cleaned. Finally, the heat treatment defined by the manufacturer especially for this post-solder alloy was applied to the ingot in the ceramic oven. All the heat treatments, applied to the parent alloys and to the post-solder alloys, are entirely described in a previous paper[8].

The electrodes were prepared as follows:

- a sample of each parent alloy or post-solder alloy was soldered (using tin) to a copper wire covered by plastic,
- it was embedded in a cold {resin+hardener} mix.,
- the surface of each electrode was polished with SiC paper from 80 to 1200 grit under water, and finished with 1μm diamond particles.

The surface of alloy exposed to saliva was a square of about 5 mm ×5 mm (parent alloy electrode) or a disk of about 35 mm^2 (post-solder alloy electrode). The surfaces of the alloys in the electrodes were observed using a Hitachi FEG-Scanning Electron Microscope, in Back Scattered Electrons mode (BSE) for the microstructure examinations, and in Secondary Electrons (SE) mode before and after the polarizations at constant potential to evaluate the relief resulting of the degradation.

A potentiostat 263A (Princeton Applied Research) was used for the electrochemical experiments (driven by the software: EGG/Princeton model 352), connected to the three electrodes (Working Electrode: the studied alloy, Auxilliary Electrode: platinum, and Potential-reference Electrode: a Saturated Calomel Electrode), immersed in a cell containing the electrolyte heated and maintained at 37°C by a Julabo F32 thermo-cryostat (electrolyte's composition given in TABLE 5).

TABLE 5 : Chemical compositions of the four post-solder alloys studied here (all contents in wt.%; manufacturer's data).

Species	Concentrations (g/L)
KCl	0.4
NaCl	0.4
$CaCl_2$, $2H_2O$	0.91
NaH_2PO_4, $2H_2O$	0.69
Na_2S, $9H_2O$	0.005
urea	1

RESULTS AND DISCUSSION

Results

Some of the obtained cyclic polarization curves obtained are plotted in Figure 1, Figure 2 and Figure 3, in which arrows show the values of the potentials thereafter imposed to a electrodes). TABLE 6 (High Noble alloys), TABLE 7 (Noble alloy), TABLE 8 (Predominantly Base alloys) and TABLE 9 (Post-solder alloys) show the Pourbaix's domains[9] which correspond to the potentials selected to be applied: first for the 10^{-6}Mol/L of dissolved species, concentration usually adopted to state if corrosion exists or not, and second for 1Mol/L (corresponding to a much more severe and visible corrosion). These tables also give the identity of the species released in the electrolyte in case of corrosion of the alloys after the 3 days-tests at imposed anodic potential, and detected by ICP; if any, qualitative data about their concentrations are provided in the same tables: "X", "A", "A+", "B", "C" and "C+" notations correspond respectively to the following ranges: X: [0 to 1ppb], A: [1 to 10 ppb], A+: [10 to 100 ppb], B: [100 to 1,000 ppb], C: [1,000 to 10,000 ppb], and C+: [higher than 10,000 ppb].

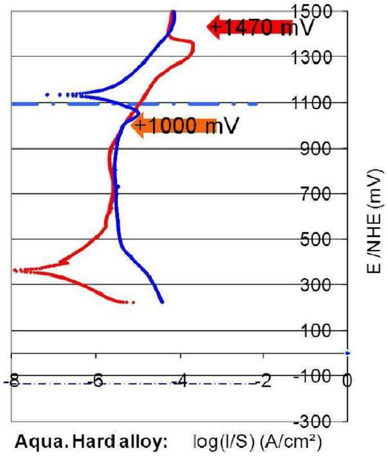


Figure 1 : The cyclic polarization curves obtained for a high noble parent alloy (Aquarius Hard) and potentials applied for the 3-days polarizations at constant high anodic potential.

The potentials lower than +1000mV/NHE were considered in order to better characterize the behaviour of the alloys (microstructure deteriorations and species lost in the electrolyte) at the potential of constant current plateau end or at the peaks of high currents. The high potential of +1470mV/NHE was applied to almost all the alloys for comparatively observing their behaviour for a same very high potential.

