Effect of Reprocessing Treatment on the Corrosion of Co–Cr Alloy in Acid Media

FLORENTINA GOLGOVICI[1], MARIANA PRODANA[1*], ANCA POPESCU[2*]
[1]University Politehnica of Bucharest, Department of General Chemistry, 1-7 Gh. Polizu Str., 011061, Bucharest, Romania
[2]University "Titu Maiorescu" of Bucharest, Faculty of Dentistry, 67A Gheorghe Petrascu Str., 031593, Bucharest, Romania

The aim of the paper is a comparison of corrosion behaviour of three Co–Cr commercial alloys in acid media before and after a reprocessing treatment which is a step in denture restorative pieces fabrication. The electrochemical tests as Tafel procedure and electrochemical impedance spectroscopy (EIS) are performed in a usual alimentary commercial environment with a pH 2.73 and the investigations are completed with inductively coupled plasma mass spectrometry (ICP-MS) determinations, in order to see the release of ions changes. Based on experimental data it is concluded that thermally reprocessing effect leads for all tree alloys to enhancement of corrosion rate and an important displacement in the resistance group at corrosion classification.

Keywords: corrosion, Co-Cr alloys, electrochemical technics, EIS, ICP-MS

The classic Co-Cr alloy was first used in 1929 and since then this type of alloy has gained a wide application as metallic biomaterial especially in dentistry. With a certain content of Ni, despite the fact that the material preserves a relatively low density, this material is much stronger, harder and presents a high elasticity module. For oral cavity this alloy has initially appeared as an alternative to precious metal restorations. Taking into account that its corrosion products are metallic ions leading to allergies and diseases, the electrochemical behaviour was widely investigated and many surface modifications have been performed to enhance corrosion rate in bioliquids [1-4]. It is to mention that in the processing time as casting, defects such as microporosity and cored matrix structure may appear leading to significant decrease of the alloy ductility. In order to improve the ductility and strength of this alloy various heat-treatments have been proposed [5]. To increase ductility and to stabilize phases, Ni addition was a choose as well, but the added nickel originates allergic reaction to people having sensitivity to metal. Thus, a Ni-free Co–Cr–Mo alloy is needed to eliminate the Ni allergic problem. Despite the fact that Ni is considered carcinogenic, there are many dentistry companies using extensively this alloy for bridges and crown.

The introduction of a new alloy Co-Cr without Ni (according to ASTM F-75, with a composition in weight percentages of 27-30% Cr, 5-7% Mo and less than 0.1% Ti, Si, Mn) [6] and of many procedures of surface modification [7, 8] for enhancing performances, led in the last decade to a new enlargement in using such alloys. Regarding their mechanical properties [9], it is to mention the resistance to traction and to flow with values of 655 and 450 MPa, respectively, the elongation higher than 8%, as well as the hardness (Rockwell) between 25 – 35 [9]. A reduced quantity of alloy has been required for casting, thus reducing cost and increasing lifespan and durability of the restoration. Co-Cr alloys without Ni are commonly used as a base metal alloy for casting of removable, partial-denture frameworks, and partial fixed restorations fabrication as well. Due to the high melting temperature required in the use of specialized casting equipment during fabrication of individual denture frameworks, despite the heat treatment previously performed on such alloys, it is expected after reprocessing activity some changes to appear in the alloy stability in bioliquids. Recently, the consumption of soft drinks is increasing, especially among children and adolescents. To date, the acid environment created by the consumption of soft drinks has not been investigated as one possible reason for the degradation of Co-Cr alloys used as biomaterial especially in dentistry [10]. Having this idea in mind the present paper aims to compare the corrosion behaviour in a strong acidic medium of three Co-Cr commercial alloys before and after reprocessing.

Experimental part

The studied materials are three commercial alloys used in dental medicine with a composition presented in table 1.

Investigated non-reprocessed metallic samples were cylinders with a 0.5 cm^2 exposed area in corrosion environment. The reprocessed metallic samples have been obtained firstly in wax disc forms which have been casted using Castomat equipment at 1350^0C.

Table 1
COMPOSITION (wt.%) OF Co-Cr ALLOYS

Alloy name	Co %	Cr %	Mo %	Mn %	Si %	C %	N %	W %	Ga %	Fe %	Ce %
Heraenium CE (HNCE) - 1	63.5	27.8	6.6	0.6	1	0.3	0.2	-	-	-	-
Wirobond C (WBC) - 2	61	26	6	-	1	0.02	-	5	-	0.5	0.5
Wirobond 280 (WBA) - 3	60.2	25	4.8	<2	<2	-	-	6.2	2.9	-	-

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* *email: prodana_mariana@yahoo.com, drancapopescu@yahoo.com*

The electrochemical cell was the classical one with three electrodes as following: the working electrode (the Co-Cr commercial alloys: Wirobond C and Wirobond 280 made by Bego Company, Heraenium CE made by Heraeus Company and reprocessed alloys), a contraelectrode (Pt plate) with a large area and a reference electrode (saturated calomel, ECS). The electrodes preparation included cleaning before each determination using abrasive paper with various granulations, washing with water and ultrasonication for 10 min in acetone in order to remove grease and impurities present on surface after polishing and drying.

