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## Influence of the chemical composition of a parent alloy used in fixed partial denture on its corrosion in an acidified Fusayama's saliva

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### ABSTRACT

The frameworks supporting ceramic in fixed partial dentures are generally constituted of several dental alloys. In the mouth, some parts of the framework may be exposed to a more or less aerated saliva and then exposed to corrosion on long times, which can be detrimental for their mechanical resistance. Commercial alloys used in frameworks have specific chemical compositions, chosen for reaching high level of mechanical strength as well as for resisting corrosion. Three ternary Ni-based alloys derived from a commercial dental one, with varying Cr and W contents, were elaborated and tested in corrosion in an artificial saliva. Electrochemical techniques were used to specify the behaviour of each new alloy (follow-up of free potential, measurement of polarization resistances, cyclic polarizations). The importance of maintaining the chromium content to resist corrosion was evidenced, and the detrimental role of the heat treatment discovered. Moreover, it is possible that the minor elements present in the commercial alloy also play an important role in the corrosion resistance. © 2009 Trade Science Inc. - INDIA

### KEYWORDS

Fixed partial denture;  
Parent alloy;  
Electrochemical  
measurements;  
Fusayama saliva.

### INTRODUCTION

The fixed partial dentures, for which one usually see only the cosmetic ceramic parts (artificial teeth), also contain metallic alloys constituting a framework almost never visible, except the post-solder alloys joining the parts of parent alloy<sup>[1]</sup>. Indeed these parent alloys are generally totally covered by ceramic, but in some

cases, the extremities of some of these parts can be in contact with the buccal milieu and then possibly subjected to corrosion, a phenomenon which can be enhanced by galvanic coupling with the post-solders if these ones play a cathodic role in the coupling. Such problem is not serious if the parent alloys are based on elements such as gold, platinum or palladium (“High Noble” or “Noble” parent alloys, as named in the

Identical alloy norm). It can be not the case for parent alloys based on nickel and chromium (belonging to the "Predominantly Base" alloys, Identical alloy norm), and this is the reason why they are, for example, rich in chromium which is unfortunately more expensive than nickel.

The purpose of the present study is to try specifying the importance for the mechanical behaviour, and for the resistance against corrosion in the buccal milieu, of the chromium content and also of the tungsten content, which is also more expensive than nickel and furthermore more difficult to include in the alloy in the melting step of the elaboration.

## EXPERIMENTAL

### Elaboration of the alloys

The commercial alloy from which the alloys of this study are derived, is the Pisces Plus (Ivoclar Vivadent®), the chemical composition of which is about 62Ni-22Cr-11W-2Al-3Si (in wt.%). Its microstructure, which was earlier described<sup>[1]</sup>, is mainly composed of a dendritic matrix, with dendrites which are more rich in tungsten in their core than in their outer parts, and of W-rich particles dispersed in the interdendritic spaces. The alloys which were synthesized in this study is a (Ni, Cr, W)-based (Al, Si)-free version of the Pisces Plus (named "PP std"), a similar ternary alloy but with a chromium content divided by 2 ("PP Cr2"), another one but with a tungsten content divided by 2 ("PP W2"), and finally another one in which the contents in Cr and in W are simultaneously divided by 2 ("PP Cr2 W2").

They were elaborated by foundry under controlled atmosphere, using a CELES High Frequency (80-300kHz) induction furnace under 300mbars of pure argon gas. Pure nickel, pure chromium and pure tungsten (>99.9%, Alfa Aesar) were melted together in a copper crucible in which they solidified thereafter. The obtained 30g-ingots were either kept in these as-cast conditions, or subjected to a heat-treatment realized respecting the real thermal cycles usually applied in the case of a prosthesis involving the Pisces Plus commercial alloy (*opaque, dentine, glazing*: already described in a previous work<sup>[1]</sup>).

### Metallography

Mounted and mirror-like polished samples were

prepared for metallography examinations (cut, embedded in a cold resin added with a strengthener (Escil®) then polished from 240-grit SiC-paper to 1200-grit, ultrasonic-cleaned, then polished with 1µm-particles). The microstructures of these samples, as-cast or heat-treated, were examined using a Scanning Electron Microscope (SEM Philips XL30) in Back Scattered Electrons mode (BSE) with a 20kV acceleration voltage.

