

Corrosion of Simple Cobalt-Chromium Alloys, Bases of Real Dental Alloys Devoted to Prosthetic Dentistry, in a NaCl Solution Simulating Human Saliva Specified by Stationary Electrochemical Techniques and EIS

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Abstract: Cobalt-based alloys containing chromium in quantity high enough represent a cheap alternative to dental alloys involving high quantities of noble metals (Au, Pt, Pd...). However, their general corrosion behaviour is not necessarily excellent and their use in the buccal milieu, which supposes contact with saliva, may lead to the release of ions to which the patient may be particularly sensible: allergic reaction, disease due to cobalt ions, associated troubles... In this work it was wished to investigate the electrochemical behaviour of extremely simplified versions of commercial cobalt-based dental alloys in a solution featuring among the ones usually used for simulating saliva. The aim was to explore the possible effects on the corrosion rate of the chromium content and of an eventual plastic deformation issued from fabrication or from mastication. Two binary alloys, Co-15wt.%Cr and Co-30Cwt.%Cr, mounted as electrodes, without or with preliminary hardening in compression, were subjected to EIS and cyclic polarization runs in a three-electrode cell heated at the human body temperature. Both alloys demonstrated high resistance against corrosion, with i_{corr} values significantly lower than $1 \mu A/cm^2$, without real effect of the chromium content (15wt.% seems enough) or of preliminary plastic deformation.

Keywords: Dental cobalt-chromium alloys, compression hardening, corrosion in artificial saliva, impedance spectroscopy, cyclic polarization.

1. INTRODUCTION

The metallic alloys used in prosthetic dentistry are, for most of them, based on very noble metals such as gold, platinum and palladium. However several manufacturers also propose cheaper alloys, for example for the frameworks strengthening the fixed partial dentures in which they are internally present. These ones generally bring good mechanical properties to prostheses and also, additionally, corrosion resistance as high as much nobler dental alloys. The best known among these dental alloys are the {nickel-chromium}-based ones. But there are also alloys based on cobalt. Cobalt-based alloys, elsewhere used in other medical fields such as bone surgery [1], are effectively also considered for dental applications [2-4] since several decades. Their characteristics such as their microstructural state [5,6], their mechanical behaviour [7,8] and their corrosion resistance in the buccal milieu [7,9] were subjected to investigations since many years.

Metallic alloys can be all possibly corroded in oxidant milieu, with as result the release of ionic

species. In the case of dental alloys this is the buccal milieu, which can act as corrosive media, because of the presence of oxidant species as oxygen dissolved in saliva. This may concern cobalt, the ions of which may promote allergic diseases [10,11]. Besides the possibility of cobalt ions generation in mouth, corrosion also may mechanically weaken the parts of cobalt alloy emerging from inside the cosmetic part of the prosthesis (Figure 1). Furthermore, mastication may induce a little plastic deformation for the thinner parts of frameworks, inducing an accelerated corrosion of the cobalt alloy with as results enhanced risk of mechanical rupture and ions release. Studying how alloys behave in corrosion in a milieu simulating the buccal milieu may be of great importance to anticipate such problems.

The purpose of the present work, in the continuity of recent studies [12-13] devoted to the dSIGN30 alloy (90Co-30Cr-4Ga-3Nb), is to investigate the roles of the content in chromium in dental cobalt-based alloys and of a plastic deformation, on the corrosion behaviour in artificial saliva, in the simplified case of binary alloys from which many real dental cobalt alloys are extrapolated. The experiences were simply done in a sodium chloride solution heated at the body temperature and not disaerated, using electrochemical impedance spectroscopy (EIS) and cyclic polarization.

