Electrochemical Behaviour of a New Dental Alloy for Restorative Works in Simulating Extreme Functional Conditions

ECATERINA VASILESCU[1*], PAULA DROB[1], STELIANA IVANESCU[2], IOAN DAN[2], CORA VASILESCU[1]
[1] Institute of Physical Chemistry "Ilie Murgulescu", Spl. Independentei 202, 060021 Bucharest, Romania
[2] SC R&D Consulting and Services SRL, 45 M. Ghiculeasa Str., 023761, Bucharest, Romania

The behaviour of the new dental Ag-17Au-10Pd-3Ti alloy in un-doped and doped with 0.05M NaF (the equivalent of the fluoride concentration from oral hygiene products) Carter-Brugirard artificial saliva of different pH values that simulate the non-uniformity conditions of the pH of the saliva from oral cavity was studied. The conditions of local acidity (till to pH = 2.5) that can appear immediately after the fastening of the dental works, when the hydrogen concentration increases in the traumatized tissues or by the hydrolysis in time of the corrosion products were reproduced; also, the local alkaline conditions (till to pH = 8.9) that can produce in the case of inflammations or in the distress periods of the body were simulated.

Keywords: un-doped and doped saliva; different pH values; corrosion rate; ion release

For restorative aesthetic works are used alloys that can be covered with porcelain "porcelain-fused-to metal alloys" (PFM) of type: Au-Pt-Pd; Au-Pd-Ag; Pd-Ag; Au-Pd; Pd-Cu [1]. But, these alloys can create some problems: Pd-Ag alloys produce the discoloration of the ceramics, Pd-Cu alloys form dark oxides that mask the dental work. Titanium alloys have lower mechanical properties than the other base metal alloys, but have a lower density and are easily tolerated by patients.

The biocompatibility in the case of a dental work (crown, bridge, etc.) means not to cause the inflammation of the pulpal or periodontal tissues (without osseointegration).

The corrosion [2-11] deteriorates the non-noble metals by local attack named pitting and sometimes deeply penetrate in the metal structure. The corrosion effects can be from the change of the aspect to the loss of the mechanical resistance; also, the metallic ions released by corrosion can reach in the digestive tract and in tissues. The ions and products generated by corrosion can have different effects: teeth discoloration, pains due to the galvanic corrosion, oral lesions, allergic dermatitis and stomatites, endodontic failures, dental implant rejection and very slowly tumorgenisis and carcinogenesis.

The extra cellular fluid [12-20] contains ions of Na^+, K^+, Fe^{2+}, Ca^{2+}, Pb^{2+}, Cl^-, HCO_3^-, OH^-, F^-, Br^-, I^-, NO_2^-, PO_4^{3-} and 18 amino acids, proteins, vitamins, etc., at a *p*H that varies from 5 to 7 and a pressure of CO_2 from 8 to 3000 mmHg.

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 hydrolyze producing important changes of the local *p*H of the biofluid; these differences can generate potential and current gradients that can accelerate the corrosion on some zones [21-27]. Consequently, it appear non-uniformities of the physiological fluid *p*H along of the metallic surface; the local acidity (up to *p*H = 2) is producted by the hydrolysis in time of the corrosion products and the local alkalinity up to *p*H = 9 in the case of the inflammations or in the distress periods of the body [28].

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

To simulate these extreme conditions, we made the experiments in normal Carter-Brugirard artificial saliva and in artificial saliva of different *p*H values: acid *p*H to simulate the acidity conditions, alkaline *p*H to simulate the alkaline conditions that can appear in the enumerated conditions, as well as *p*H ≈ 5 that exists in oral cavity immediately after a meal. Also, Carter-Brugirard artificial saliva doped with 0.05M NaF (that reproduces the fluoride concentration from the oral hygiene products) of normal, acid and alkaline *p*H values was used.

Experimental part

Ag-Au-Pd-Ti alloy was obtained by vacuum melting and contains 70% Ag, 17% Au, 10% Pd and 3% Ti, only non-toxic elements.