### Preparation of the electrodes and electrochemical runs

Some parts of alloys cut in the as-cast ingots and in the heat-treated ingots were used for realizing the electrodes. They were tin-soldered with an electrical wire, embedded in a cold resin (the same as for the metallography samples), and polished until a mirror-like surface state was obtained. The area of emerging alloy, which was thereafter in contact with the electrolyte, was of a variable shape. The determination of the surfaces was then done by scanning the main areas of the electrodes and thereafter by determining the alloy surface fraction by image analysis using the Adobe Photoshop software. The measured surfaces varied from 0.2 to 1.2 cm<sup>2</sup>.

The electrochemical experiments were performed using a 37°C-heated three-electrodes cell and a potentiostat / galvanostat (Princeton Applied Research, model 263A), driven by a computer (supporting the software M352 of EGG/Princeton). The artificial saliva was an acidified version of the Fusayama one, the composition of which is displayed in TABLE 1. The pH was decreased to 2.3 using lactic acid (concentration: 90%). Such artificial saliva has been often used for studying the corrosion behaviour of various dental alloys in the past, based on Au, Pt or Pd<sup>[2-6]</sup> as well as on less noble metals: Ag or Hg<sup>[2,4,7]</sup>,

**TABLE 1 : The used fusayama saliva, before acidification with lactic acid**

Components	Concentrations (g/L)
KCl	0.4
NaCl	0.4
CaCl <sub>2</sub> , 2H <sub>2</sub> O	0.906
NaH <sub>2</sub> PO <sub>4</sub> , 2H <sub>2</sub> O	0.690
Na <sub>2</sub> S, 9H <sub>2</sub> O	0.005
urea	1

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and even on Ni or Co<sup>[2,4,7-9]</sup>. The electrolyte temperature was constant and equal to 37°C, thanks to a Julabo F32 device. In the electrochemical cell, the Working Electrode was one of the eight electrodes of the studied alloys, the Counter Electrode was a platinum disk-like electrode and the Reference Electrode was a Saturated Calomel Electrode (reference in potential: 241.5mV versus Hydrogen Normal Electrode).

Each electrochemical experiment was composed of:

\* record of the free potential (i.e. corrosion potential  $E_{\text{corr}}$ ) of the immersed working electrode during about 2 hours, with two measurements of polarization resistance ( $R_p$ ) at  $t=1\text{h}$  and  $t=2\text{h}$  (scan rate of 10mV/min from  $E_{\text{corr}} - 20\text{mV}$  to  $E_{\text{corr}} + 20\text{mV}$ ),

\* cyclic polarization between the cathodic domain and the anodic domain: increase in potential from  $E_{\text{corr}} - 150\text{mV}$  up to 1.225V/SCE (scan rate of 1mV/min), followed by decrease in potential from 1.225V/SCE down to the initial value  $E_{\text{corr}} - 150\text{mV}$ , with the same scan rate.

The results were thereafter compared to the Pourbaix's diagrams<sup>[10]</sup> of Ni, Cr and W.

## RESULTS AND DISCUSSION

### Chemical compositions of the obtained alloys

The general chemical compositions of the obtained alloys were determined by the Wavelength Dispersion Spectrometry technique (WDS) using a Castaing's electronic microprobe (Cameca SX50 or SX100). This was done in not focalized mode (magnification  $\times 400$ ), in five locations in each sample. The results are given in TABLE 2, in which the chemical composition of the commercial Pisces Plus (manufacturer's data) is reminded for comparison.

Globally the targeted values are well respected, with chromium and tungsten contents not far from the Pisces Plus ones (a little too high for Cr and, on the contrary, a little too low for tungsten) in the case of the As-cast PP std and the Heat-treated PP std. The half contents in chromium (PP Cr2 and PP Cr2W2) and half contents in tungsten (PP W2 and PP Cr2W2) are, in contrast, very close to the contents of Pisces Plus after division by 2.