As testing electrolyte a soft drink was used with a *p*H 2.73. The most important components of the electrolyte are: acidifying agents (citric, phosphoric and ascorbic acids), sugar caramel, emulsifying agents, arabic gum, plant extracts, natural flavours.

The immersion periods of time have been 0, 48, and 96 h respectively.

Electrochemical determinations have been performed at 298 K temperature with an AutoLab PGSTAT 12 *EcoChemie* potentiostat using potentiodynamic polarization method (1 mVs^{-1} scan rate) and electrochemical impedance spectroscopy procedure (within frequency range 100 KHz and 100 mHz).

Determination of ions release level was performed with ELAN DRC-e induced plasma coupled spectrometer (ICP-MS). For ICP/MS determinations sample preparation involves acid digestion, in a well determined volume of HNO_3 65%; after digestion, the samples were diluted 100 times and liquid fractions were analyzed.

Results and discussions

The potentiodynamic polarization investigation of Heraenium CE (HNCE), Wirobond C (WBC) and Wirobond 280 (WBA) non-reprocessed thermally in an acid environment with a *p*H 2.73 is presented in curves of figure 1 (a-c) at the indicated immersion times.

From this figure it is observed that in the same time with the increase of the immersion time for each alloy a shift of corrosion potential toward for more electronegative values is taking place, in the same time with an increase of current density along the anodic branch of curve. As another result is an increase of corrosion rate of all biomaterials. After „Tafel region" the passive domain of alloys appears at anodic polarization. In the cases of both Wirobond alloys, the curves at 48 and 96 immersion hours are pretty close to each other leading to the approximately the same values for electrochemical parameters. The passive domains are pretty large in these situations as well.

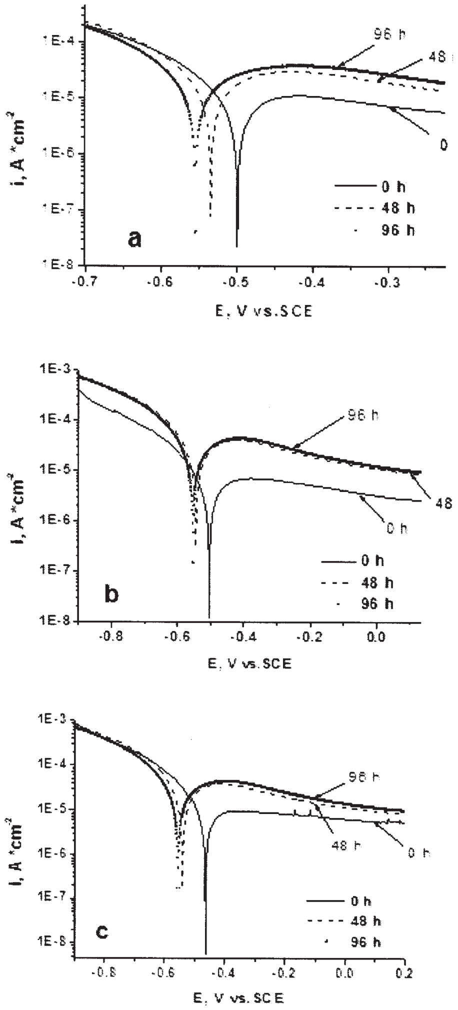

Fig. 1. Polarization curves for a) type 1, b) type 2 and c) type 3 alloys at various immersion times in acid media

Electrochemical kinetic parameters have been computed from figures 1 using two procedures as following: Tafel slope extrapolation and polarization resistance. Values for corrosion potential, (E_{corr}), corrosion density (i_{cor}), gravimetric corrosion rate, (K_g), penetration index (P), anodic slope, (B_a), cathodic slope (B_c) and polarization resistance are given in table 2.

From the data of table 2 all the studied alloys at initial time are included in conventional stability scale „very stable" in the corrosion resistance group (corrosion classification) with coefficient 3. With the increase of immersion time, at both 48 and 96 h, the corrosion resistance group corresponding to corrosion rate is stable with coefficient 4.

