Corrosion Stability of a New Dental Alloy for Restorative Metal-Polymer Works

ECATERINA VASILESCU[1*], PAULA DROB[1], CORA VASILESCU[1], DANIEL MARECI[2], JULIA CLAUDIA MIRZA-ROSCA[3]

[1] Institute of Physical Chemistry "Ilie Murgulescu", 202 Spl. Independentei, 060021, Bucharest, Romania

[2] Technical University "Gh. Asachi", 71 Bd. Mangeron, 700050, Iasi, Romania

[3] Las Palmas de Gran Canaria University, Mechanical Engineering Department, 35017 Tafira, Spain

With the aim to increase the corrosion resistance of the dental silver-palladium alloys, a new dental Ag-20Pd-5Au-1.5Ti alloy was elaborated; titanium, the new element introduced in the composition of this alloy is very resistant to corrosion and has favourable effects on its resistance. The behaviour of the new Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard artificial saliva un-doped and doped with 0.05M NaF of different pH values (to simulate the extreme conditions that can appear in oral cavity for long term working periods) and Ringer-Brown solution (that reproduce "in vitro" the human fluid) is studied in this paper. The electrochemical techniques of the potentiodynamic and linear polarization and electrochemical impedance spectroscopy were used. Also, the open circuit potentials and corresponding open circuit potential gradients (due to the saliva pH and content non-uniformities) variations versus the exposure time (5000 h) were registered. Both in Carter-Brugirard saliva and Ringer-Brown solution, the new dental Ag-20Pd-5Au-1.5Ti alloy exhibited a passive metal behaviour with electropositive corrosion potentials, relative large passive potential ranges and low passive current densities. From EIS data, an electric equivalent circuit with two time constants was modelled: the first time constant represents the passive film and the second constant illustrates the charge transfer reactions through this passive layer.

Keywords: new dental Ag-20Pd-5Au-1.5Ti alloy; Carter-Brugirard artificial saliva un-doped and doped with 0.05M NaF of different pH values; Ringer-Brown solution; corrosion rates; electric equivalent circuits

The dental alloys are generally used for many years and need to resist to mechanical load and degradation caused by oral fluid, temperature and pH changes. Moreover, corrosion in mouth is a continuous process and the ions released by the dental alloys in oral fluid are removed continuously with abrasion of food, liquids and toothbrushes [1-8].

Generally, there are three different types of dental alloys: conventional casting alloys used without ceramics or polymers, bonding alloys used with high and medium fusing ceramics and polymers and universal alloys used without and with low fusing ceramics and polymers [9,10].

Dental alloys based on noble metals used for crown and bridge applications have high price and was necessary to introduce a large number of alternative casting alloys of low cost. These alloys with silver, palladium, copper, nickel, chromium, etc., have to be accompanied by the continuous check of the tarnish and corrosion resistance in order to assure a long term durability and good aesthetic results [11-15].

Dental alloys may induce adverse biological reactions such as gingival swelling and erithema, mucosal pain and lichenoid reactions. Although these troubles are often due to other than the material itself they can be induced by the metallic ions released during corrosion. So, in order to decrease the risks, it is necessary to test the dental alloys regarding their resistance to corrosion [16-20].

Palladium-silver based dental alloys [11,21-26] represent one of the alternative materials used for dental crows and bridges because they have very high corrosion resistance. However, metal ion may be released from prosthetic works by corrosion reactions occurring during their exposure in the oral cavity; palladium, silver and copper ions were detected in the artificial saliva [22,27,28].

Immediately, after the fixation of a dental work, at the contact with tissues appear exudates that contain fibrin and chloride ions at a relative low *p*H (5 or smaller, till to 2), because the hydrogen concentration increases in the traumatic tissues [21,29]. In few hours appears an inflammatory response that can increase the pH value till 9 [21,29,30]. Also, the electrochemical cells with differential aeration can be formed.

Moreover, the dental alloys are used for very long term (10-20 years) and in this period it is possible that different oxides from the passive film to hydrolyse, producing important changes of the local *p*H of the biofluid [31,32].