**TABLE 2 : Chemical compositions of the initial Pisces Plus (in wt.%; manufacturer's data) and of the four ternary alloys derived from the precedent one (in wt.%; WDS microprobe measurements)**

ments	Ni	Cr	W	Al	Si	ot
s Plus lar dent)	61.5	22.0	11.2	2.3	2.6	M mei
ast std"	64.4 ± 0.5	23.5 ± 0.2	9.9 ± 0.2			
heat-treated std"	63.4 ± 0.4	25.0 ± 0.2	8.9 ± 0.2	/	/	
ast Cr2"	72.7 ± 1.5	11.6 ± 0.2	11.7 ± 0.4			
heat-treated Cr2"	73.5 ± 0.6	11.7 ± 0.4	11.6 ± 0.5	/	/	
ast W2"	73.1 ± 1.2	23.1 ± 1.5	4.9 ± 1.0			
heat-treated W2"	not meas.	not meas.	not meas.	/	/	
ast Cr2W2"	80.6 ± 0.7	11 ± 0.1	5.4 ± 0.2			
heat-treated Cr2W2"	81.2 ± 0.7	11 ± 0.2	5.3 ± 0.3	/	/	

### Microstructures of the obtained alloys

There are no real differences between the eight microstructures, as illustrated by selected micrographs in Figure 1. Indeed, first the differences of chemical compositions between the four alloys of this study did not induce any changes in the microstructures, and this is also true between the as-cast condition and the heat-treated condition. However one can note that the microstructure is dendritic in all cases, but there are no pronounced grain boundaries or interdendritic boundaries, when the samples are observed at high magnification. In fact, the two very distinct levels of grey which can be seen (and which allow distinguishing the dendritic network) are only due to severe chemical micro-segregations during solidification. The too short heat treatment did not change this heterogeneous chemical distribution: "Oxidation cycle": 5 min at 1010°C, "1<sup>st</sup> opaque": 1 min bellow 900°C, "2<sup>nd</sup> opaque": 1 min bellow 890°C, "1<sup>st</sup> and 2<sup>nd</sup> Dentin": 1 min bellow 870°C and "Glazing": 1 min bellow 830°C, with in addition, of course, some time spent for increase and decrease in temperature.

These microstructures are a little different from the real Pisces Plus, although it presented the same dendritic structure enhanced by segregations at solidification. Indeed it also contained small particles

(white when seen with the SEM in BSE mode) obviously extremely rich in tungsten, dispersed in the interdendritic (dark in BSE mode) spaces.