Table 2
ELECTROCHEMICAL PARAMETERS FOR Co-Cr STUDIED ALLOYS BEFORE REPROCESSING AT DIFFERENT IMMERSION TIME

Alloy	Immersion time, h	Tafel slope method						Polarization resistance method	
		E_{corr}, mV	i_{corr}, $\mu A/cm^2$	K_g, g/m^2h	P, mm/year	B_a, mV	$-B_c$, mV	R_P, Ω	i_{corr}, $\mu A/cm^2$
Type 1-HNCE	0	-479	3.74	0.0415	0.0455	60	92	6200	2.543
	48	-516	6.82	0.0758	0.083	92	93	3164	6.347
	96	-537	12.4	0.1378	0.151	105	115	2141	11.131
Type 2-WBC	0	-477	2.87	0.0355	0.036	125	127	14335	1.908
	48	-525	12.8	0.158	0.1632	126	129	2647	10.45
	96	-537	14.1	0.174	0.1798	129	130	2103	13.369
Type 3-WBA	0	-449	4.288	0.054	0.0557	110	101	7194	3.178
	48	-525	11.59	0.146	0.1505	108	132	2569	10.039
	96	-540	11.2	0.141	0.1454	116	117	2656	9.522

Table 3
ELECTROCHEMICAL PARAMETERS FOR Co-Cr STUDIED ALLOYS AFTER REPROCESSING AT DIFFERENT IMMERSION TIME

Alloy	Immersion time, h	Tafel slope method						Polarization resistance method	
		E_{corr}, mV	i_{corr}, μA/cm^2	K_g, g/m^{2}h	P, mm/year	B_a, mV	$-B_c$, mV	R_P, Ω	i_{corr}, μA/cm^2
HNCE (1)	0	- 507	11.55	0.1284	0.14056	168	136	2580	12.649
	48	- 506	13.05	0.1451	0.15882	168	128	2144	14.713
	96	- 507	13.83	0.1537	0.16831	166	136	2196	14.781
WBC (2)	0	-506	15.11	0.1871	0.1927	179	128	2168	14.947
	48	-509	21.03	0.2604	0.2682	161	131	1584	19.8
	96	-509	33.59	0.4159	0.4284	168	198	1221	32.32
WBA (3)	0	- 484	9.095	0.1146	0.11814	169	135	2679	12.1641
	48	-514	13.83	0.1743	0.17965	167	148	2086	16.3327
	96	-520	21.03	0.2651	0.27318	158	135	1338	23.6250

If we compare the behaviour of Co-Cr alloys studied in strong acid media, we can see that, at initial time all three alloys have close behaviour but having different values for corrosion potential and for current density; after 96 h the behaviour for all of them is almost similar.

Regarding the potentiodynamic study for thermal reprocessed alloys, the same conditions regarding tested electrolyte, with the same *p*H have been used. The corresponding curves for the same immersion times for these cases, as for non-reprocessed alloys are presented in figure 2, respectively.

It is observed that with the immersion time increase in acid media (2.73 *p*H) there are not modifications of polarization curve regarding the shape, current density, and corrosion potential for the sample of Heraenius CE alloy. Such data lead to the conclusion of the stability of this alloy for this period of time in acid media despite the reprocessing.

For the other two alloys samples tested after reprocessing it is to observe a small shift to the electronegative direction of corrosion potential (fig. 2b and 2c) and an increase of corrosion density. The passivation domains have been appeared in both cases before and after reprocessing. The corrosion products are probably mainly citrates and phosphates of the metallic ions.

Electrochemical corrosion parameters corresponding to polarization curves for reprocessed alloys have been computed using two procedures as following: Tafel slope extrapolation and polarization resistance; the corresponding values are listed in table 3.

All values from table 3 represent a corrosion rate more amplified than before reprocessing and this feature justifies the inclusion of all Co-Cr alloys in stability corrosion range in group 6, „relative stable", due to the obtained penetration index between 0.1 and 0.5 mm/year.

The comparison of the three studied reprocessed alloys was performed for 0 and 96 h immersion time in acid media. In both cases the alloys have behaviour pretty close to each-other as can be seen from data of table 3. For initial immersion time the best behaviour is for Wirobond 280 sample, but after 96 h immersion the Heraenium CE alloy presents the best corrosion resistance.