With the aim to increase the corrosion resistance of the silver-palladium alloys, a new dental Ag-20Pd-5Au-1.5Ti alloy was elaborated; titanium, the new element introduced in the composition of this alloy is very resistant to corrosion and has favourable effect on its resistance. The behaviour of the new Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard artificial saliva un-doped and doped with 0.05M NaF of different *p*H values (to simulate the extreme conditions that can appear in oral cavity for long term working period) and Ringer-Brown solution (that reproduce "in vitro" the human fluid) is studied in this paper.

Experimental part

Cylindrical electrodes (obtained from ingots of the new Ag-20Pd-5Au-1.5Ti alloy) were grinded with metallographic paper of different granulations, fixed in a Stern-Makrides hold system, rinsed with distilled water, degreased in boiling benzene and dried.

All measurements were carried out in:

- artificial Carter-Brugirard saliva of *p*H = 2.46 (that can appears in the case of using the acid drinks) and *p*H = 5.4 (that can appear after a meal), *p*H = 7.89 (normal *p*H), *p*H = 8.96 (that can appear in case of infections or inflammations); saliva composition is (g/L): NaCl – 0.7; KH_2PO_4 – 0.26; KSCN – 0.33; Na_2HPO_4 – 0.19; urea – 0.13; $NaHCO_3$ – 1.5;
- artificial Carter-Brugirard saliva doped with 0.05M NaF (like in the products of oral hygiene) of *p*H = 2.54 and *p*H = 5.52 (obtained by HCl addition), *p*H = 8.21 (normal pH), *p*H = 8.81 (obtained by KOH addition);

* *email: ec_vasilescu@yahoo.com*

- Ringer-Brown solution with the composition (g/L): NaCl – 6; KCl – 0.4; $CaCl_2.2H_2O$ – 0.2; natrium lactate – 3.05; *p*H = 7:

Temperature was kept at $37^0 \pm 1^0C$.

The electrochemical techniques of potentiodynamic and linear polarization and electrochemical impedance spectroscopy (EIS) were used. Also, the open circuit potentials, E_{oc} and corresponding open circuit potential gradients (due to the saliva *p*H, $\Delta E_{oc}(pH)$ and content, $\Delta E_{oc}(c)$ non-uniformities) variations versus the exposure time (5000 h) were registered.

Cyclic potentiodynamic measurements were applied beginning from -0.5 V till to +4 V (versus SCE) using a scan rate of 10 mV/s. A Voltalab 80 equipment with VoltaMaster 4 programme was used. From the obtained voltagraphs were determined the main electrochemical parameters that characterize the alloy corrosion resistance: E_{corr} – corrosion potential; E_p – passivation potential; E_T – transpassive potential; ΔE_p – passivation potential range; i_{corr} – corrosion current density; i_p – passive current density.

Linear polarization measurements (Tafel curves) were applied for a range of ± 300 mV around the open circuit potential, with a scan rate of 10 mV/sec. The same Voltalab equipment with VoltaMaster 4 programme, which provided the values of the corrosion current (i_{corr}) and rate (V_{corr}) was used. The total quantity of ions released in solution (ion release rate), expressed in ng/cm² was determined with the formula:

$$ion\ release\ rate = 1.016 x V_{corr} x 10^5 \quad (1)$$

where V_{corr} = corrosion rate in mm/yr.

The electrochemical impedance spectroscopy (EIS) was applied at open circuit potential using a PAR 263A potentiostat connected with a PAR 5210 lock-in amplifier. The amplitude of the AC potential was 10 mV and single sine wave measurements at frequencies between 10^{-1} and 10^5 Hz were performed for each sample.

Results and discussions

Corrosion stability in Carter-Brugirard saliva un-doped and doped with 0.05M NaF of pH ≈ 2.5

Cyclic polarisation curves (fig. 1) show good behaviour of Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva of *p*H ≈ 2.5, un-doped and doped with 0.005M NaF: corrosion potential, E_{corr} has electropositive values (table 1) that characterize a state of immunity for Au, Pd and Ag and of passivity for Ti on the Pourbaix diagrams [33]; passivation potential range, ΔE_p is large, about 2 V and the passive current density, i_p has very low values in this potential range (table 1), revealing a passive, stable, resistant state. Doping with 0.05 M NaF brings slight increase of the main electrochemical parameters (table 1) but without affecting the good stability of this new dental alloy.

