PITTING CORROSION OF A DENTAL COPPER ALLOY IN ARTIFICIAL SALIVA

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Abstract: The corrosion behaviour of a copper based dental alloy (GAUDENT) in a simulated saliva environment was studied by potentiodynamic polarization and by electrochemical impedance spectroscopy (EIS). It was established that the metallurgical processing (melting in air and manually casting) influences negatively the corrosion resistance. The keeping of this alloy in solution reduces the thermodynamic tendency to corrosion but not influence appreciably the type and intensity of the corrosion. In all cases a pitting corrosion was evidenced.

Keywords: *Gaudent, cyclic polarisation, corrosion current, EIS*

INTRODUCTION

The biocompatibility of dental alloys is an important and controversial problem for practitioner physicians. This depend both on the release of metallic ions from the material and on their cytotoxicities. These factors depend mainly on alloy composition, pre-treatment of materials and environmental medium. The release of corrosion products may elicit an adverse biological reaction in the host, several authors reporting

increased concentrations of local and systemic trace metals in association with metal implants [1, 2]. Accelerated corrosion and a tissue response, as discoloration, or foreign body response, that can be related directly to identifiable corrosion products have been demonstrated in the tissues surrounding multiple-part devices [3, 4]. Corrosion products may cause local pain and swellings in the region of implant [5] and may ultimately result in a cascade of events leading to periprosthetic bone loss [3]. Excess of metal ions, especially chromium, cobalt and nickel are suspected to induction of tumors e.g. malignant fibrous histiocytoma [6]. The toxicities of these elements, metabolic, bacteriological, immunological or carcinogenic, generally apply to soluble forms and may not apply to the degradation products of prosthetic implants

The GAUDENT is a copper-based dental casting alloy, containing over 80 % copper and 10 % aluminum. Earlier studies suggest that copper-based alloys eliminate the Cu ions and other corrosion products in such concentrations that can affect the viability and proliferation of lymphocyte and seem to be very important for the cytotoxic effect. However, when considering any toxic effects of copper it is essential to remember that copper is found naturally, is indispensable for life, and that any potential harm is linked to a great number of factors. Nevertheless, the copper is more dangerous because this element is a chemical modifier. Copper induces greater carcinogenic activity of nickel than it has by itself.

In the earlier papers [7, 8], the corrosion behavior of a GAUDENT S sample was analyzed in various corrosion media: weak acidic saliva of Fusayama–Mayer type, a weak basic saliva of Rondelli type, and in inorganic and organic acidic solutions (pH = 1.35 respectively 2.64).

In Fusayama–Meyer saliva was evidenced a pitting corrosion; characterized by a breakdown potential of approximately 1550 mV (SCE) and a re-passivation potential of 650 mV (SCE). In acidic solution and presence of Cl^-, the casting alloy shows a generalized corrosion starting from a potential of 700 mV (SCE), while in the presence of SO_4^{2-} and Cl^- ions the corroding effect starts from a potential of −50 mV (SCE), corrosion process being accomplished by other electrochemical reaction taking place in the corrosion medium. Recently, the behavior of Gaudent alloy in Fusayama–Mayer and a Ringer type solution was analyzed, the measurements have been emphasized the fact that from thermodynamic point of view the artificial saliva seem to be more aggressive than the Ringer solution but, kinetically, the corrosion rate in Ringer solution is approximately five time greater than in artificial saliva [9]. Present study analyses in a new manner the corrosion behavior of Gaudent alloy in Afnor type artificial saliva.

EXPERIMENTAL

A commercially Gaudent S sample vas used, its composition, determined with an emission spectrophotometer BAIRD - model DV6, being: 82.4% Cu, 9.95% Al, 4.15% Ni, 2.13% Fe and 1.35% Mn. Another sample was obtained by air melting and centrifugal casting of the commercial sample.

The corrosion media was an AFNOR type artificial saliva with composition: NaCl – 0.7 g/L, KCl – 1.2 g/L, Na_2HPO_4 H_2O – 0.26 g/L, $NaHCO_3$ – 1.5 g/L, KSCN – 0.33 g/L, urea – 1.35 g/L and pH = 7.6.

The open circuit potential measurements (OCP) and the polarization curves recording were performed with the electrochemical system VOLTALAB-32 (Radiometer,

Copenhagen). Experimental data were acquired and processed with the VoltaMaster 2 software. A saturated calomel electrode (SCE) was used as reference and platinum as auxiliary electrode.

The working electrode, made from alloy sample was processed into a cylindrical shape and mounted in a polytetrafluoroethylene support. In these conditions the surface exposed to corrosion and measure was a one-dimensional circular area. Before experimental determinations the samples were mechanically polished with abrasive SiC paper up to a granulation number of 2500 mesh and then rinsed in distilled water and ethanol.