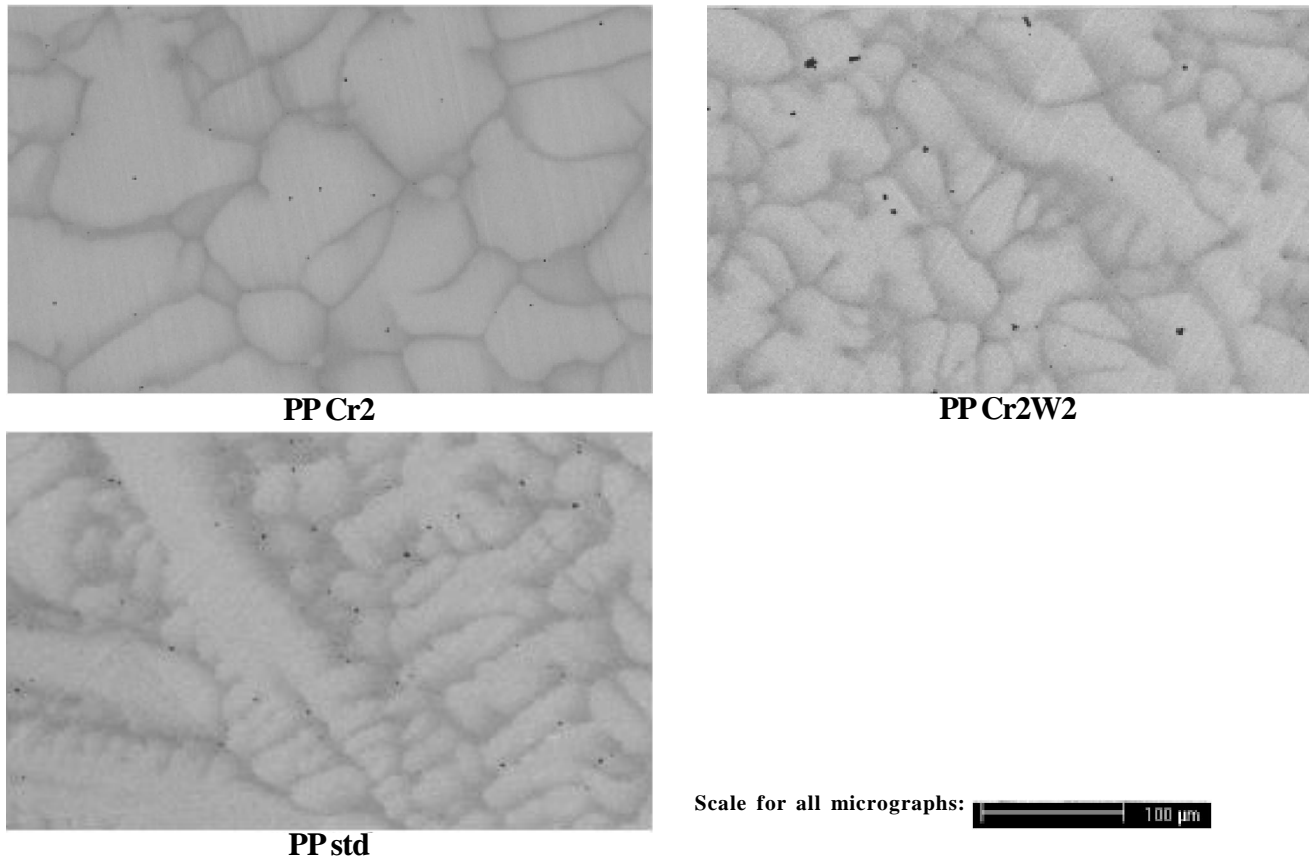


Figure 1: Microstructures of three of the four studied alloys in the as-cast state (SEM micrographs, BSE mode)

### Electrochemical measurements

During the two hours before cyclic polarization, the free potentials of the as-cast alloys are very different (Figure 2, TABLE 3). The PP std alloy remains at a high level of potential (near +140 mV/HNE) while the PP Cr2 and the PP W2 are at a very low one (near -50 mV/HNE). The PP Cr2W2 is in

an intermediate position (slow decrease from +50 down to +10 mV/HNE). In the heat-treated state, all PP alloys are at a low potential (several tens mV / HNE) for PP std, PP W2 and PP Cr2W2, especially the PP Cr2 alloy (near -170 mV/HNE). The best heat-treated alloy is the Pisces Plus, the free potential of which varies but which finishes to be stabilized

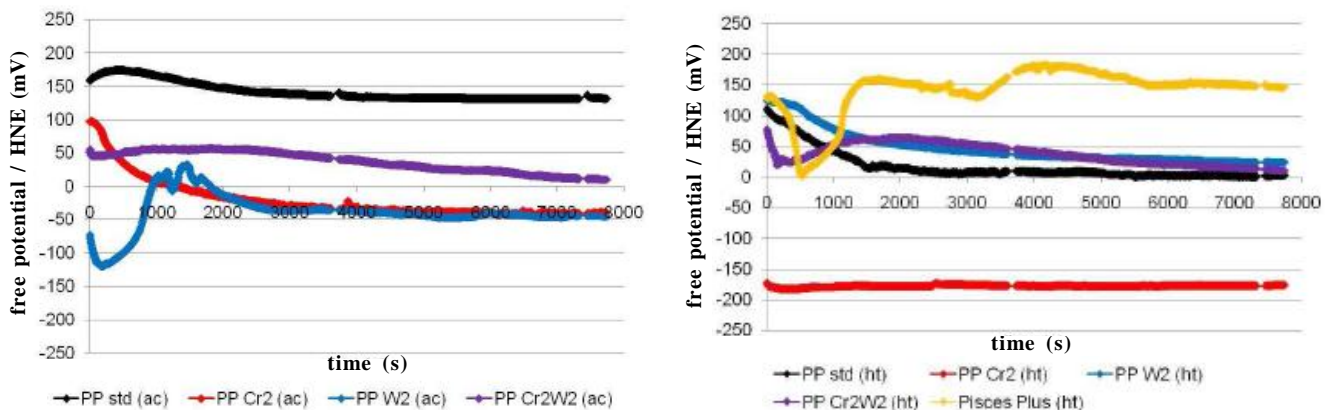


Figure 2 : Evolution, over about 2 hours, of the free potential of the as-cast alloys (left) and of the heat-treated alloys (right)

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near +150 mV/HNE.