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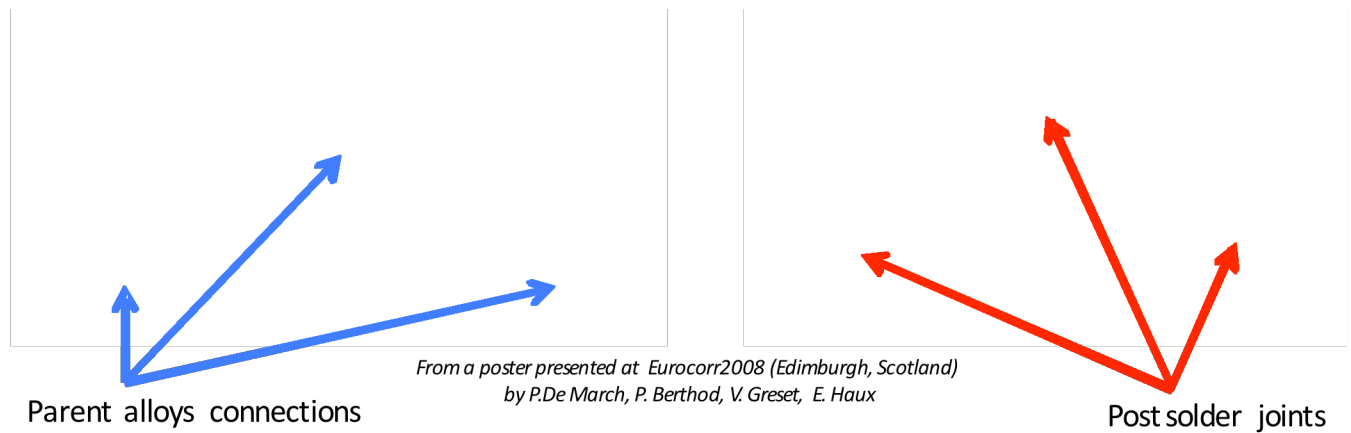


Figure 1: Metallic parts belonging to the frameworks strengthening fixed partial dentures, emerging from the cosmetic part of the prosthesis (artificial teeth) and thus exposed to the buccal milieu.

2. EXPERIMENTAL

2.1. Elaboration of the Alloys

Two alloys, Co-15Cr and Co-30Cr (chemical compositions in wt.%), were considered in this work. They are really simple since they do not contain other elements, the effects of which may hide the effect of the chromium content and of a preliminary plastic deformation. The effect of chromium may be enhanced by the great difference in chromium content (Cr in the second alloy: twice the first one). They were elaborated by foundry from parts of pure elements (Co and Cr, mainly from Alfa Aesar, purity > 99.9 wt.%). Cobalt and chromium were separately weighed to obtain charges of about 40 gram. They were then melted in order to constitute the two binary alloys. For that each charge was placed in the water-cooled crucible of a High Frequency Induction furnace (CELES). In both cases the charge was thereafter isolated from laboratory air by a silica tube. In this one three cycles $\{7 \times 10^{-2}$ millibars – vacuum; incorporation of 600 mbars of pure Argon $\}$ were applied. The final internal atmosphere was of about 300 millibars of pure Ar).

Melting of the charge and its homogenization were achieved by heating up to about 4kV and by an isothermal stage of three minutes in the liquid state. Rather fast cooling led to solidification and solid state cooling. Finally two compact ingots, one of the Co-15wt.%Cr composition (“Coalloy15”) and one of the Co-30wt.%Cr composition (“Coalloy30”), were obtained.

2.2. Machining, Metallography Preparation and Observations

Two parallelepipeds (dimensions: about 6 mm × 6 mm × 4 mm) were machined in each ingot. In both

cases one of the two parts was devoted to metallographic characterization in the as-cast condition and to the realization of the “as-cast” working electrode, and the second one was subjected to compression and thereafter the realization of the “hardened” electrode.

The observations of the as-cast alloys, after embedding in cold resin and grinding/polishing, were carried out by electron microscopy using a Scanning Electron Microscope (SEM) from JEOL (JSM 6010LA model). The Energy Dispersion Spectrometer (EDS) equipping this SEM allowed the microstructure observations in Back Scattered Electrons (BSE) mode and the semi-quantitative chemical analysis to control the obtained chemical composition. BSE observations and EDS measurements were done under a 20kV acceleration voltage.