Cylindrical electrodes 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.

An electrochemical glass cell with three electrodes was used: central working electrode, auxiliary platinum electrode (grid to have a bigger surface) and a reference saturated calomel electrode (SCE) connected with the working electrode by a Haber-Luggin capillary placed very close by the working electrode surface to avoid the apparition of some supplementary potential drops.

All measurements were carried out in:

- artificial Carter-Brugirard saliva of *p*H = 2.5 and *p*H = 5.5 (obtained by HCl addition), *p*H = 7.9 (normal *p*H), *p*H = 8.9 (obtained by KOH addition); 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 of the same *p*H values was used to reproduce the fluoride ion content from the usual teeth pastes and gels.

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

The electrochemical techniques of potentiodynamic and linear polarization were used.

* *email: evasiles@chimfiz.icf.ro*

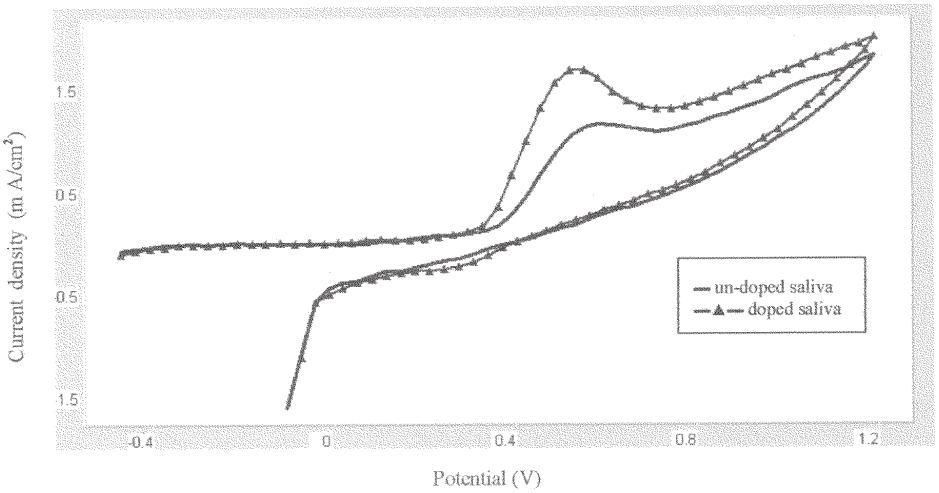

Fig. 1 Cyclic potentiodynamic curves in un-doped and doped Carter-Brugirard saliva of *p*H = 2.5 at 37°C for Ag-17Au-10Pd-3Ti alloy

Cyclic potentiodynamic polarization measurements were applied beginning from -0.5 V up to +1.2 V (versus SCE) using a running rate of 10 mV/sec. Equipment Voltalab 80 with VoltaMaster 4 programme was used. From the obtained voltammograms 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. If the reverse branch of the cyclic voltammogram presents smaller currents than of the direct branch, so, the studied material has very stable passivation behaviour. If the reverse branch shows the bigger currents than of the direct branch it results that pitting corrosion exists.

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 that provided the values of the corrosion current (i_{corr}) and rate (V_{corr}) were used. The total quantity of ions released in solution ("ion release") in ng/cm² was determined with formula:

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

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

Results and discussions

Behaviour in un-doped and doped with 0.05M NaF Carter-Brugirard saliva of pH = 2.5

Un-doped artificial Carter-Brugirard saliva of *p*H = 2.5 is more aggressive than the normal Carter-Brugirard saliva [31], but, since this *p*H value can appear in the functional time of a dental work, these limit conditions using very acid *p*H saliva were simulated. From the cyclic potentiodynamic polarization curve (fig. 1) it resulted that the Ag-17Au-10Pd-3Ti alloy is self passivation, without appearing the active-passive dissolution potential domain, but with a relative, large passivation potential range (table 1). Corrosion potential has a favorable, electropositive value, for the oral environment, placed on the Pourbaix diagrams [31] in the passivation potential range of titanium, in the immunity potential range of palladium, gold and silver. Passivation current density is small, denoting a passive film resistant to corrosion. The current peak registered at the potential of +0.6 V is due to the silver oxidation to Ag^+ ions [31].