Linear polarization curves were recorded at small scan rate of the electrode potential (dE/dt = 0.5 mV/s) in the potential range ($E_{corr} \pm 100$ mV). The cyclic potential curves were registered at 10 mV/s scan rate and the potential range (–350…+1500…-350 mV). Corrosion currents were evaluated by polarization resistance method, known as the Stern-Geary method [10].

$$J_{corr} = \frac{b_a \cdot b_c}{2.303(b_a + b_c) R_p}, \quad [mA.cm^{-2}] \tag{1}$$

where: R_p is the polarization resistance at corrosion potential, b_a and b_c – Tafel parameters (the slopes of the linear portions of the anodic and cathodic curves).

The measurements were performed both for recent (fresh) polished surface and for old surfaces – maintained after grinding for different periods in artificial saliva.

Electrochemical Impedance Spectroscopy (EIS), using a PAR 263 A potentiostat with PAR 5210 amplifier and ZsimpWin software, also characterized the sample. The amplitude of the AC potential was 10 mV and single shine wave measurements at frequencies between 10^{-1} and 10^5 Hz were performed for the sample.

The structural changes of alloy surface after electrochemical corrosion were analyzed by optical microscopy, with a MC1 apparatus (IOR – Bucharest, Romania) provided with digital camera.
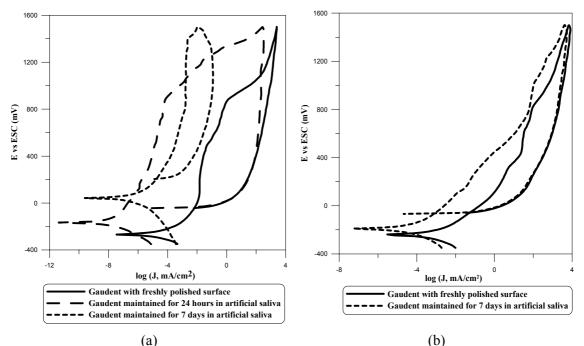
RESULTS AND DISCUSSIONS

For establish the corrosion type and for evaluate the main parameters of the corrosion process, the cyclic polarization curves were registered both for fresh finished surface of the electrode and for surface maintained 24 or 168 hours (7 days). All measurements were made comparatively for both commercial sample (non processed sample) and for casting sample.

The cyclic polarization curves in semi-logarithmic E = f(log J) coordinates, are presented in Figure 1.

The analysis of these cyclic polarization curves point out that in all cases a pitting corrosion takes place, both for freshly cleaned surface and for old surface.

The main corrosion parameters, evaluated from linear and cyclic polarization curves are presented in Table 1.

(a)   (b)

Figure 1. *Cyclic polarization curves on Gaudent in artificial saliva for different immersion times: (a) Commercial; (b) Casting sample*

Table 1. *Main corrosion parameters for Gaudent in Afnor saliva*

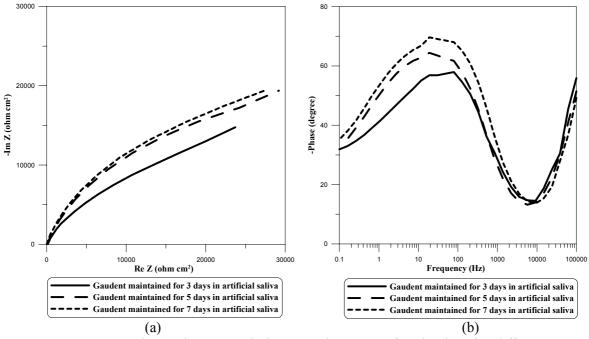| Sample	E_{cor} mV(ESC)	R_p (Ω cm^2)	J_{cor} (μA/cm^2)	E_{BD} mV(ESC)	E_{RP} mV(ESC)	ΔE, (mV)
Alloys with freshly polished surface						
Commercial sample	-193	2,79 10^3	4,42	707	-44	751
Casting sample	-175	1,39 10^3	5,12	750	-60	810
Alloys maintained for 24 hours in artificial saliva						
Commercial sample	-147	8,19 10^4	0,097	1330	-52	1382
Casting sample	-160	4,02 10^4	1,90	883	-12	895
Alloys maintained for 7 days in artificial saliva						
Commercial sample	+100	2,12 10^4	0,42	1340	200	1140
Casting sample	-145	2,99 10^3	2,46	1000	-60	1060

Analyzing the data contained in Table 1 one find that at initial moment of immersion in artificial saliva the two sample shows relatively high negative values of corrosion potential (E_{cor}) – indicating a increased tendency to instantaneous corrosion at immersion in solution. Instantaneous corrosion currents densities (J_{cor}) are enough large, of 5.10^{-6} A/cm^2 order, and indicate a high corrosion rate. Breakdown potentials (E_{BD}), comparable for the two samples, have small values - which can be find in oral cavity, while the repassivation potential (E_{RP}) are very small, closed of the corrosion potential, this saying greater imperfect passivity domain (ΔE).

By maintaining the sample in artificial saliva for one or seven days the corrosion potential increases, this indicating a certain passivation of the alloy. The difference between the two samples is significantly; while in the case of commercial sample (laminated material) the corrosion potential increases with approximately 300 mV, in the case of the casting sample the increase is only 30 mV. This fact indicates that the

commercial sample passivates better than the casting sample. Corresponding, the instantaneous corrosion current decreases more little in the casting sample.