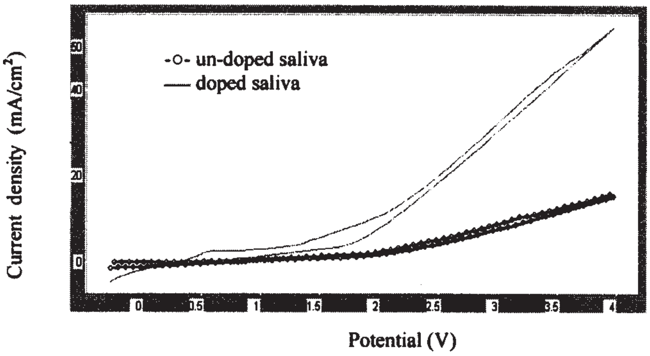

Fig. 1. Cyclic potentiodynamic curves for Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva of *p*H ≈ 2.5 at 37°C

From linear polarisation measurements (Tafel curves) it resulted a low corrosion rate (table 2) in "Very Stable" category and a very reduced quantity of ions released in un-doped Carter-Brugirard saliva. In doped saliva, the corrosion rate is placed in "Stable" resistance class (table 2); a corrosion rate of 0.013 mm/year conducts to a thinness of the alloy with 0.13 mm after 10 years of continuous using in saliva of this extreme *p*H value and doping with NaF. Because, this very acid *p*H value can accidentally appear in oral cavity, the alloy can be considered very stable.

In the doped saliva, both the corrosion rates and ion release rates have higher values due to its higher corrosivity produced by the aggressive fluoride ion.

Corrosion stability in Carter-Brugirard saliva un-doped and doped with 0.05M NaF of pH ≈ 5.4

In Carter-Brugirard saliva of *p*H ≈ 5.4, the same good behaviour resulted (fig. 2, table 1): electropositive corrosion potentials placed in the immunity domain of Au, Pd and Ag and in the passivity domain of Ti [33]; large passivation potential range and low passive current densities, namely a very good corrosion resistance. Slight higher values of all electrochemical parameters appeared in doped saliva, without to influence the alloy stability.

Corrosion rates (table 2) placed the Ag-20Pd-5Au-1.5Ti alloy in the „Very Stable" resistance class both in un-doped and doped saliva.

Table 1

MAIN ELECTROCHEMICAL PARAMETERS FOR Ag-20Pd-5Au-1.5Ti ALLOY IN CARTER-BRUGIRARD SALIVA AT 37°C

*p*H	E_{corr} (V)	E_p (V)	E_T (V)	ΔE_p (V)	i_p (μA/cm²)
≈ 2.5	-0.201	-0.201	+2.0	2.201	3.7
≈ 2.5 + NaF	-0.210	-0.210	+1.9	2.110	10
≈ 5.4	-0.230	-0.230	+2.0	2.230	4.8
≈ 5.4 + NaF	-0.237	-0.237	+1.2	1.437	9.1
≈ 8	-0.076	-0.076	+2.1	2.176	8.5
≈ 8 + NaF	-0.162	-0.162	+1.2	1.362	9.4
≈ 9	-0.197	-0.197	+2.1	2.297	9.5
≈ 9 + NaF	-0.196	-0.196	+1.2	1.396	14.5

Table 2
CORROSION RATES AND ION RELEASE RATES FOR Ag-20 Pd-5Au-1.5Ti ALLOY IN CARTER-BRUGIRARD SALIVA AT 37°C

*p*H	i_{corr}(μA/cm²)	V_{corr} (μm/an)	Category	Ion release rate (ng/cm²)
≈ 2.5	0.21	1.81	VS	182.88
≈ 2.5 + NaF	1.59	13.58	S	1379.73
≈ 5.4	0.84	7.21	VS	732.54
≈ 5.4 + NaF	0.86	7.38	VS	750.41
≈ 8	0.92	7.91	VS	803.66
≈ 8 + NaF	1.06	9.08	VS	922.53
≈ 9	0.93	8.02	VS	815.24
≈ 9 + NaF	1.34	11.44	S	1162.30