Since the domains of existence of the species  $\text{Ni}^{\text{II}}$  ( $\text{Ni}^{++}$ ),  $\text{Cr}^{\text{III}}$  ( $\text{Cr}^{+++}$  or  $\text{Cr}(\text{OH})_3$ ) and  $\text{W}^{\text{VI}}$  ( $\text{WO}_3$ ) are very large in potential range, these great differences of potential given before do not generally induce changes of the concerned E-pH domains for the three elements. All alloys, during this free immersion in the Fusayama saliva, are either in the domains of stability of  $\{\text{Ni}^{++}, \text{Cr}^{+++}, \text{WO}_3\}$  if the considered corrosion criterion is 1  $\mu\text{Mol/L}$  of dissolved ion species or in the stability domains of  $\{\text{Ni}^{++}, \text{Cr}(\text{OH})_3, \text{WO}_3\}$  if the chosen criterion is 1 Mol/L.

Concerning the polarization resistances, they are generally at high levels, but there are significant differences between alloys and also between an as-cast alloy and the same heat-treated (TABLE 3). The highest values were obtained for the as-cast PP; they are much higher than for the heat-treated PP std (x100), the  $R_p$  of which are ten times lower than for the heat-treated Pisces Plus. This let think that the polarization resistance of an as-cast Pisces Plus should be higher than the 400-700k $\Omega$  cm<sup>2</sup> of the as-cast PP std. The lowest values of  $R_p$  were obtained for the PP Cr2, with also a detrimental effect of the heat-treatment (0.7-0.8 decreased to 0.4-0.5k $\Omega$  cm<sup>2</sup>). Other very low values were obtained for the other Cr-impoverished alloys: the PP Cr2W2 the  $R_p$  of which are decreased by comparison to the PPW2 alloy. The decrease in W content (PP W2) affected the value of polarization resistance of the PP std only for the as-cast condition.

Cyclic polarization runs were performed for all alloys for the two conditions (as-cast and heat-treated). One of these curves is given in Figure 3 for illustration. One can see that the as-cast PP std seems to behave as an auto-passive alloy since no anodic peak before passivation can be seen before the anodic current became almost constant. Nevertheless one can think that the not decreased chromium content allowed developing an oxide or hydroxide of  $\text{Cr}^{\text{III}}$  on surface since a beginning of transpassivation is visible when the E-increasing part of the curve (in red in Figure 3) is quitting the  $\text{Cr}^{\text{III}}(\text{OH})_3$  domain to penetrate in the  $\text{HCr}^{\text{VI}}\text{O}_4^-$  one.

In Figure 4, only the E-increasing parts of the cyclic polarization curves are plotted, for all as-cast alloys

**TABLE 3 : Free potentials and polarization resistances before cyclic polarization**

Alloys	Corrosion criterion	$E_{\text{corr}} / \text{HNE (mV) at } t = \dots$			$R_p$ (k $\Omega\text{m} \times \text{cm}^2$ )	
		0h	1h	2h	at t = 1h	at t = 2h
Pisces Plus	value of $E_{\text{corr}}$	+129	+154	+150		
(heat-treated)	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			64	89
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				
PP std	value of $E_{\text{corr}}$	+160	+139	+136		
As-cast	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			441	703
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				
PP std	value of $E_{\text{corr}}$	+109	+10	+2		
Heat-treated	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			4.7	4.8
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				
PP Cr2	value of $E_{\text{corr}}$	+97	-35	-41		
As-cast	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			0.8	0.7
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				
PP Cr2	value of $E_{\text{corr}}$	-175	-178	-178		
Heat-treated	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3 / \text{W}_2\text{O}_5 / \text{WO}_2$			0.4	0.5
	1 Mol/ L	$\text{Ni}^{++} / \text{Ni}^0 \text{Cr}(\text{OH})_3 \text{WO}_3 / \text{W}_2\text{O}_5 / \text{WO}_2$				
PP W2	value of $E_{\text{corr}}$	-82	-35	-45		
As-cast	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			4.8	2.9
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				
PP W2	value of $E_{\text{corr}}$	+125	+37	+24		
Heat-treated	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			7.6	8.2
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				
PP Cr2W2	value of $E_{\text{corr}}$	+46	+44	+12		
As-cast	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			1.5	1.5
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				
PP Cr2W2	value of $E_{\text{corr}}$	+73	+49	+15		
Heat-treated	1 $\mu\text{Mol} / \text{L}$	$\text{Ni}^{++} \text{Cr}^{+++} \text{WO}_3$			2	1.7
	1 Mol/ L	$\text{Ni}^{++} \text{Cr}(\text{OH})_3 \text{WO}_3$				

together (left), and for all heat-treated alloys together (right) while the characterization of the whole curves of cyclic polarization led to the results presented in TABLE 4.