2.3. Hardening

The parallelepipeds especially machined for that were subjected to compression allowing a plastic deformation important enough to obtain a hardened version of the same alloys. An electrochemical testing machine (manufacturer: MTS Systems, model: Alliance RF/150 model), of a 150kN capacity, equipped with auto-adjustable platens, was used.

2.4. Corrosion Properties

Thus, for each alloy an as-cast parallelepiped part and a plastically deformed parallelepiped part were available to perform the electrochemical characterization of corrosion. They were immersed in a liquid cold resin mixture but without submersion as for the metallographic samples. After total stiffening they were extracted from the plastic mould. They were

Table 1: Chemical Composition of the Two Alloys (Full Frame)

Alloys	Coalloy15		Coalloy30	
Average ± standard deviation	Co	Cr	Co	Cr
	Bal.	15.9 ±0.2	Bal.	30.7 ±0.2

placed in a vice, sewed a little and the denuded part of an electrical wire was inserted in the resulting slot by compression. Incorporated again in the mould additional liquid cold resin mixture was poured to totally immerse the upper part of the sample as well as the denuded copper of the electric wire. The metallic part of the obtained electrode was then ground until the 1200-grit paper, washed and dried. The obtained working electrodes were each associated to a platinum counter electrode and a Saturated Calomel Electrode (SCE). The three electrodes were then placed in a double-walled three-electrode cell containing a 9g/L NaCl aqueous solution simulating saliva. This one was prepared from distilled water and by the dissolution of NaCl crystals. Its pH was adjusted to 7.4 by addition of diluted HCl (for acidification) or diluted NaOH (for basification). The double-walled cell was heated to 38°C by water circulation from a Julabo F32 thermocryostat, in order to obtain 37°C for the electrolyte.

Two different apparatus were used for the electrochemical experiments for specifying the corrosion behaviour of the alloys.

First, runs of Electrochemical Impedance Spectroscopy were performed using a Versastat potentiostat (Princeton Applied Research-EGG) equipped with an electronic card allowing EIS experiments. The test were driven, and thereafter exploited, using the Versastudio software. The applied potential followed a sinusoidal variation around the corrosion potential (centred on E_{corr}), with an amplitude of 10mV, for a frequency decreasing from 100,000Hz down to 1Hz. What was wished with these experiments: determining the transfer resistance R_t (corrected from the electrolyte resistance R_e) and the double-layer capacity C_{dl} . The second used apparatus was an older potentiostat (model 263A) from Princeton Applied Research, driven by the M352 software of EGG/Princeton. The open circuit potential E_{ocp} was first determined, then the working electrode was polarized at $E_{ocp} - 150\text{mV}$. The applied potential increased thereafter up to 1.225 V at 1 mV s^{-1} . After having reached 1.225 V the potential decreased at -1 mV/s down to the initial value ($E_{ocp} - 150\text{mV}$).

3. RESULTS AND DISCUSSION

3.1. Chemical Compositions and Microstructures of the Obtained Alloys; Hardness

The chemical compositions of the two alloys, as analysed using the SEM and its EDS device, are globally well respected (Table 1), despite a chromium content a little higher than expected. The as-cast microstructures of both alloys are logically single-phased, as suggested in the SEM/BSE micrographs in Figure 2. No detectable chemical segregation possibly occurred during solidification can be noted.