General commentaries

The five High Noble parent alloys (dSIGN98, Aquarius Hard, dSIGN91, Lodestar and W) and the four post-solder alloys (.585,.615,.650 and LFWG) are all rich in gold and their base-element (Au) is still in its immunity domain for an applied potential equal to +1,000mV / ENH. The other noble elements, Pt and Pd, are passivated for this same value of applied potential. After 3 days of exposure at this potential, no noblest parent alloys has lost any elements in the electrolyte, at least with quantities really detectable by ICP. The ICP measurements only revealed the presence of Zn (e.g. dSIGN98 and dSIGN59) or Sn (e.g. W and dSIGN59) species in the electrolyte after tests. Gold is also in its immunity state after 3-days immersion of each of the post-solder alloys with polarization to +1000mV. In contrast, these alloys contain other metals, less noble, and this in great quantities favoring their presence after test in significant quantities in the artificial saliva (Cu: about 20wt.% in mass, Zn: 16wt.% in LFWG, Ga: 7wt.% in .585). Ag is in its corrosion domain but seemingly suffers rather low corrosion despite its content which is sometimes very high in the alloy (from 13wt.% in .615 and .650 up to 27wt.% in LFWG). Indium, which can be present in the alloy in more or less high amounts (from 1.4wt.% in Aquarius Hard up to 8.5wt.% in Lodestar), was never really found in saliva.

TABLE 6 : High noble alloys - the different potentials applied during 3 days to the alloys, position in the Pourbaix's diagram, corresponding species stable (criteria: 1Mol/L and 10^{-6} Mol/L), and ICP results.

dSIGN98	**86% Au**	**12% Pt**	**2%Zn**		
1 Mol/L	$Au(OH)_3$	PtO_2	Zn^{++}		
10^{-6}Mol/L	$Au(OH)_3$	PtO_2	Zn^{++}		
E = +1470mV	*B*	*C*	*C*		
1 Mol/L	Au^0	PtO_2	Zn^{++}		
10^{-6}Mol/L	Au^0	PtO_2	Zn^{++}		
E = +1000mV	*X*	*X*	*B*		
Aqu. Hard	**86% Au**	**8.5% Pt**	**2.6% Pd**	**1.4% In**	
1 Mol/L	$Au(OH)_3$	PtO_2	$Pd(OH)_4$	In^{+++}	
10^{-6}Mol/L	$Au(OH)_3$	PtO_2	$Pd(OH)_4$	In^{+++}	
E = +1470mV	*B*	*B*	*B*	*B*	
1 Mol/L	Au^0	PtO_2	$Pd(OH)_2$	In^{+++}	
10^{-6}Mol/L	Au^0	PtO_2	$Pd(OH)_2$	In^{+++}	
E = +1000mV	*X*	*X*	*X*	*X*	
dSIGN91	**60% Au**	**31% Pd**	**1.0% Ga**	**8.4% In**	
1 Mol/L	$Au(OH)_3$	$Pd(OH)_4$	Ga_2O_3	In^{+++}	
10^{-6}Mol/L	$Au(OH)_3$	$Pd(OH)_4$	Ga^{+++}	In^{+++}	
E = +1470mV	*A*	*A*	*A*	*A*+	
1 Mol/L	Au^0	$Pd(OH)_2$	Ga_2O_3	In^{+++}	
10^{-6}Mol/L	Au^0	$Pd(OH)_2$	Ga^{+++}	In^{+++}	
E = +1000mV	*X*	*X*	*X*	*A*	
Lodestar	**52% Au**	**39% Pd**	**1.5% Ga**	**8.5% In**	
1 Mol/L	$Au(OH)_3$	$Pd(OH)_4$	Ga_2O_3	In^{+++}	
10^{-6}Mol/L	$Au(OH)_3$	$Pd(OH)_4$	Ga^{+++}	In^{+++}	
E = +1470mV	*A*	A+	*A*+	*A*+	
1 Mol/L	Au^0	$Pd(OH)_2$	Ga_2O_3	In^{+++}	
10^{-6}Mol/L	Au^0	$Pd(OH)_2$	Ga^{+++}	In^{+++}	
E = +1000mV	*A*	*A*	*A*	*A*	
W	**54% Au**	**26% Pd**	**16%Ag**	**1.5% In**	**2.5% Sn**
1 Mol/L	$Au(OH)_3$	$Pd(OH)_4$	Ag^+ / Ag_2O_3	In^{+++}	$Sn(OH)_4$
10^{-6}Mol/L	$Au(OH)_3$	$Pd(OH)_4$	Ag^+	In^{+++}	$Sn(OH)_4$
E = +1470mV	*A*	*A*	*A*	*A*	*C*
1 Mol/L	Au^0	$Pd(OH)_2$	Ag^+	In^{+++}	$Sn(OH)_4$
10^{-6}Mol/L	Au^0	$Pd(OH)_2$	Ag^+	In^{+++}	$Sn(OH)_4$
E = +1000mV	*X*	*X*	*X*	*X*	*B*
1 Mol/L	Au^0	Pd^0	Ag^0	In^{+++}	$Sn(OH)_4$
10^{-6}Mol/L	Au^0	Pd^0	Ag^+	In^{+++}	$Sn(OH)_4$
E = +500mV	*A*	*X*	*A*	*A*	*C*