One can see that the E-increasing parts of the cyclic polarization curves are very different from one another. For the as-cast alloys the best results were obtained by the PP std alloy, with the higher corrosion potential and the lowest corrosion current. At higher potentials (in the anodic part) there is seemingly a passivation plateau (anodic current remains small, lower than 10<sup>-5</sup> A/cm<sup>2</sup>) but there is a perturbed part (probably pitting) before that transpassivation occurs (which demonstrates that the alloy was effectively passivated, by chromia or tri-

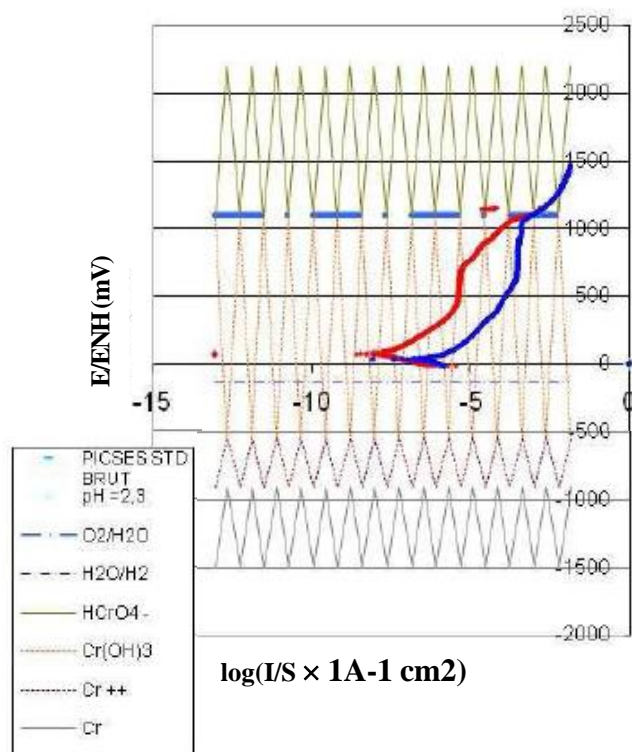


Figure 3: Example of cyclic polarization curve (as-cast PP std)

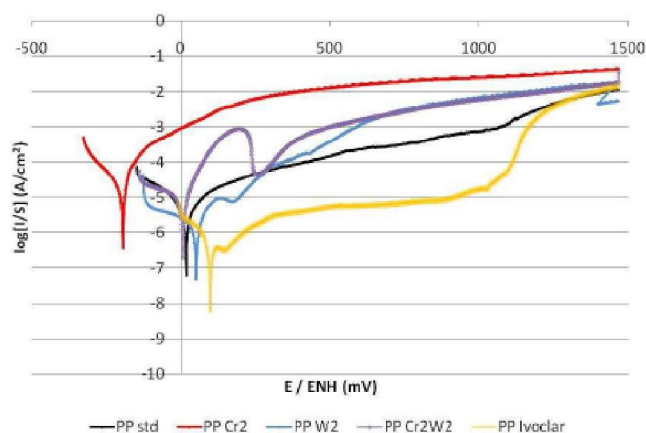
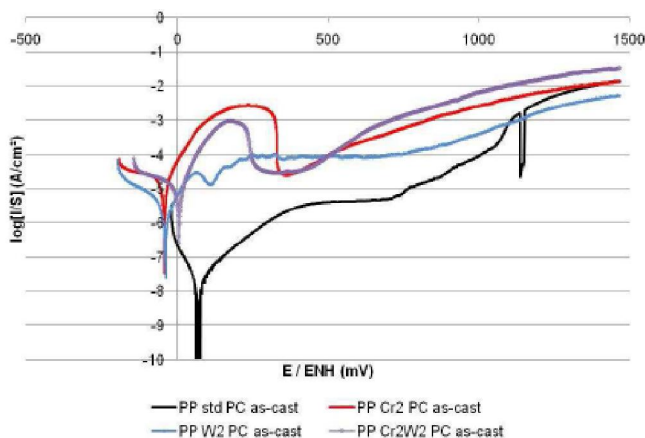


Figure 4: E-increasing parts of the cyclic polarization curves for the as-cast alloys (left) and for the heat-treated alloys (right)

currents along the passivation plateau) and a pronounced transpassivation near 1100mV/HNE shows that the surface was probably wholly covered by chromia or by the tri-hydroxide of chromium.