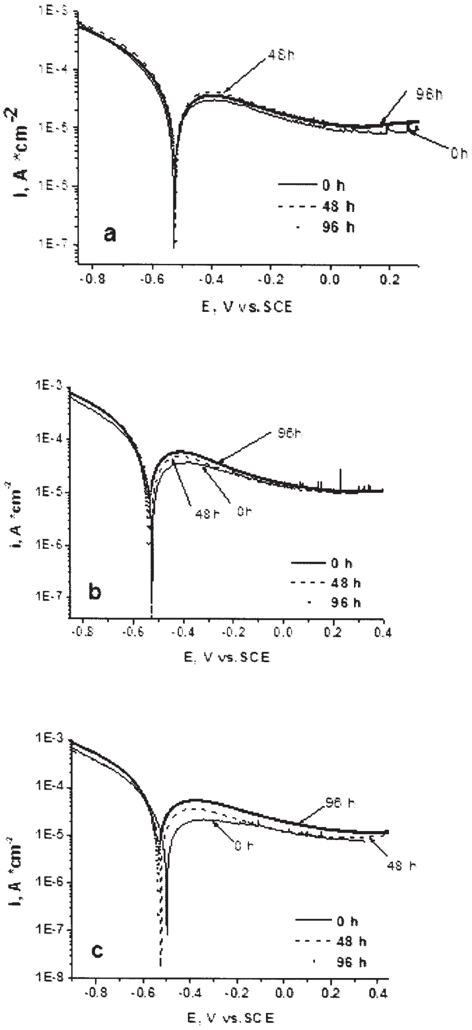

Fig. 2. Polarization curves for the Heraenium CE (a), Wirobond C (b) and Wirobond 280 (c) alloys thermal reprocessed and immersed in acid media at 0, 48, and 96 h , respectively

In order to show the reprocessing effect on the three studied Co-Cr alloys, we present comparatively in figure 3 the polarization curves for non-reprocessed and reprocessed alloys at initial time of immersion.

From all cases illustrated in figure 3 it is to observe that thermal processing of the three types of Co-Cr alloys lead to a shift of corrosion potential to more electronegative

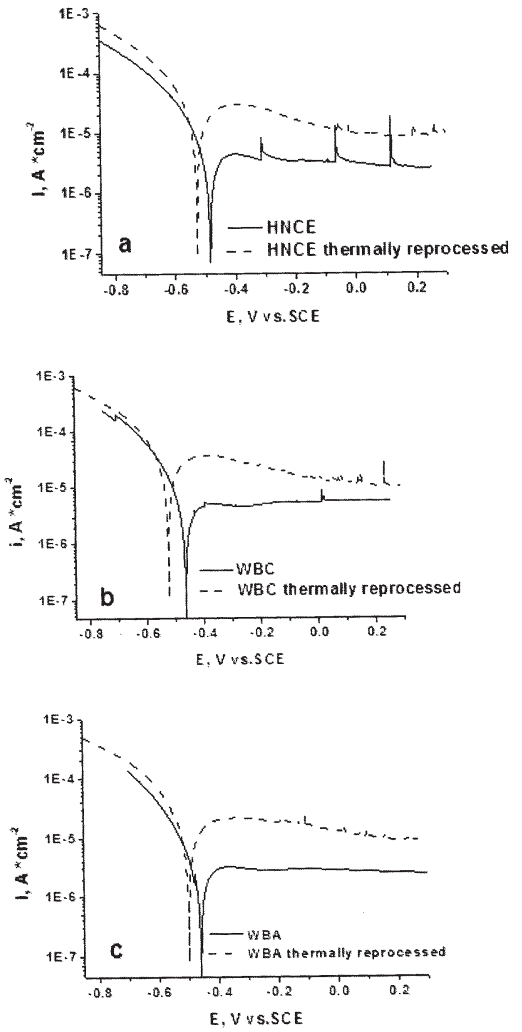

Fig. 3. The polarization curves of Co-Cr alloys before and after thermally reprocessed for initial time of immersion in acid media at 298 K temperature

values, and to an increase of anodic current density. In fact an increase of corrosion rate is taking place. However for initial moment on immersion it can be seen that the thermal reprocessing of alloys has a negative influence on corrosion behaviour in acid media with a *p*H 2.73.

After 96 h immersion in acid media (fig. 4) the behaviour of the three alloys is different. In the cases of HNCE and WBC alloys the thermal processing led to a small shift of corrosion potential to more electropositive values and a small increase of current density. For the third alloy (WBA) practically no change in corrosion behaviour has been observed.

Nyquist and Bode diagrams are presented in figure 5 for the first type (HNCE) alloy at various immersion times. From Nyquist diagram it is observed the presence of a capacitive open semicircle with a diameter that is decreasing with the increase of immersion time. This fact is an indication of a decrease of polarization resistance (semicircle diameter) leading to an increase of corrosion rate with the increase of immersion time and confirming data from polarization curves. Bode diagram reveals the presence of a single time constant corresponding to a single semicircle on Nyquist diagram. The maximum of phase angle is shifting to smaller frequencies values and is slightly decreasing together with the increase of immersion time in acid media. The maximum value of phase angle has values around -80° for all immersion times indicating a capacitive behaviour for the interface created in this way.