The behaviour of Ag-17Au-10Pd-3Ti alloy (fig. 1) in doped saliva of *p*H = 2.5 is similar with that from un-doped saliva of the same *p*H value, namely self-passivation with a large potential range. Corrosion potential (Table 1) in doped saliva is a little more electropositive than in un-doped saliva and the passive potential range is a little more narrow. The same peak at +0.6 V was registered.

From Tafel linear polarization curve were determined the corrosion rates that have a relative low values in un-doped saliva and slightly bigger in doped saliva. The alloy is arranged in category "Stable" (table 2).

Table 1
MAIN ELECTROCHEMICAL PARAMETERS FOR Ag-17Au-10 Pd-3Ti ALLOY IN ARTIFICIAL CARTER-BRUGIRARD SALIVA AT 37°C

*p*H	Saliva	E_{corr} (V)	E_p (V)	E_T (V)	ΔE_p (V)	i_p ($\mu A/cm^2$)
2.5	Un-doped	-0.24	-0.24	+0.40	0.64	45.2
	Doped	-0.22	-0.22	+0.32	0.54	61.5
5.5	Un-doped	-0.22	-0.22	+0.35	0.57	35.5
	Doped	-0.19	-0.19	+0.40	0.59	28.9
7.9	Un-doped	-0.14	-0.14	+0.10	0.24	68.8
	Doped	-0.20	-0.20	+0.40	0.60	21.9
8.9	Un-doped	-0.12	-0.12	+0.39	0.51	25.9
	Doped	-0.19	-0.19	+0.40	0.59	18.8

pH	Saliva	i_{corr} ($\mu A/cm^2$)	V_{corr} ($\mu m/yr.$)	Ion release (ng/cm^2)
2.5	Un-doped	0.60	20.26	2058.4
	Doped	1.26	42.35	4302.8
5.5	Un-doped	0.91	30.39	3087.6
	Doped	0.49	16.65	1691.6
7.9	Un-doped	0.21	7.05	716.8
	Doped	0.87	29.41	2988.1
8.9	Un-doped	1.87	62.64	6364.2
	Doped	0.62	20.90	2123.4

Table 2
CORROSION RATES AND "ION RELEASE" FOR Ag-17Au-10 Pd-3Ti ALLOY IN ARTIFICIAL CARTER-BRUGIRARD SALIVA AT 37°C

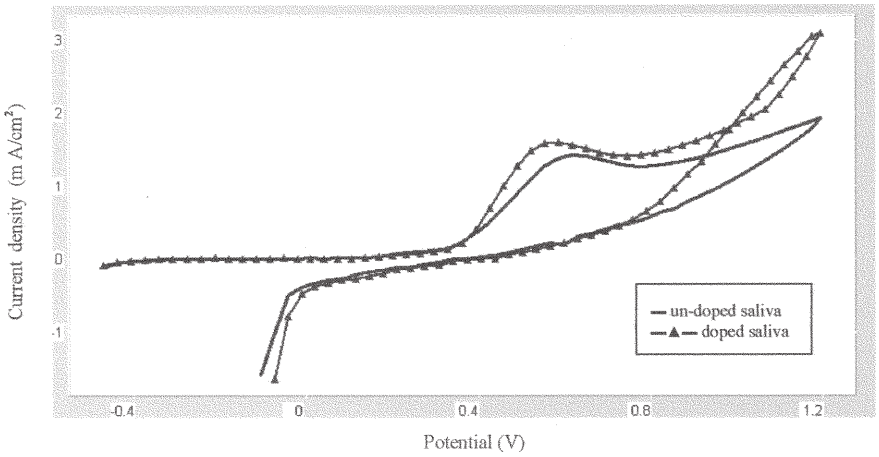

Fig. 2 Cyclic potentiodynamic curves in un-doped and doped Carter-Brugirard saliva of *p*H = 5.5 at 37°C for Ag-17Au-10Pd-3Ti alloy

The total quantity of ions released (table 2) is relative slow, so, the alloy releases in the surrounding tissues and in the oral cavity small quantities of ions both in un-doped and doped saliva.