VS –Very Stable; S – Stable

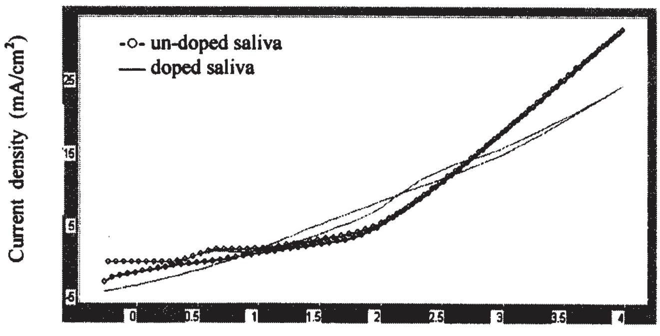

Fig. 2. Cyclic potentiodynamic curves for Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva of *p*H ≈ 5.4 at 37°C

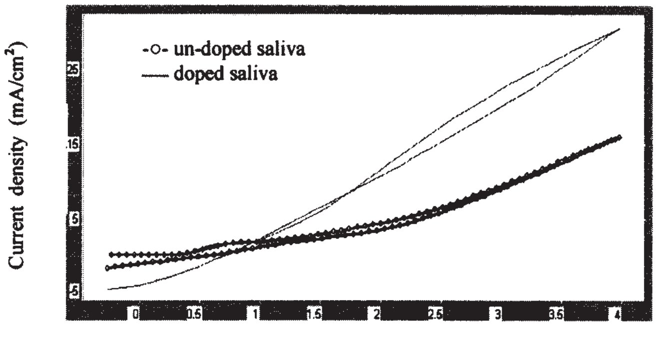

Fig. 3. Cyclic potentiodynamic curves for Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva of *p*H ≈ 8 at 37°C

Corrosion stability in Carter-Brugirard saliva un-doped and doped with 0.05M NaF of pH ≈ 8

In normal saliva of *p*H ≈ 8, the Ag-20Pd-5Au-1.5Ti alloy is very resistant (fig. 3 and table 1) having noble corrosion potential, a very large passivation potential range, reduced passive current densities and reduced corrosion rates specifically for „Very Stable" state; correspondingly, the ion release rates are low both in un-doped and doped saliva (table 2).

Corrosion stability in Carter-Brugirard saliva un-doped and doped with 0.05M NaF of pH ≈ 9

The alkaline Carter-Brugirard saliva of *p*H ≈ 9 influenced slightly negative the behaviour of the Ag-20Pd-5Au-1.5Ti alloy as following: the corrosion potentials (fig. 4 and table 1) present more active values than in neutral saliva, still placed in the immunity domain of Au, Pd and Ag and in the passivity domain of Ti [33]; the passive current densities are little higher and corrosion rates (table 2) characterise a „Very Stable" behaviour in un-doped saliva and a „Stable" class in doped saliva. However, a corrosion rate of 0.011 mm/yr. conducts to alloy thinness with 0.1 mm after 10 years of continuous working in this saliva. So, the alloy can be considered resistant taking into account that, this *p*H value can appear only accidentally and very rarely in oral cavity.

Stability of the new Ag-20Pd-5Au-1.5Ti alloy from the monitoring of the open circuit potentials

From figure 5 can be observed that the open circuit potentials E_{oc} have slight oscillations with the tendency to be more electropositive for 5000 exposure hours; this behaviour emphasize a stable passive state and a good anticorrosive resistance. The shift of E_{oc} to positive values shows the increase of the passive film thickness and the decrease of the corrosion rate [34]. The initial variations of E_{oc} values suggest some dissolution and re-passivation processes of the passive film [35].