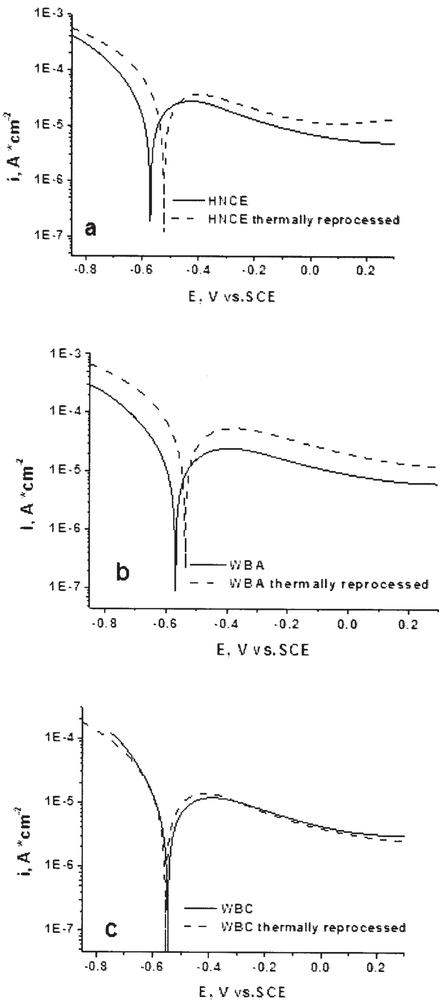

Fig. 4. Polarization curves of Co-Cr alloys in initial state and after thermally reprocessed in acid media after 96 h immersion in acid media at 298 K temperature

The behaviour during immersion in acid media with a *p*H 2.73 of the other two Co-Cr alloys (WBC and WBA) is very similar to this one (fig. 5 (c, d, e and f)).

As can be observed from these figures at the initial moment the best corrosion behaviour is for WBC alloy, but after 96 h immersion for all three alloys the behaviour is similar. It is a confirmation for data obtained in potentiodynamic determinations.

In the case of Co-Cr all recasting alloys the results obtained with EIS, represent a confirmation of data obtained using extrapolation of Tafel plots and polarization resistance. Open semicircles have been obtained for Nyquist diagrams, with a single maximum for phase angle corresponding for Bode diagram. The behaviour in all immersion times is similar for alloy type 1 - HNCE (fig.6a and b), and thus not significant changes with the increase of immersion time have been observed. In the case of other two types of alloys WBC and WBA, respectively (figs. 6 c, d and 6 e, f), in the same time with the increase of immersion time in acid media, an increase of the diameter of capacitive semicircle and decrease of the maximum phase angle have been observed. The value of maximum phase angle is between -75 ÷ -80^0, denoting the capacitive behaviour of the interface electrode/electrolyte.

According to figures 6 the corrosion behaviour of the three alloys immediately after immersion in acid media is close to each-other, but after 96 h of immersion there appear differences and the best corrosion resistance remains for the WBC alloy.