Breakdown potentials are relative small for both fresh surface and for old surface, and (700…750 mV (SCE)), but the values increase sensible during the prolonged maintenance in solution. The repassivation potentials (E_{RP}) are very small, close to the corrosion potential, thus that the imperfect passivity domain is unusual large (comprised between 750 and 1400 mV) for both type of surfaces. The "hysteresis loop" area, which is a measure of corrosion process intensity, is enough great. Taking into account all these one can point out that the Gaudent alloy is very susceptible to pitting corrosion in Afnor saliva, the process taking place at relative small over-potentials with high intensities of corrosion currents. The maintaining of the alloy in solution conducts to an increase of the corrosion resistance. This effect can be explained both by increase of oxide thickness and by saline deposits on the metal surface.

Electrochemical Impedance Spectroscopy confirms this behavior supplementary. The quality of fitting to the equivalent circuit was judged by the "chi squared" value that was less than $2 \cdot 10^{-4}$. Instead of pure capacitors, constant phase elements (Q) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data. The electrochemical impedance data for commercial Gaudent in artificial saliva after 3, 5 and 7 days immersion are shown in Figure 2.

(a) (b)

Figure 2. *Impedance data recorded on Gaudent in artificial saliva for different immersion times: (a) Nyquist plots; (b) Bode-phase plots*

The Nyquist plot (Figure 2a) shows that impedance increases with time. Two time constant, well separated in the frequency domain, can be clearly observed on the Bode plot (Figure 2b). For the commercial sample in Afnor saliva the experimental data are best described with the equivalent circuit presented in Figure 3.
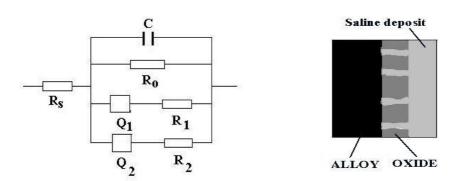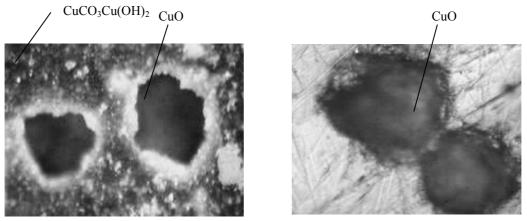
Figure 3. The equivalent circuit for the corroding system considered

Polarization resistance (R_p) is represented by the sum of the R_0, R_1, R_2 and the resistance of the solution, R_s. From the Stern-Geary equation, it follows that the higher the R_p, the lower is the corrosion rate and the lower is the ion release.

This circuit satisfy the experimental data within in the limit of 1...2 % errors and confirms the complexity of the corrosion process in the case of this alloy.

By microscopic analysis of electrochemical treated sample confirms the advanced pitting corrosion and saline sediments on alloy surface.
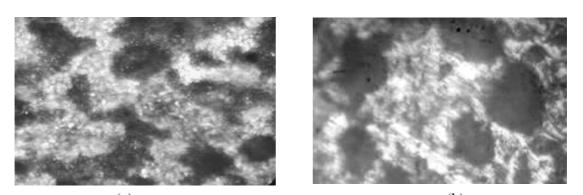

(a)   (b)

Figure 4. The micrographs of the commercial Gaudent(laminated) after andodic polarization at 1500 mV(SCE) in Afnor saliva (a) – saline sediments and after saline removing (b)

The microphotographs presented in Figure 4a point out that, besides the pitting localized attack, saline sediment is deposed on the surface. This sediment, having a greenish color, is most probably the copper hydroxycarbonate resulted during the reaction between copper and oxygen in the presence of CO_2 dissolved in solution. The pitting attack is better observed after mechanical remove of the saline deposit (Figure 4b).

Figure 5 presents the micrographs of the casting sample surface after electrochemical treatment (anodic polarization) (a) and after salts remove. For both laminated and casting samples, the micrographs were achieved for sample maintained 24 hours in saliva and then polarized at +1500 mV.

(a)   (b)

Figure 5. The micrographs of the casting Gaudent(laminated) after anodic polarization at 1500 mV(SCE) in Afnor saliva (a) – saline sediments and after saline removing (b)

The corrosion type do not modify nor by casting processing not even by keeping in solution. The pitting attack is much more visible in the case of the commercial alloy, but in the case of the casting alloy the pits are very extended, the surface appearance being characteristic that one of the generalized corrosion.

CONCLUSIONS

- Gaudent alloy is very susceptible to pitting corrosion in artificial saliva, the process taking place at relative small over-potentials with high intensities of corrosion currents.
- The EIS Bode-phase plots show two maxims. The EIS spectra are best fitting using an equivalent circuit (EC). The EC is consistent with the model of a two-layer structure: the inner layer could consist of CuO and the other layer of saline sediments.
- The microscopic analysis confirms the advanced pitting corrosion and saline sediments on alloy surface.

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