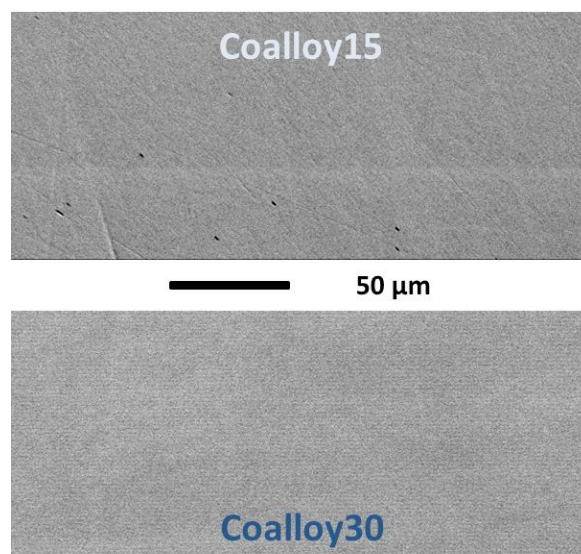


Figure 2: The microstructures of the two studied alloys as observed with the SEM in BSE mode.

3.2. Compression Runs

The two alloys were subjected to compression test until reaching 8.5 to 9% of total deformation. The corresponding curves are plotted together in Figure 3. For Coalloy15, after an elastic deformation until about 340 MPa (yield strength) the applied stress was increased up to about 730 MPa in the plastic domain, with as result a longitudinal permanent deformation of about -4%. For Coalloy30, the elastic deformation finished for about 320 MPa and the plastic one for about 600 MPa (resulting longitudinal permanent deformation: -6%).

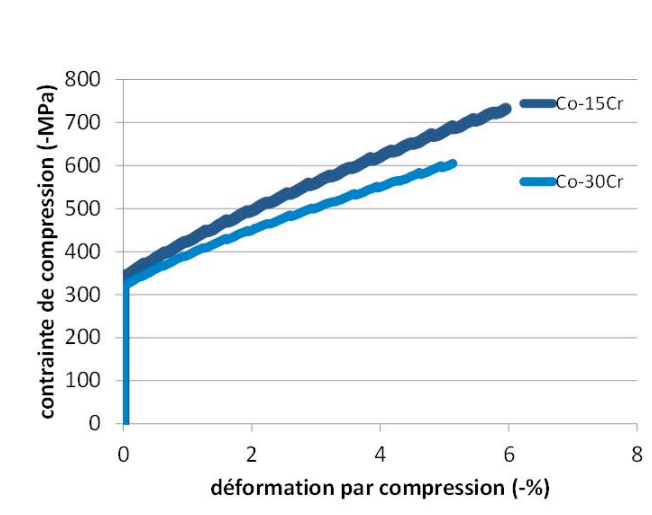


Figure 3: The compression curves of the two studied alloys.

3.3. EIS Results

The EIS results were plotted according to the Nyquist representation ($-Z_{im}(\omega) = Z_{real}(\omega)$). Unfortunately the semi-circles were only partly obtained for the {1 Hz; 100kHz} frequency range, as illustrated in Figure 4 (as-cast Coalloy15), Figure 5 (hardened Coalloy15); Figure 6 (as-cast Coalloy30) and Figure 7 (hardened Coalloy30). This problem, which is sometimes encountered with highly alloyed steels, suggests very high values of the transfer resistance. One can note that the obtained part of circle becomes more and more unbend when the immersion time increases (from $t = 0$ min to 60 min), suggesting that the transfer resistance goes on increasing.