TABLE 7 : Noble alloy - the different potentials applied during 3 days to the alloys, position in the Pourbaix's diagram, corresponding species stable (criteria: 1Mol/L and 10^{-6} Mol/L), and ICP results.

dSIGN59	59% Pd	28%Ag	2.7% In	8.2% Sn	1.3% Zn
1 Mol/L	$Pd(OH)_2$	Ag^+	In^{+++}	$Sn(OH)_4$	Zn^{++}
10^{-6}Mol/L	$Pd(OH)_2$	Ag^+	In^{+++}	$Sn(OH)_4$	Zn^{++}
E = +1000mV	*X*	*A*	*A*	*C*	*C*
1 Mol/L	Pd^0	Ag^0	In^{+++}	$Sn(OH)_4$	Zn^{++}
10^{-6}Mol/L	Pd^0	Ag^0/Ag^+	In^{+++}	$Sn(OH)_4$	Zn^{++}
E = +400mV	*X*	*X*	*X*	*A*	*B*

TABLE 8 : Predominantly base alloys - the different potentials applied during 3 days to the alloys, position in the Pourbaix's diagram, corresponding species stable (criteria: 1Mol/L and 10^{-6} Mol/L), and ICP results.

4ALL	61% Ni	26% Cr	11% Mo
1 Mol/L	NiO_2	$HCrO_4^-$	MoO_3
10^{-6}Mol/L	Ni^{++}	$HCrO_4^-$	$HMoO_4^-$
E = +1470mV	*C+*	*C+*	*C+*
1 Mol/L	Ni^{++}	$Cr(OH)_3$	MoO_3
10^{-6}Mol/L	Ni^{++}	Cr^{+++}	$HMoO_4^-$
E = +1000mV	*B*	*A+*	*A+*
Pisces Plus	**62% Ni**	**22% Cr**	**11% W**
1 Mol/L	NiO_2	$HCrO_4^-$	WO_3
10^{-6}Mol/L	Ni^{++}	$HCrO_4^-$	WO_3
E = +1470mV	*C+*	*C+*	*C+*
1 Mol/L	Ni^{++}	$Cr(OH)_3$	WO_3
10^{-6}Mol/L	Ni^{++}	Cr^{+++}	WO_3
E = +1000mV	*C+*	*C*	*C*