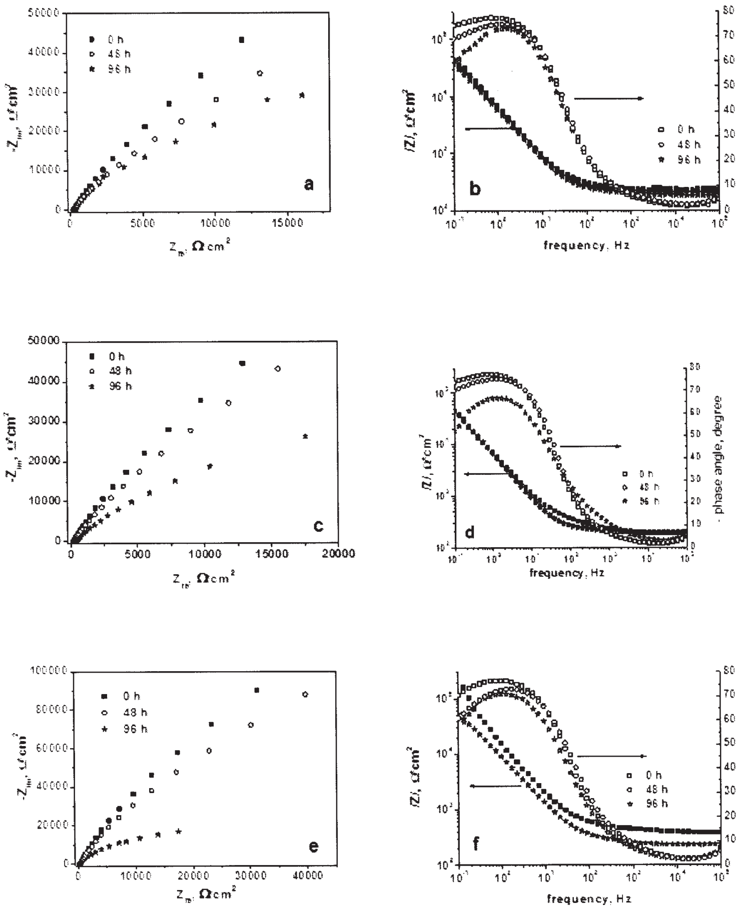

Fig.5. Nyquist and Bode diagrams for: type 1 alloy-HNCE (a, b); type 2 alloy - WBC (c, d); type 3 alloy - WBA (e, f) in acid media at various immersion time

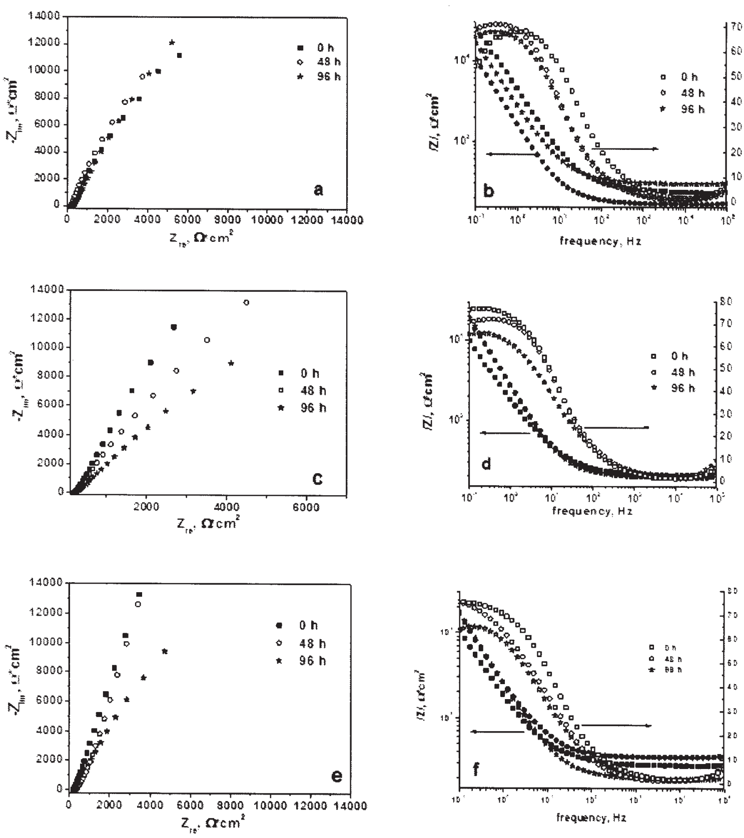

Fig. 6. Nyquist and Bode diagrams for: HNCE (a, b); WBC (c, d); WBA (e, f) in acid media at various immersion times

In order to compare the influence of recasting process of the three alloys on their electrochemical stability, the diagrams presented in figures 7 are analysed.

From figure 7 it is to conclude that in the cases of HNCE and WBA alloys the reprocessing lead to capacitive semicircles with a smaller diameter indicating an increase of susceptibility to corrosion in acid media. For the WBC alloy, there have not been observed changes in its susceptibility to corrosion after recasting. These observations confirm the results obtained from polarization curves with the help of Tafel slope and polarization resistance methods.