### General commentaries

It appeared first in this study that the microstructure of the four alloys is seemingly independent on the contents in Cr and in W: the same qualitative microstructure is obtained whatever the Cr content and W content.

Second, the microstructure of the one of the four

hydroxide of chromium). The three other as-cast alloys display worse behaviours, with lower corrosion potentials and higher corrosion currents. If the as-cast PP Cr2 and PP Cr2W2 seemed to become passive (anodic peaks followed by decrease in anodic current) this passivation is probably not uniform and unstable since current remain high for higher potentials.

The heat-treated PP std, PP W2 and PP Cr2W2 led to similar corrosion potentials and corrosion currents, with a partial and unstable passivation (anodic peaks for the PP Cr2 W2 and the PP W2), with maybe a passivation already achieved for the PP std (lower current than for the precedent alloys for high anodic potentials, and visible transpassivation  $\text{Cr}^{\text{III}}$  (chromia or hydroxide)  $\rightarrow$   $\text{Cr}^{\text{VI}}$ ). The worst alloy is the heat-treated PP Cr2 alloy which displays the lowest corrosion potential and the highest corrosion current: it is obviously entirely in the active state. The best one remains the heat-treated Pisces Plus, which led to the highest corrosion potential and the lowest corrosion density of current. Its passivation is efficient (very low anodic

elaborated alloys, which was wanted to be a simplified version of the commercial Pisces Plus, is a little different than the latter one. If the dendritic network and the heterogeneous distribution of elements between core (white in BSE mode, rich in W) and surrounding zones of dendrites (dark in BSE mode, impoverished in W) are common to the real parent alloy and its ternary model, the first one presents additional particles (white in BSE mode) precipitated here and there in the interdendritic spaces. For its relatively high chromium content, it seems that the 11.2 wt.% of tungsten in the Pisces Plus is a little higher than the limit of solubility of

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**TABLE 4 : Exploitation of the cyclic polarization curves (with Tafel calculations for the two parts)**

Alloys	Corrosion criterion	$E_{corr} \uparrow$ /NHE (mV)	$I_{corr}$ /NHE (nA/cm <sup>2</sup> )	$E_{corr} \downarrow$ /NHE (mV)	Beta (mV/decade)	
					$\beta_a$	$\beta_c$
Pisces Plus		+98	near 100	+45		
(heat-treated)	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3$			$E \uparrow$ : too high	$E \uparrow$ : 92
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3$			$E \downarrow$ : 52	$E \downarrow$ : too high
PP std		+70	27	+34		
As-cast	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3$			$E \uparrow$ : 139	$E \uparrow$ : 75
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3$			$E \downarrow$ : 151	$E \downarrow$ : 254
PP std		+17	near10000	-79		
Heat-treated	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3$			$E \uparrow$ : too high	$E \uparrow$ : too high
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3$			$E \downarrow$ : too high	$E \downarrow$ : too high
PP Cr2		-42	near10000	+23		
As-cast	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3$			$E \uparrow$ : 88	$E \uparrow$ : too high
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3$			$E \downarrow$ : 121	$E \downarrow$ : 250
PP Cr2		-195	near10000	+74		
Heat-treated	1 $\mu$ Mol / L	$\uparrow Ni^{++} Cr^{+++} WO_3/W_2O_5/WO_2$ $\downarrow Ni^{++} Cr^{+++} WO_3$			$E \uparrow$ : 42	$E \uparrow$ : 138
	1 Mol/ L	$\uparrow Ni^{++}/Ni^0 Cr(O)_3 WO_3/W_2O_5/WO_2$ $\downarrow Ni^{++} Cr(OH)_3 WO_3$			$E \downarrow$ : too high	$E \downarrow$ : too high
PP W2		-38	near10000	-97		
As-cast	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3$			$E \uparrow$ : too high	$E \uparrow$ : too high
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3$			$E \downarrow$ : too high	$E \downarrow$ : too high
PP W2		+50	4070	-91		
Heat-treated	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3/W_2O_5$			$E \uparrow$ : 94	$E \uparrow$ : too high
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3/W_2O_5$			$E \downarrow$ : 79	$E \downarrow$ : 389
PP Cr2 W2		+6	near10000	-70		
As-cast	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3$			$E \uparrow$ : 79	$E \uparrow$ : too high
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3$			$E \downarrow$ : 71	$E \downarrow$ : 79
PP Cr2 W2		+7	near10000	-94		
Heat-treated	1 $\mu$ Mol / L	$E \uparrow Ni^{++} Cr^{+++} WO_3$ $E \downarrow Ni^{++} Cr^{+++} WO_3/W_2O_5$			$E \uparrow$ : 76	$E \uparrow$ : too high
	1 Mol/ L	$E \uparrow Ni^{++} Cr(OH)_3 WO_3$ $E \downarrow Ni^{++} Cr(OH)_3 WO_3/W_2O_5$			$E \downarrow$ : 722	$E \downarrow$ : 269