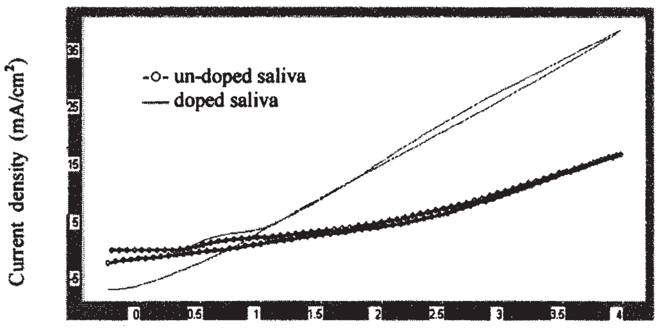

Fig. 4. Cyclic potentiodynamic curves for Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva of *p*H ≈ 9 at 37°C

A different behaviour was observed in Carter-Brugirard saliva of *p*H ≈ 5.4, where the open circuit potential became slight more active (more electronegative), but the medium value reached till present is -200 mV, a value that also characterizes a good passive state and corrosion resistance.

In neutral (*p*H ≈ 8) and alkaline (*p*H ≈ 9) Carter-Brugirard saliva, the open circuit potentials reached after 5000 exposure hours values of -100 mV, respectively +100 mV, specifically for a very stable passive state.

All values of the open circuit potentials are placed in the immunity domain of Au, Pd and Ag and in the passivation domain of Ti [33].

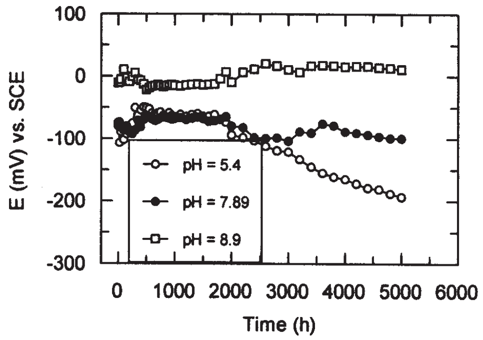

Fig. 5. E_{oc} vs. time for Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva of different *p*H values

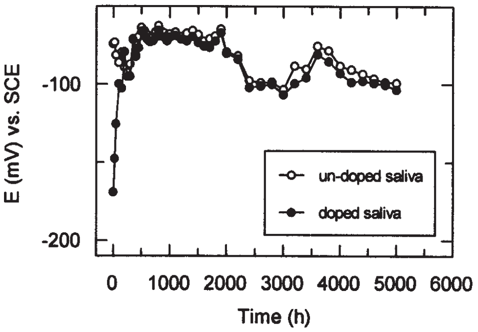

Fig. 6. E_{oc} vs. time for Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva un-doped and doped with 0.05M NaF at *p*H ≈ 8

From figure 6 it resulted no differences between the values of open circuit potentials in un-doped and doped saliva of *p*H 8. This fact confirms the good anticorrosive resistance of the new Ag-20Pd-5Au-1.5Ti alloy

Stability of the new Ag-20Pd-5Au-1.5Ti alloy from the monitoring of the open circuit potential gradients

Due to the non-uniformities of the saliva *p*H and composition, along the same dental work can appear the potential gradients $\Delta E_{oc}(pH)$, respectively $\Delta E_{oc}(c)$ that can accelerate the corrosion. Four potential gradients were simulated and calculated:

$$\Delta E_{oc1}(pH) = E_{oc}^{pH=5.4} - E_{oc}^{pH=7.89} \quad (2)$$

$$\Delta E_{oc2}(pH) = E_{oc}^{pH=5.4} - E_{oc}^{pH=8.96} \quad (3)$$

$$\Delta E_{oc3}(pH) = E_{oc}^{pH=7.89} - E_{oc}^{pH=8.96} \quad (4)$$

$$\Delta E_{oc4}(c) = E_{oc}^{pH=7.89} - E_{oc}^{NaF} \quad (5)$$

These potential gradients were monitored for 5000 h till present. In table 3, low values of these gradients (from 0.0004 V to 0.182 V) appeared; these values can not initiate or keep local or galvanic corrosion, because, only differences of 0.6 – 0.7 V [36-39] can generate these types of corrosion.