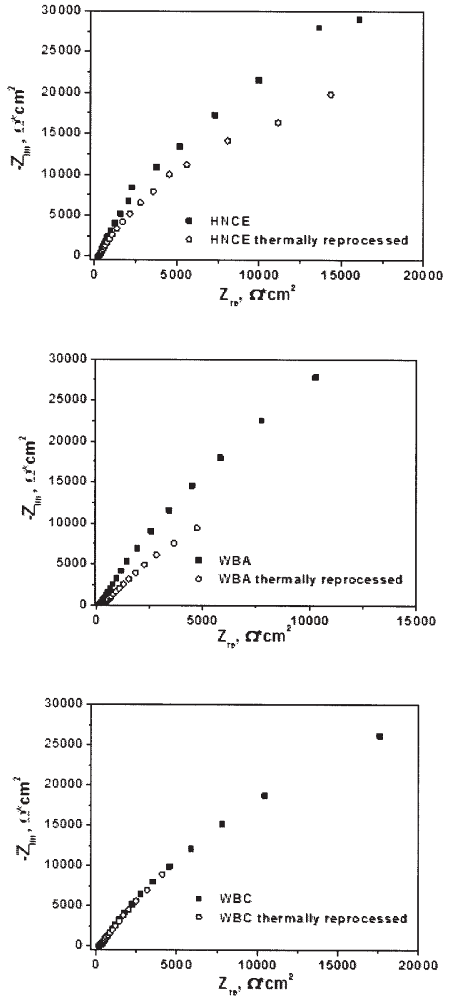

Fig. 7. Nyquist diagrams for the three alloys thermally non-reprocessed and reprocessed at initial time of immersion in acid media

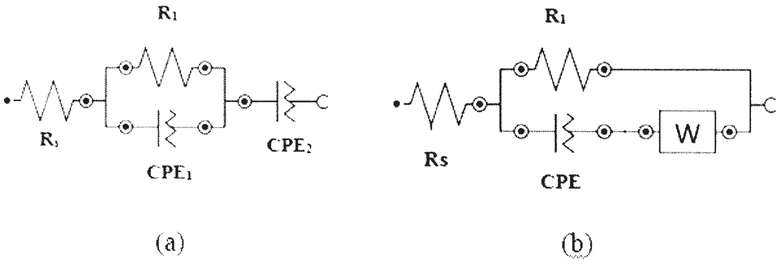

Fig. 8. Schematic representation of the electrical equivalent circuit diagram for: (a) the non-reprocessed thermally alloys; (b) the thermally reprocessed alloys

The obtained Nyquist and Bode spectra were interpreted on the basis of equivalent electrical circuits as electrochemical models of the interface, using specialized fitting software Nova 1.10. Figure 8 exhibits the proposed equivalent circuit used for fitting the experimental data for non-reprocessed alloys.

The elements of this circuit are: Rs – ohmic resistance of electrolyte solution; R_1 and CPE_1 are linked with the interface film/electrolyte, while the CPE_2 is associated with the passive film. R_1 represents the charge transfer resistance (polarization resistance) and CPE_1 is a constant phase element associated with the electric double layer. Change in CPE2 constant phase element can be used as an indication of passive film thickness change. Each CPE has two components: Y_0 and the exponent n. Table 4 contains the values of the equivalent circuit elements from figure 8a for the best fitting of experimental data.

The constant phase element CPE_1 takes into account the deviation of electrochemical double layer from pure capacitive behaviour. The value of parameter n is the associated with the nonuniform distribution of current as a result of roughness or surface defects. As can be seen from table 4, the value of n in most cases is very close to 1 indicating a behaviour that approaches that of an ideal capacitor.

After 48 h immersion time, the decrease of charge transfer resistance and the increase of CPE_1 values are observed, indicating the dissolution through the pores or surface defects of the alloy in contact with the electrolyte. After 96 h of alloy immersion in acid media at *p*H 2.73 it can be seen that the charge transfer resistance value increases, leading to the idea that on the surface of the alloy appear insoluble corrosion products which hinders the charge transfer process.

It can be said that on the alloy surface takes place several processes, the most important being the dissolution of the alloy through pores or defects and the formation of insoluble corrosion products which are deposited on the alloy surface. Depending on the rate of the two processes, the value of charge transfer resistance (polarization resistance) increases or decreases.

For thermally processed alloys was proposed another electrical equivalent circuit (fig. 8b) for fitting the experimental data obtained by electrochemical impedance spectroscopy.

As can be seen, in the case of thermally processed Co-Cr alloys, in the used equivalent circuit model a Warburg

Alloy	Immersion time, h	Rs, Ω	R$_1$, Ω	CPE$_1$		CPE$_2$	
				Y$_0$(S s^n)× 10^6	n	Y$_0$ (S s^n))× 10^6	n
HNCE	0	420	57.6	9.97	0.856	16.6	0.887
	48	389	30	53.2	0.814	26.2	0.918
	96	454	49.6	5.96	0.98	17	0.852
WBC	0	400	46.1	6.34	0.886	15.9	0.882
	48	380	28.1	9.79	0.89	15.8	0.861
	96	388	127	5.89	0.855	18.3	0.783
WBA	0	330	53.9	3.03	0.768	15.3	0.877
	48	344	34.1	3.47	0.988	14.7	0.855
	96	391	38.7	3.2	0.952	55.8	0.65