Behaviour in un-doped and doped with 0.05M NaF Carter-Brugirard saliva of pH = 5.5

In un-doped Carter-Brugirard saliva of *p*H = 5.5, the Ag-17Au-10Pd-3Ti alloy presented a typical behaviour of self-passivation metal (fig. 2). The corrosion potential is more electropositive than those from the un-doped saliva with the highest acidity (table 1) due to the more reduced aggressivity of this saliva, being in the same domain of the immunity for gold, silver and palladium and of passivity for titanium. The peak from the potential of +0.7 V belongs to the formation of the same Ag^+ ions.

Fluoride ions do not act on the main electrochemical parameters (fig. 2 and table 1), these being a little more favorable than in the absence of the fluoride ions.

The corrosion rates and "ion release" have low values (table 2) placing the alloy in the resistance category "Stable".

Behaviour in un-doped and doped with 0.05M NaF Carter-Brugirard saliva of pH = 7.9

In normal un-doped Carter-Brugirard saliva of *p*H = 7.9, the environment in which the alloy works most of the time, a behaviour of passive metal (fig. 3) was registered. The corrosion potential has a nobler value than in saliva of acid *p*H values (table 1) and is placed in the same domain of immunity and passivity of the constituent metals. The peak from +0.6 V corresponds to dissolution of silver as Ag^+ ions.

In doped Carter-Brugirard saliva of normal *p*H, fluoride ions have a negative influence on the main electrochemical parameters, that present more active values (fig. 3 and table 1).

In un-doped saliva, the corrosion rate determined from Tafel slope shows that the Ag-17Au-10Pd-3Ti alloy is very resistant, being classified as "Very Stable" (table 2); the total quantity of ions (table 2) released in Carter-Brugirard saliva of *p*H = 7.9 is with one size order lower than of the other studied *p*H values.

In doped saliva, the corrosion rates and "ion release" (table 2) presented higher values than in un-doped saliva and placed the alloy in the resistance class "Stable" in comparison with "Very Stable" in un-doped saliva.

Behaviour in un-doped and doped with 0.05M NaF Carter-Brugirard saliva of pH = 8.9

In un-doped alkaline Carter-Brugirard saliva that simulated the case of inflammations or infections, the Ag-17Au-10Pd-3Ti alloy is self-passivated (fig. 4), presenting a large passive potential range; the corrosion potential (table 1) has the noblest value from those four values of studied *p*H; also, the passive current density is low, specific for a passive, stable, resistant layer. The same peak of silver dissolution appears at the potential of +0.6 V.

In doped alkaline Carter-Brugirard saliva, fluoride ions activated the corrosion potential (fig. 4 and table 1) but enlarged the passive potential range and reduced the passive current density.

From Tafel curve it results a higher corrosion resistance in doped saliva, than in un-doped saliva, but the alloy is placed in the "Stable" category (table 2). The total quantity of ions released in corrosion environment is reduced.

Conclusions

Electrochemical studies concerning the behaviour of Ag-17Au-10Pd-3Ti alloy in un-doped and doped with 0.05M NaF Carter-Brugirard saliva of acid, neutral and alkaline *p*H values pointed out the following:

- in un-doped Carter-Brugirard saliva, the corrosion rate and "ion release" placed the Ag-17Au-10Pd-3Ti alloy in