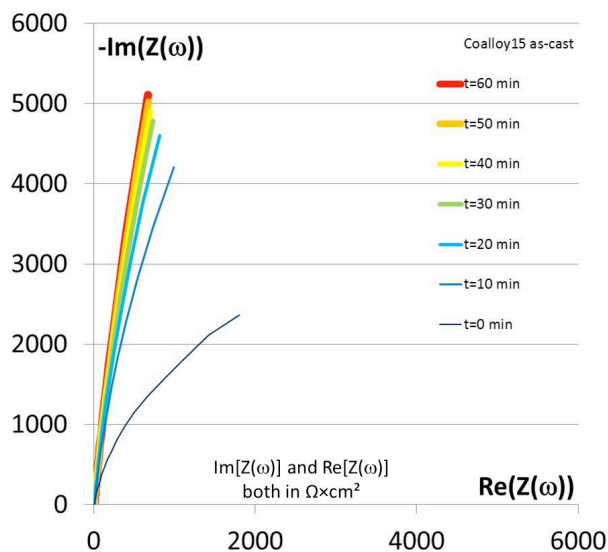


Figure 4: The six EIS results acquired for $t = 10, 20, 30, 40, 50$ and 60 minutes after immersion of the as-cast Coalloy15, plotted according to the Nyquist representation.

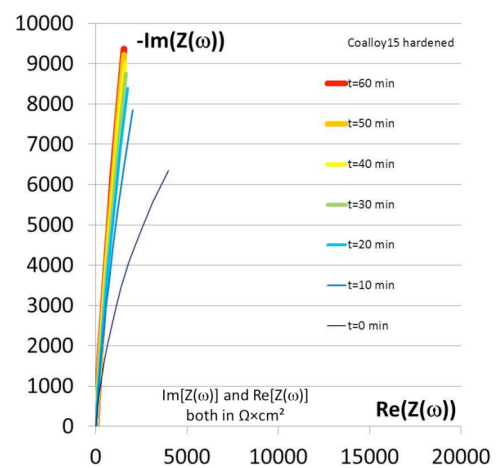


Figure 5: The six EIS results acquired for $t = 10, 20, 30, 40, 50$ and 60 minutes after immersion of the hardened Coalloy15, plotted according to the Nyquist representation.

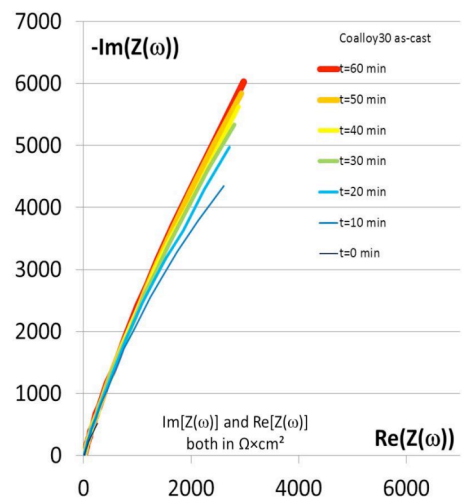


Figure 6: The six EIS results acquired for $t = 10, 20, 30, 40, 50$ and 60 minutes after immersion of the as-cast Coalloy30, plotted according to the Nyquist representation.

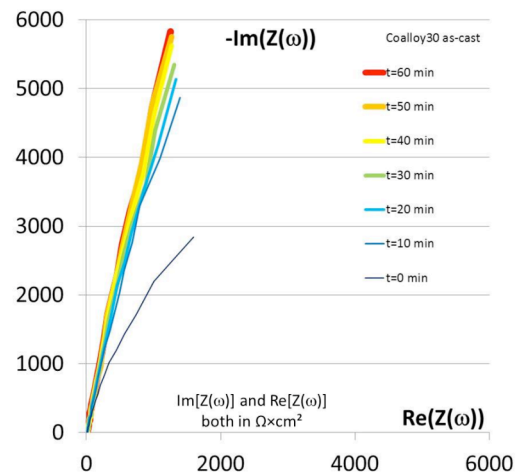


Figure 7: The six EIS results acquired for $t = 10, 20, 30, 40, 50$ and 60 minutes after immersion of the hardened Coalloy30, plotted according to the Nyquist representation.