Stability of the new Ag-20Pd-5Au-1.5Ti alloy in Ringer-Brown solution

Potentiodynamic polarisation curve in Ringer-Brown solution (fig. 7) exhibited a passive metal behaviour with an electropositive corrosion potential (E_{corr} = -0.247 V), a relative large passive potential range (ΔE_p = 0.597 V), a low passive current density (i_p = 21 μA/cm^2) and an increase of the passive current density at +0.35 V due to the dissolution of silver as Ag^+ ions [33].

From electrochemical impedance spectroscopy (EIS) were obtained Bode spectra at E_{oc} (fig. 8); these spectra show two phase angles at about -65^0 and -75^0; the first angle indicates some charge transfer processes through the passive film due to the dissolution of Ag as Ag^+ ions; the second angle show a near capacitive behaviour, characterizing a passive film.

The electric equivalent circuit (fig. 9) was modelled with two time constants: the first time constant is for the passive film and is illustrated by the polarisation resistance, R_1 and the constant phase element CPE_1; the second constant is for the charge transfer reactions and is showed by the resistance, R_2 and the constant phase element, CPE_2.

It resulted a high value for resistance R_1 (5.5 10^5 Ω cm^2), reflecting a very stable passive layer, and high value for resistance R_2 (1.1 10^5 Ω cm^2), indicating reduced charge transfer processes [40,41]. Also n_1 parameter has a value closed to 1 (0.92), characterizing an almost ideal capacitor, namely a very good passivity [42]. These facts confirm the

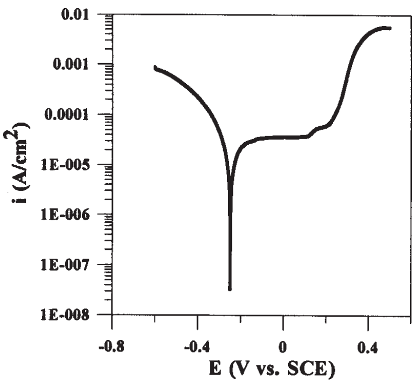

Fig. 7. Potentiodynamic curve for Ag-20Pd-5Au-1.5Ti alloy in Ringer-Brown solution

Table 3
OPEN CIRCUIT POTENTIAL GRADIENTS FOR Ag-20Pd-5Au-1.5Ti ALLOY IN CARTER-BRUGIRARD SALIVA AT 37^{0}C

Time (h)	$\Delta E_{oc1}(pH)$ (V)	$\Delta E_{oc2}(pH)$ (V)	$\Delta E_{oc3}(pH)$ (V)	$\Delta E_{oc4}(c)$ (V)
100	-0.016	-0.092	-0.076	+0.014
500	+0.013	-0.029	-0.042	+0.002
1000	+0.003	-0.050	-0.053	+0.002
2000	-0.015	-0.084	-0.070	+0.0004
3000	-0.018	-0.110	-0.093	+0.003
4000	-0.077	-0.150	-0.013	+0.005
5000	-0.094	-0.182	-0.088	+0.004

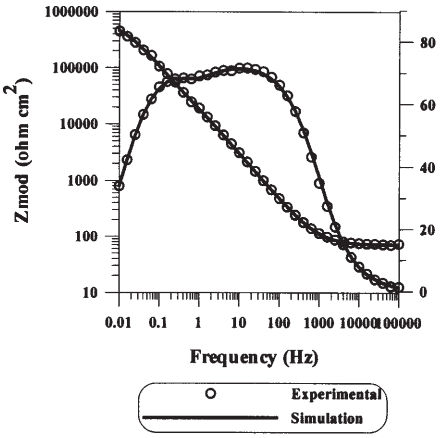

Fig. 8. Bode spectra for Ag-20Pd-5Au-1.5Ti alloy in Ringer-Brown solution at E_{oc}

good anticorrosive resistance of the new dental Ag-20Pd-5Au-1.5Ti alloy in Ringer-Brown solution.