Table 4
VALUES OF THE CIRCUIT PARAMETERS FOR NONREPROCESSED THERMALLY Co-Cr ALLOYS

Table 5
VALUES OF THE CIRCUIT PARAMETERS FOR THERMALLY REPROCESSED Co-Cr ALLOYS

Alloy	Immersion time, h	R_s, Ω	$R_1 \times 10^3$, Ω	CPE_1		$W \times 10^3$, S
				$Y_0 \times 10^6$, S s^n	n	
HNCE	0	150	40.2	83.5	0.859	1.3
	48	158	27.6	136	0.995	0.99
	96	188	66.9	146	0.864	1.32
WBC	0	148	46.2	205	0.899	1
	48	120	78.5	136	0.9	1.44
	96	122	24	269	0.987	0.755
WBA	0	115	50.1	135	1	0.916
	48	206	70.9	158	1	0.643
	96	173	36.8	250	0.893	1.04

Table 6
IONS RELEASE IN SOLUTION AFTER VARIOUS IMMERSION TIME

Sample	Immersion time (h)	Co (ppm)	Cr (ppm)	Mo (ppm)	Mn (ppm)	Al (ppm)	Ga (ppm)	Si (ppm)	W (ppm)	Fe (ppm)
1 - HNCE	24	0.064	0	0	0.06	0	0	0	0	0.043
	48	7.853	0	1.153	0.23	0.034	0	0	0	1.238
	96	7.95	0	1.153	0.26	0.172	0	0	0	1.848
1 – HNCE reprocessed	24	0.327	0	0.016	0.02	0.012	0.004	3.273	0	0.276
	48	0.333	0	0.016	0.23	0.012	0.011	3.273	0	1.809
	96	2.009	0	0.323	0.34	0.074	0.011	3.273	0	2.540
2 - WBC	24	0.006	0.003	0	0.01	0.011	0.004	3.248	0	0.280
	48	5.327	0.003	0.785	0.07	0.011	0.004	3.248	0.723	0.431
	96	5.388	0.003	0.785	0.08	0.033	0.004	3.248	0.723	0.621
2 - WBC reprocessed	24	0.134	0.019	0.006	0.01	0.017	0.007	6.673	0.008	0.409
	48	0.136	0.019	0.006	0.13	0.017	0.007	6.673	0.008	0.537
	96	5.906	0.019	1.01	0.14	0.078	0.007	6.673	0.845	0.742
3 - WBA	24	0.007	0.029	0	0.01	0.018	0.006	6.756	0	0.417
	48	0.121	0.029	0	0.11	0.018	0.006	6.756	0	0.770
	96	0.203	0.029	0	0.12	0.075	0.006	6.756	0	1.226
3 - WBA reprocessed	24	0.358	0.057	0.024	0.03	0.029	0.026	10.23	0.047	0.552
	48	7.680	0.057	1.403	0.51	0.047	0.343	10.23	2.391	1.858
	96	13.11	0.057	3.23	0.93	0.195	0.54	10.23	4.342	3.154

element appears, indicating that after heating, Co-Cr alloys form a porous film enables to allowing the diffusion of electrolyte through it.

The main working steps in ions determinations are samples mineralization and samples dissolution according to the protocol described in experimental part. The results are presented in table: [6].

From this table it can be seen that after reprocessing WBC and WBA alloys release in solution a higher amount of metallic ions. The metal ion concentrations are in the range of ppm. The highest amount of ion release is from the WBA alloy followed by WBC alloy. Therefore, the best stability is for the HNCE alloy.

In the case of HNCE non-processed alloy the amount of Co ions release is higher compared to the amount of Co ion release after reprocessing. In this case Si ions appear in solution by immersing reprocessed alloy, despite the fact that Si ions were not present in solution in the case of nonprocessed alloy. The amount of Mn ions released in solution is almost the same before and after processing; Mo ions amount is smaller for reprocessed alloy.

In the case of reprocessed dental WBC alloy the amounts of ion release are higher compared with the released ions from the same alloy before reprocessing. The differences are more significant for Co, Mo and Si. For WBA alloy, after reprocessing the amount of Si ions released is higher, but for the other ions the amount was almost the same.

Conclusions

Based on experimental data it has been established that, in general, the corrosion rate and ions release in strong acid media is higher after reprocessing procedure. In majority of investigated cases an increase of stability corrosion group in corrosion classification is taking place. The electrochemical methods as Tafel plots, polarization resistance and EIS confirm this conclusion and ions release measurements from ICP-MS determinations lead to the same conclusion for all three tested alloys. After reprocessing, both Wirobond types alloys release in solution a higher amount of metallic ions. Such amounts are in the range of ppm. The highest amount of ion release is from the WBA alloy, followed by WBC alloy. The best stability is for the Heraenium CE alloy.

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