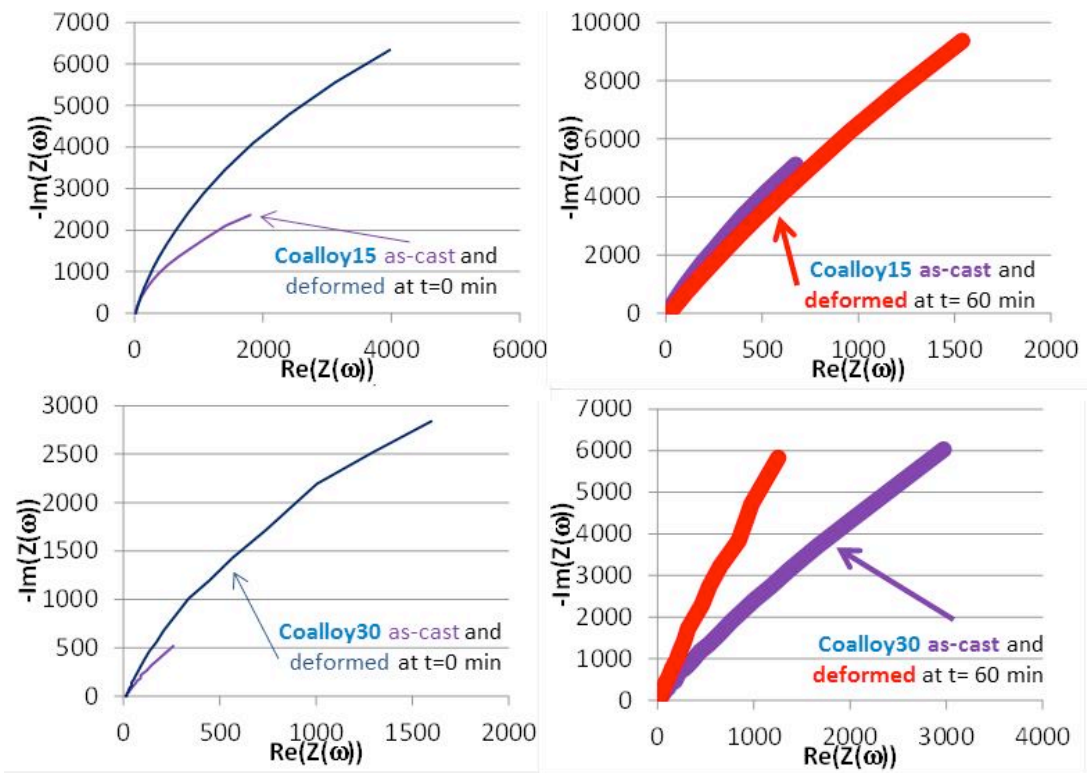


Figure 8: Comparison of the Nyquist plots between the as-cast states and the hardened states after immersion and after 1 hour of immersion, for the two alloys.

The EIS Nyquist curves are gathered in four graphs in Figure 8 to better observe the effect of hardening. One can see that the curves tend to be significantly more unbend (better transfer resistance) after plastic deformation than in the as-cast state, just after immersion as well as after one hour of immersion. Hardening seems being beneficial for the corrosion behaviour of these two alloys.

3.4. Cyclic Polarization Results

The obtained polarization curves are plotted in Figure 9 for the Coalloy30 in its as-cast condition and after hardening, and in Figure 10 for both alloys after plastic deformation. The first remark that can be done is the hysteresis shown by three of the four cyclic polarization curves. Indeed, except the one of the as-cast Coalloy 30, all of them present a corrosion potential higher in the potential-decreasing part than in

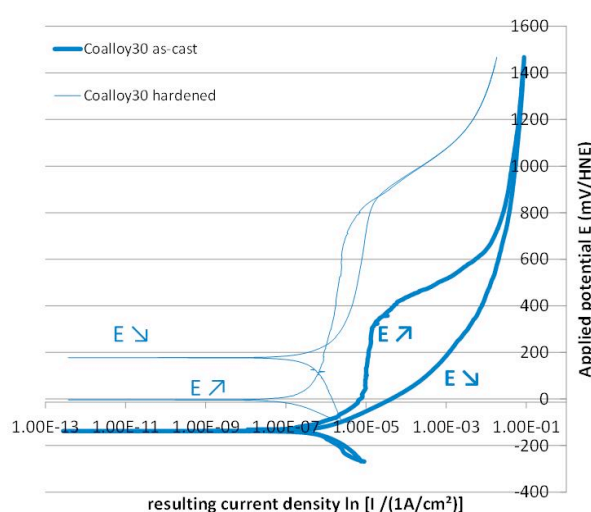


Figure 9: The cyclic polarization curves of the Coalloy 30 in its as-cast state and in its hardened state.