Conclusions

Cyclic polarisation curves show good behaviour of Ag-20Pd-5Au-1.5Ti alloy in Carter-Brugirard saliva of different *p*H values, un-doped and doped with 0.005M NaF: self-passivation, large passive potential range, very low values of passive current density, revealing a passive, stable, resistant state. Doping with 0.05 M NaF brings slight increase of the main electrochemical parameters but without affecting the good stability of this new dental alloy.

From linear polarisation measurements it resulted a low corrosion rate in “Very Stable” category and a very reduced quantity of ions released in un-doped Carter-Brugirard saliva.

Open circuit potentials haves slight oscillations with the tendency to be more electropositive for 5000 exposure hours; this behaviour emphasize a stable passive state and a good anticorrosive resistance.

The open circuit potential gradients, monitored for 5000 exposure hours in Carter-Brugirard saliva un-doped and doped with 0.05M NaF presented very low values which cannot initiate and keep local or galvanic corrosion.

In Ringer-Brown solution, Ag-20Pd-5Au-1.5Ti alloy exhibited a passive metal behaviour with an electropositive corrosion potential, a relative large passive potential range, a low passive current density.

From EIS data, an electric equivalent circuit with two time constants was modelled: the first time constant is for the passive film and the second constant is for the charge transfer reactions through this passive layer.

Acknowledgements: This work has been supported by Romanian National Research Plan, contract number MNT-7-024/2010. The authors gratefully acknowledge this support.

References

1. GIL, F.J., FERNANDEZ, E., MANERO, J.M., PLANELL, J.A., CORTADA, M., GINER, L., J. Biomed. Mater. Eng., **5**, 1995, p. 161
2. VERMILYEA, S.G., CAI, Z., BRANTLEY, W.A., MITCHELL, J.C., J. Prosthodont., **5**, 1996, p. 288
3. KIKUCHI, M., TAKADA, Y., KIYOSUE, S., YODA, M., WOLDU, M., CAI, Z., OKUNO, O., OKABE, T., Dent. Mater., **19**, 2003, p. 174
4. FISCHER, J., J. Biomed. Mater. Res., **15**, 2000, p. 678
5. OHKUBO, C., SHIMURA, I., AOKI, T., HANATANI, S., HOSOI, T., HATTORI, M., ODA, Y., OKABE, T., Biomaterials, **24**, 2003, p. 3377
6. MARECI, D., SUTIMAN, D., CRETESCU, I., CAILEAN, A., MIRZA ROSCA, J.C., Rev. Chim. (Bucharest), **59**, no. 8, 2008, p. 871
7. HUANG, H.H., Electrochim. Acta, **47**, 2002, p. 2311
8. MARECI, D., CHELARIU, R., GORDIN, D.M., UNGUREANU, G., GLORIANT, T., Acta Biomater., **5**, 2009, p. 3625