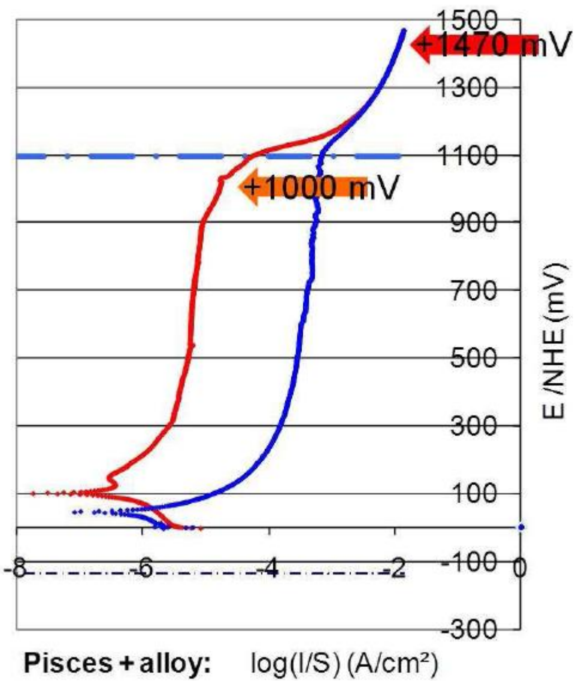


Figure 2 : The cyclic polarization curves obtained for a predominantly base alloy (Pisces +) and potentials applied for the 3-days polarizations at constant high anodic potential.

TABLE 9 : Post-solder alloys - the different potentials applied during 3 days to the alloys, position in the Pourbaix's diagram, corresponding species stable (criteria: 1Mol/L and 10^{-6} Mol/L), and ICP results.

.585	59% Au	16% Ag	18% Cu	7.2% Ga
1 Mol/L	$Au(OH)_3$	Ag^+	Cu^{++}	Ga_2O_3
10^{-6}Mol/L	$Au(OH)_3$	Ag^+	Cu^{++}	Ga^{+++}
E = +1470mV	*C*	*A+*	*C+*	*C+*
1 Mol/L	Au^0	Ag^+	Cu^{++}	Ga_2O_3
10^{-6}Mol/L	Au^0	Ag^+	Cu^{++}	Ga^{+++}
E = +960mV	*A*	*A*	*B*	*B*
1 Mol/L	Au^0	Ag^0	Cu^{++}	Ga_2O_3
10^{-6}Mol/L	Au^0	Ag^+	Cu^{++}	Ga^{+++}
E = +475mV	*X*	*A*	*A+*	*A+*
.615	**61% Au**	**13% Ag**	**17% Cu**	**7.6% In**
1 Mol/L	Au^0	Ag^0	Cu^0/Cu^{++}	In^{+++}
10^{-6}Mol/L	Au^0	Ag^0/Ag^+	Cu^{++}	In^{+++}
E = +430mV	*X*	*X*	*A+*	*A*
.650	**65% Au**	**20% Cu**	**13% Ag**	**2% Ga**
1 Mol/L	Au^0	Cu^0/Cu^{++}	Ag^0	Ga_2O_3
10^{-6}Mol/L	Au^0	Cu^{++}	Ag^0/Ag^+	Ga^{+++}
E = +430mV	*X*	A+	*X*	*X*
LFWG	**56% Au**	**27% Ag**	**16% Zn**	
1 Mol/L	$Au^0/Au(OH)_3$	Ag_2O_3/Ag^+	Zn^{++}	
10^{-6}Mol/L	$Au(OH)_3$	Ag^+	Zn^{++}	
E = +1470mV	*A+*	*A*	*C*	
1 Mol/L	Au^0	Ag^+	Zn^{++}	
10^{-6}Mol/L	Au^0	Ag^+	Zn^{++}	
E = +1000mV	*A*	*A*	*C*	
1 Mol/L	Au^0	Ag^0	Zn^{++}	
10^{-6}Mol/L	Au^0	Ag^+ /Ag^0	Zn^{++}	
E = +490mV	*X*	*X*	*B*	