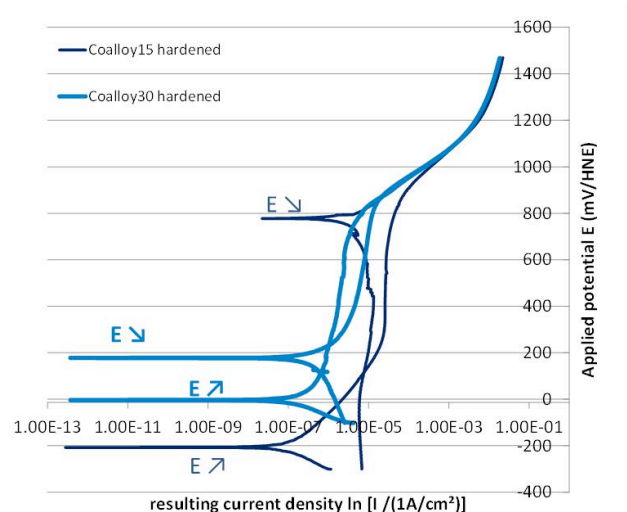


Figure 10: The cyclic polarization curves of the Coalloy15 and Coalloy 30 in their hardened states.

the potential-increasing part. A second remark is the higher values of anodic current density during the decrease in potential than during the previous increase in potential.

Further analysis is done in Tables 2 and 3. First, a Tafel-type exploitation of the part centered on E_{corr} in the potential-increasing part of the polarization curves led to the Tafel cathodic and anodic coefficients (β_a and β_c) presented in Table 2, together with the values of E_{corr} and I_{corr} . With values rather close to 120 mV per decade of current β_c is typical of the $\text{H}^+ + \text{e} \rightarrow \frac{1}{2} \text{H}_2$ cathodic reaction, while the values of β_a are too high to be representative of the $\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}$ or $\text{Cr} \rightarrow \text{Cr}^{2+} + 2\text{e}$ or $\text{Cr}^{3+} + 3\text{e}$ anodic reactions. The values of the corrosion potential (E_{corr}) are higher for the Coalloy30 than for the Coalloy15 but the corrosion current density (I_{corr}) is lower for the Coalloy15 than for the Cr-richest alloy. These two contradictory observations do not

allow clearly saying which among these two alloys is the best resistant. With an increase in corrosion potential and a decrease in corrosion current density it seems, in contrast, that hardening should improve the corrosion resistance of the Coalloy30. However, one can say that, in all cases, the corrosion current density is remarkably low, with values all under $1 \mu\text{A}/\text{cm}^2$.

By looking at the I_{cp} values in Table 3, one can see that passivating is rather easy for both alloys, as-cast or hardened. Furthermore reaching the passivation state seems easier for the Coalloy30 than for the Coalloy 15, and easier after hardening than before. Curiously the anodic current density seems higher when passivated than before overpassing the corrosion potential. During the potential-decreasing phase a new corrosion potential appears, more or less higher than the one observed during the potential-increasing part.