W in the (Ni, Cr)-matrix, even if the latter is not homogeneous chemically. This is not the case for the ternary alloys for which the tungsten content is generally lower (PP std) or very lower (PP W2 and PP Cr2W2) than in the real Pisces Plus. One time only the content in tungsten is a little higher in an alloy of this study (PP

Cr2) but this alloy also contains a low content in chromium. It is possible that chromium tends to decrease the limit of solubility of W in nickel, what could explain the absence of W-rich particles in that alloy which contains a little more tungsten than the Pisces Plus. One can add here some results of thermodynamic calculations performed with the Thermo-Calc version N software working with a database containing the systems involving Ni, Cr and W: for the four chemical compositions of this study the alloys (at their thermodynamically stable state at high temperature) are all single-phased (Ni FCC solid solution containing all Cr and W atoms). Unfortunately, it was not really possible to see if a W-rich second phase can be present in small mass fractions, by performing such calculations for the Pisces Plus since this one also contains significant amounts of other elements (Al, Si). It is true that all these alloys are not in any thermodynamical stable state, anyway.

Such W-rich particles are maybe of great interest for the behaviour in corrosion of the Pisces Plus since W, which forms  $WO_3$ , whatever the ion-concentration criterion considered, can accelerate passivation. Indeed, these particles are directly exposed to the electrolyte and can react independently of the corrosion of the alloy itself. This maybe explains the better corrosion behaviour of the Pisces Plus.

Concerning the electrochemical measurements, it appears that the results, in terms of free potential, polarization resistances, corrosion potential, corrosion current and anodic currents in the "passivation" plateau were very dispersed among the alloys, as-cast or heat-treated. Nevertheless it clearly appeared that the decrease in chromium significantly deteriorates the corrosion behaviour of the ternary alloy. This is not a surprise, of course, but in this situation (acidified Fusayama saliva at 37°C), for the PP Cr2 and also the PP Cr2W2, the chromium content is obviously under a limit in chromium separating good behaviours and very bad behaviours. The effect of a decrease in tungsten content is less marked in general. A more interesting observation is the detrimental effect of the heat-treatment usually applied in practice: the corrosion behaviour is noticeably deteriorated. It is possible that this can be also true for the commercial Pisces Plus itself since the as-cast PP std has seemingly better polarization

resistances than the heat-treated Pisces Plus. Studying a not treated Pisces Plus may be interesting.

This commercial alloy displayed anyway the best behaviour in corrosion. The presence of free W-rich precipitates may help by a pre-passivation by  $WO_3$ , or by deposition on the alloy surface of precipitated species formed from anions and cations, formed during the early steps of corrosion, involving chromium and tungsten for example (as encountered in some austenitic stainless steels containing several percents of molybdenum), which allows waiting to a real passivation with oxide or hydroxide of chromium. The presence of Al and Si, and maybe also of rare earth (Mischmetal is mentioned in the chemical composition of the manufacturer), may explain this superiority of the Pisces Plus.

### CONCLUSIONS

It is not necessary to employ noble metals as parent alloys for framework destined to support fixed partial dentures to achieve very good resistance against corrosion, even in the case of aerated acidified solutions simulating saliva. Passivable nickel-chromium alloys permit reaching high level of performance but their chemical composition needs to be well chosen for allowing them to efficiently resist corrosion thanks to an early development of a passivation layer but which must be very stable and protective. Chromium must be rated at high levels of contents and attention must be given to possible effect of heat-treatment included in the elaboration procedure of the prosthesis.

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