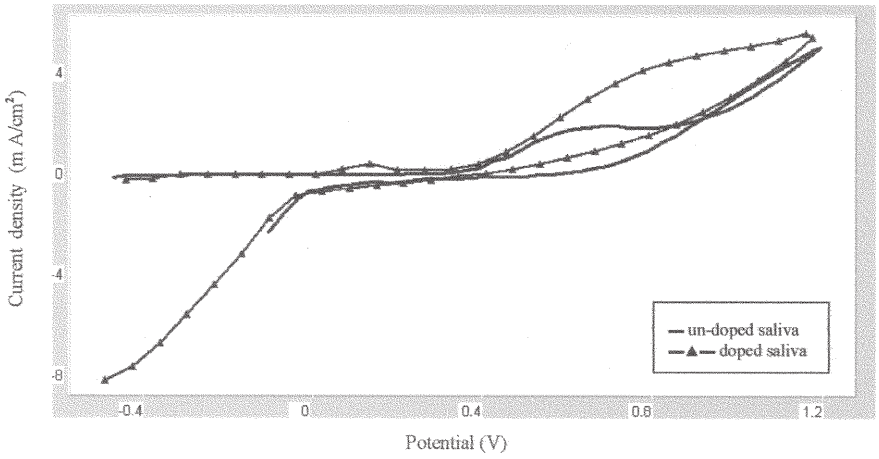

Fig. 3 Cyclic potentiodynamic curve in un-doped and doped Carter-Brugirard saliva of *p*H = 7.9 at 37°C for Ag-17Au-10Pd-3Ti alloy

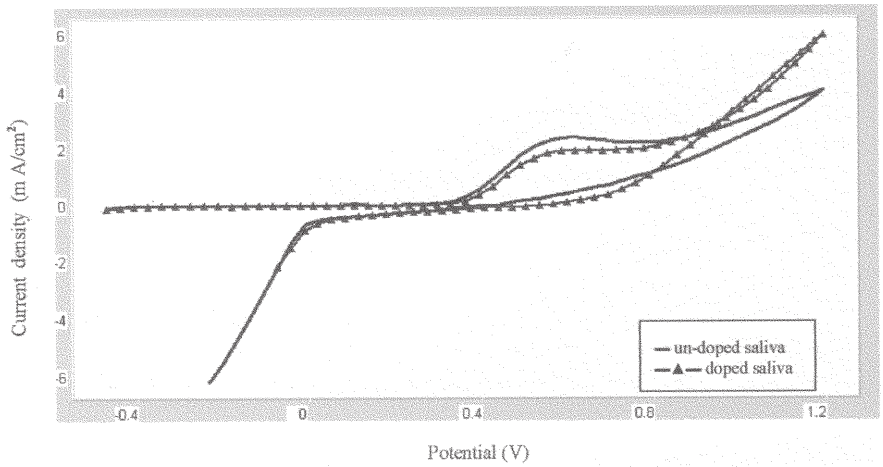

Fig. 4 Cyclic potentiodynamic curve in un-doped and doped Carter-Brugirard saliva of *p*H = 8.9 at 37°C for Ag-17Au-10Pd-3Ti alloy

"Very Stable" resistance class only in normal saliva; in saliva of very acid (2.5), relative acid (5.5) and alkaline (8.9) *p*H values that simulate the extreme functional conditions, the alloy is "Stable";

- in doped with 0.05M NaF Carter-Brugirard saliva, slightly more aggressive, the studied alloy takes part in "Stable" resistance class both in normal saliva (*p*H = 7.9) and in acid (*p*H = 2.5 and *p*H = 5.5) or alkaline (*p*H = 8.9) saliva.