Table 2: Electrochemical Characteristics Issued from the Tafel Exploitation of the Potential-Increasing Part of the Cyclic Polarization Curves

Alloy (state)	β_a (mV/decade)	β_c (mV/decade)	E_{corr} (mV/HNE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
Coalloy15 (as-cast)	/	/	/	/
Coalloy15 (hardened)	172.9	114.2	-206.8	0.1405
Coalloy30 (as-cast)	115.5	128.1	-85.9	0.6485
Coalloy30 (hardened)	166.0	89.4	-4.9	0.1922

Table 3: Electrochemical Data Characterizing the Condition of Obtaining of the Passive State and the Corrosion Properties of the Passivated Alloys

Alloy (state)	I_{cp} ($\mu\text{A}/\text{cm}^2$)	$E_{\text{passivation}}$ (V/HNE)	$I_{\text{passivation}}$ (nA/cm 2)	New E_{corr} (mV/HNE)
Coalloy15 (as-cast)	/	/	/	/
Coalloy15 (hardened)	24.5	305.5	24.5	777.5
Coalloy30 (as-cast)	8.17	19.5	8.17	-112.5
Coalloy30 (hardened)	0.715	129.5	0.715	177.5

3.5. General Commentaries

Concerning the mechanical properties of these cobalt-chromium binary alloys it appeared first that adding more chromium (30 instead only 15wt.%) to cobalt, potentially favorable for the corrosion resistance, obviously induced also a little loss in yield resistance. It is true that pure cobalt (HCP at room temperature) possesses an intrinsic high yield strength (135 to 200MPa). Its Young's modulus is comparable those of steels and thus rather high, 210 GPa (against only 25GPa for chromium, BCC at room temperature). It is consequently not surprising to observe a decrease in tensile properties when more and more chromium is added to cobalt.

Concerning the EIS results a high chromium content tends to appear globally rather beneficial for the corrosion behavior of the alloy. This can be considered as logical since chromium has a recognized role to favor passivation and therefore resistance. The higher the chromium content the higher the availability of this element to constitute the passivation layer. For a given Cr content the behavior of the pre-hardened version tends to be also globally a little better than the as-cast version. One can think to an easier action of Cr when the microstructure is perturbed by hardening (atomic and dislocation defects favorable for the migration of Cr for taking part to passivation).

Concerning the cyclic polarization tests, one can notice that the obtained curves present an hysteresis which is notably characterized by a new corrosion potential shown during the decrease in potential which is higher than the one observed during the preceding increase in potential, for both alloys and both states. This can be easily explained by the further development of passivation and to the following thickening of the passivation layer during exposure to high anodic potential.

To finish one can underline that, although that the electrodes, made of the Co-15wt.%Cr or Co-30wt.%Cr alloys, plastically deformed or not, were polished again just after their immersion in the artificial saliva for performing the electrochemical runs for corrosion characterization, it seems that they rapidly get passive, at least partly. Indeed, the experiences of electrochemical impedance spectroscopy lead to incomplete circles suggesting transfer resistances already very high, and the corrosion current densities recorded at the beginning of the cyclic polarization runs were very low. Furthermore there were almost no real

anodic peaks. One can suspect that the alloys were thus already passivated when they started to be anodically polarized and increasing the applied potential beyond E_{ocp} only finished to passivate the alloys. The current densities, which appeared curiously higher than the I_{corr} value determined by Tafel characterization, were simply higher because of the higher potential to which the alloys were exposed: the alloys were seemingly already passivated when the Tafel part of the experiment was being done. In general, the open circuit or corrosion potentials were rather high and the corrosion current very low.

CONCLUSIONS

Despite that some differences were seen between the two alloys or between the two states for a given alloy, it is too early to affirm anything about the role of the chromium content or of the hardening. But the most important is that both alloys are very resistant against corrosion in this {9g/L NaCl; pH=7.4} solution often considered as valuable artificial saliva. The chromium content seems to be not important if it is at least higher than 15wt.% and plastic deformation or hardening possibly induced by mastication for the thinnest parts of metallic parts of dental prostheses did not lead to any catastrophic deterioration of this good behavior in corrosion. One can conclude by saying that, for these basis alloys, whatever their possible hardening, no significant release of ions, and thus corresponding induced allergy, is to be feared.

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