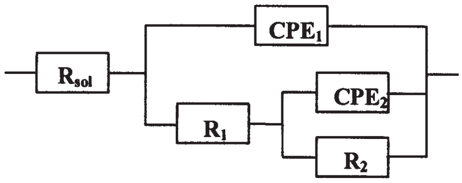

Fig. 9. Electric equivalent circuit with two time constants

9. AL-HITY, R.R., KAPPERT, H.F., VIENNOT, S., DALARD, F., GROSGOGEAT, B., Dent. Mater., **23**, 2007, p. 679
10. MANARANCHE, C., HORNBERGER, H., Dent. Mater., **23**, 2007, p. 1428
11. JOSKA, L., PODDANA, M., LEITNER, J., Dent. Mater., **24**, 2008, p. 1009
12. LE GOFF, A.H., JOIRET, S., ABOURAZZOUK, D., Electrochim. Acta, **43**, 1998, p. 53
13. BERNARD, M.C., ABOURAZZOUK, D., LE GOFF, A.H., Corros. Sci., **35**, 1993, p. 809
14. HANAWA, T., HIROMOTO, S., ASAMI, K., Appl. Surf. Sci., **183**, 2001, p. 68
15. NEWMAN, S., CHAMBERLAIN, R.T., NUNEZ, L.J., J. Biomed. Mater. Res., **15**, 1981, p. 615
16. SCHMALZ, G., GARHAMMER, P., Dent. Mater., **18**, 2002, p. 396
17. SUTIMAN, D., CAILEAN, A., CRETESCU, I., MARECI, D., Rev. Chim. (Bucharest), **59**, no. 4, 2008, p. 417
18. MAN, I., PIRVU, C., DEMETRESCU, I., Rev. Chim. (Bucharest), **59**, no. 6, 2008, p. 615
19. POPA, M.V., DEMETRESCU, I., VASILESCU, E., DROB, P., IONESCU, D., VASILESCU, **C.**, Rev. Chim. (Bucharest), **54**, no.7, 2003, p. 583
20. MARECI, D., CHELARIU, R., IVANESCU, I., GORDIN D.M., CRETESCU, I., GLORIANT, T., Rev. Chim. (Bucharest), **60**, no. 8, 2009, p. 787
21. MEYER, J.M., RECLARU, L., J. Mater. Sci. Mater. M., **6**, 1995, p. 534
22. SARKAR, N.K., BERZINS, D.W., PRASAD, A., Dent. Mater., **16**, 2000, p. 374
23. CAI, Z., VERMILYEA, S.G., BRANTLEY, W.A., Dent. Mater., **15**, 1999, p. 202
24. PINASCO, M.R., ANGELINI, E., CORDANO, E., MAGI, E., ROSALBINO, F., J. Mater. Sci. Mater. M., **11**, 2000, p. 837
25. ENDO, K., OHNO, H., MATSUDA, K., ASAKURA, S., Corros. Sci., **45**, 2003, p. 1491
26. SUN, D., MONAGHAN, P., BRANTLEY, W.A., JOHNSTON, W.M., J. Mater. Sci. Mater. M., **13**, 2002, p. 435
27. NIEMI, L., MINNI, E., IVASKA, A., J. Dent. Res., **65**, 1986, p.888
28. GOEHLICH, V., MAREK, M., Dent. Mater., **6**, 1990, p. 103
29. SCHIFF, N., GROSGOGEAT, B., ISSAC, M., DALARD, F., Biomaterials, **23**, 2002, p. 1995
30. FOVET, Y., GAL, J.Y., TOUMELIN-CHEMLA, F., Talanta, 53, 2001, p. 1053
31. POPA, M.V., DEMETRESCU, I., SUH, S.H., VASILESCU, E., DROB, P., IONITA, D., VASILESCU, **C.**, Bioelectrochemistry, **71,** 2007, p. 126
32. POPA, M.V., VASILESCU, E., DROB, P., VASILESCU, **C.**, DEMETRESCU, I., IONITA, D., J. Mater. Sci. Mater. M., **19,** 2008, p. 1
33. POURBAIX, M., Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston, 1974
34. BLACKWOOD, D.J., CHNA, A.W.C., SEAH, K.H.W., THAMPURAN, R., TEOH, S.H., Coros. Sci., **42**, 2000, p. 481
35. EVANS, U.R., Corrosion of Metals, E. Arnold, London, 1969, p. 898
36. SHEELA, G., RAMASAMI, M., RAO, C.R.K., PUSHPAVANAM, M., Bull. Electrochem., **17**, 2001, p. 347
37. FUSAYAMA, T., KATAYORI, T., NOMOTO, S., J. Dent. Res., **42**, 1963, p. 1183
38. SHALABY, L.A., Corros. Sci., **11**, 1971, p. 767
39. THOMPSON, N.G., BUCHANAN, R.A., J. Biomed. Mater. Res., **13**, 1979, p. 35
40. AL-MAYOUF, A.M., AL-SWAYIH, A.A., AL-MOBARAK, M.A., AL-JOBAB, A.S., Mater. Corros., **55**, 2004, p. 524
41. MARSH, J., GORSE, D., Electrochim. Acta, **43**, 1998, p. 659
42. TAMILSELVI, S., MURUGARAJAN, R., RAJENDRAN, N., Mater. Corros., **58**, 2007, p. 113

Manuscript received: 2.11.2009