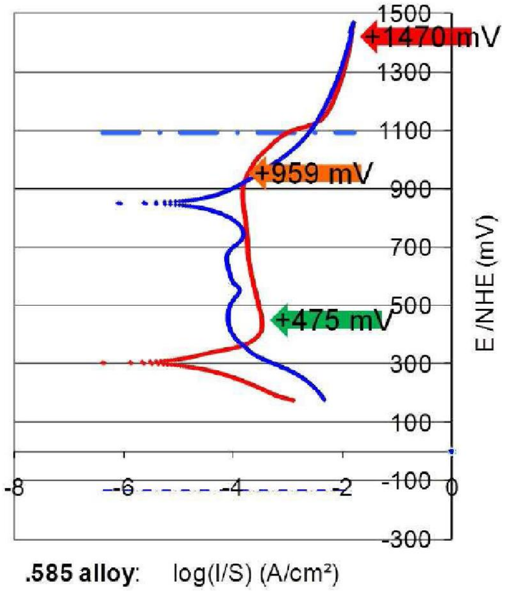
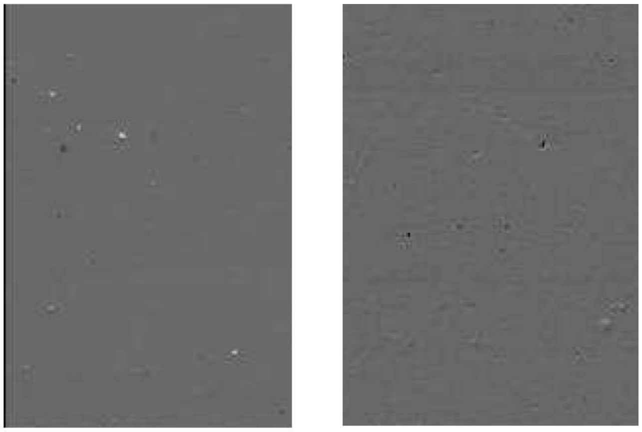


Figure 3 : The cyclic polarization curves obtained for a post-solder alloy (.585) and potentials applied for the 3-days polarizations at constant high anodic potential.

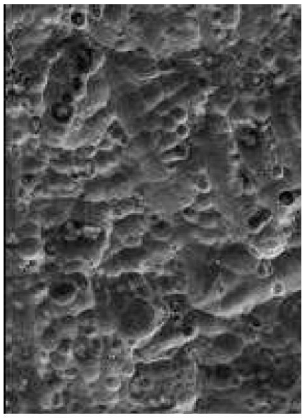
Nickel (the base element of the two Predominantly Base parent alloys) is in its corrosion domain at +1000mV in the present acidic conditions (pH=2.3). It may be significantly corroded if exposed to this potential, this resulting in the presence in more or less high quantities of nickel oxidized species in the electrolyte.

Exposing the electrodes at +1470mV/NHE often led to severe corrosion of the alloys, this resulting in high concentrations of metallic ions or hydroxides in the electrolyte. This is true not only for the Predominantly Base 4ALL and Pisces Plus alloys but also for the High Noble dSIGN98 and the .585 post-solder alloy. SEM micrographs illustrating the degradation of one of these alloys when exposed to different high potentials during 3 days are presented in Figure 4.



Microstructure before polarization at high potential

Microstructure after polarization at +1000mV/NHE for 3 days



Microstructure after polarization at +1470mV/NHE for 3 days

Scale for all micrographs:

Figure 4 : Corrosion state of the predominantly base parent alloy 4ALL before and after exposure to different constant high anodic potentials during 3 days.

CONCLUSION

The High Noble and Noble dental alloys as well as the post-solder alloys studied here are very corrosion-resistant, thanks to their high contents in elements such as gold, platinum or palladium. The two Predominantly Base alloys are also very corrosion resistant, thanks to the fact that their main elements can get easily passivated, chromium notably. In contrast, their exposure for a long time to high anodic potentials may lead to detectable or severe corrosion. Fortunately, such high potentials (+1000mV/NHE) are not achievable in real situation since this should suppose for example that saliva is extremely aerated on long times, while anodic potentials 500mV higher are strictly not possible to observe in normal conditions. But it was interesting to see that the alloys, even the ones coming from the High Noble class, did not show the same behaviours.

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