References

1. Handbook of Materials for Medical Devices, ASM International, Davis, J. R., Material Park, 2003, p. 220
2. ROBIN, A., MEIRELIS, J. P., Mater. Corros., **58**, 2007, p. 173
3. CONTU, F., ELSENER, B., BOHNI, H., J. Biomed. Mater. Res., **62**, 2002, p. 412
4. AZIZ-KERRZO, M., CONROY, K. G., FENELON, A. F., FARRELL, S. T., BRESLIN, C. B., Biomaterials, **22**, 2001, p. 1531
5.HODGSON, A., MUELLER, Y., FORSTER, D., VIRTANEN, S., Electrochim. Acta, **41**, 2002, p. 1913
6. FONSECA, C., BARBOSA, M. A., Corros. Sci., **43**, 2001, p. 547
7. LAVOS-VALERETO, I. C., WOLYNEC, S., RAMIRES, I., GUASTALDI, A. C., COSTA, I., J. Mater. Sci. Mater. Med., **15**, 2004, p. 55
8. CONTU, F., ELSENER, B., BOHNI, H., Corros. Sci., **46**, 2004, p. 2241
9. THAIR, L., KAMACHI MUDALI, U., ASOKAMANI, R., RAJ, B., Mater. Corros., **55**, 2004, p. 358
10. SOUTO, R. M., LAZ, M. M., REIS, R. L., Biomaterials, **24**, 2003, p. 4213
11. LUIZ DE ASSIS, S., WOLYNEC, S., COSTA, I., Electrochim. Acta, **51**, 2006, p. 1815
12. CAHOON, J. R., HILL, L. D., J. Biomed. Mater. Res., **12**, 1978, p. 805
13. RUCK, T. C., FULTON, J. F., Medical Physiology and Biophysics, 18, W.B. Sounders, 1960
14. RECLARU, L., MEYER, J. M., Biomaterials, **19**, 1998, p. 85
15. NAKAGAWA, M., MATSUYA, S., SHIRAISHI, T., OHTA, M., J. Dent. Res., **78**, 1999, p. 1568
16. DE MELE, M. F. L., CORTIZO, M. C., J. Appl. Electrochem., **30**, 2000, p. 30
17. SCHIFF, N., GROSGOGEAT, B., LISSAC, M., DALARD, F., Biomaterials, **23**, 2002, p. 1995
18. IBRIS, N., MIRZA ROSCA, J. C., J. Electroanal. Chem., **526**, 2002, p. 53
19. NAKAGAWA, M., MATSUYA, S., UDOH, K., Dent. Mater. J., **21**, 2002, p. 83
20. AL-MAYOUF, A. M., AL-SWAYIH, A. A., AL-MOBARAK, N. A., AL-JABAB, A. S., Mater. Chem. Phys., **86**, 2004, p. 320
21. POPA, M. V., VASILESCU, E., DROB, P., VASILESCU, C., Rev. Chim. (Bucuresti), **54**, 2003, p. 855
22. POPA, M. V., DEMETRESCU, I., VASILESCU, E., DROB, P., IONITA, D., VASILESCU, C., Rev. Roum. Chim., **50**, 2005, p. 394
23. POPA, M. V., VASILESCU, E., DROB, P., VASILESCU, C., DEMETRESCU, I., IONITA, D., J. Mater. Sci. Mater. Med., **19**, 2008, p. 1
24. MARECI, D., UNGUREANU, G., AELENEI, D. M., MIRZA ROSCA, J. C., Mater. Corros., **58**, 2007, p. 848
25. SOVAR, M. M., TIHAN, G. T., MICULESCU, F., MITRAN, V. Rev. Chim. (Bucuresti), **58**, nr. 9, 2007, p. 886
26. POPESCU, R., IONITA, D., MINCULESCU, F. Rev. Chim. (Bucuresti), **59**, nr. 1, 2008, p. 17
27. ALDEA, E., BADEA, N., DEMETRESCU, I., Rev. Chim. (Bucuresti), **58**, nr. 9, 2007, p. 918
28. CAPOSI, M., IONITA, D., MICULESCU, F., DEMETRESCU, I., Rev. Chim. (Bucuresti), **58**, nr. 10, 2007, p. 875
29. CAI, Z., NAKAJIMA, H., WOLDU, M., BERGLUND, A., BERGMAN, M., OKABE, T., Biomaterials, **20**, 1998, p. 186
30. VAN NOORT, R., J. Mater. Sci., **22**, 1987, p. 3801
31. POURBAIX, M., Atlas of Electrochemical Equilibria in aqueous solutions, Pergamon Press, New York, 1966

Manuscript received: 6.06.2008