STUDY OF CORROSION BEHAVIOR UNDER SIMULATED PHYSIOLOGICAL CONDITIONS OF THE DENTAL CoCrMoTi ALLOYS

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Lucrarea prezintă rezultatele experimentale asupra comportării la coroziune a unor aliaje dentare de tip CoCrMo, aliate cu diferite conținuturi de titan (0,1%; 1%; 3%; 3,5%; 4%; 4,5% şi 5%). Aliajele au fost elaborate într-un cuptor cu inducție cu vid înaintat, în sarje de cate 100g, fiind apoi turnate centrifugal în epruvete de formă cilindrică Φ10 mm. S-a urmărit punerea în evidență a influentei alierii cu titan asupra comportarii la coroziune în două medii fiziologice artificiale, respectiv soluție perfuzabilă de NaCl şi soluție Ringer. Pentru ambele soluții s-a pus în evidență influența benefică a alierii cu titan asupra rezistentei la coroziune prin construirea curbelor potentiodinamice. Astfel potențialele de coroziune s-au deplasat spre dreapta, la valori mai electropozitive, iar curenții de coroziune au avut valori absolute foarte mici, fiind situate în domeniul $0,3x10^{-2} \div 5,8x10^{-2}$ μA/cm^2 pentru coroziune în soluție perfuzabilă şi $3x10^{-2}$-$400x10^{-3}$ μA/cm^2 pentru coroziune în soluție Ringer.

This paper presents the experimental results on the corrosion behavior of several experimental dental alloys type CoCrMo, alloyed with different contents of titanium (0,1%; 1%; 3%; 3,5%; 4%; 4,5% and 5%). The alloys (about 100g) were elaborated in high vacuum induction furnace, in ingots about 100g, and then centrifugal casted in cylinder samples about Φ10mm. The goal was to put in evidence the influence of titanium alloying on corrosion behavior in two simulated body fluids, respectively NaCl infusion solution and Ringer solution. For both liquids the beneficial influence of titanium alloying was put in evidence by potentiodynamic curves. So, the corrosion potentials were displaced on the right, to electropositive values, and the corrosion density currents were very small in absolute values, in the range of $0,3x10^{-2} \div 5,8x10^{-2}$ μA/cm^2 for infusion solution and $3x10^{-2}$-$400x10^{-3}$ μA/cm^2 for Ringer solution, respectively.

Keywords: dental cobalt alloys, titanium alloying, corrosion resistance

1. Introduction

Cobalt-based alloys are widely used for manufacturing various devices either implanted in the body by surgery (their applications including hip

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prosthesis, knee plates and screws for osteosynthesis), or basic structures for heart valves [1], or prosthesis, with different applications in dentistry [2]. Removable partial dentures are such prosthesis, which can be inserted and take it out voluntary, by the patient, in and out from the oral cavity. These components consist from a metallic part and an acrylic one. Cobalt - chromium- molybdenum alloys used for partial removable dentures are known to have excellent corrosion resistance and outstanding mechanical properties (e.g. high stiffness). The cobalt dental alloys have diversified over time, aiming at creating both new products [3,4] and new technologies to process them [5-10]. The use of Co-Cr-Mo alloys is usually carried out by centrifugal casting, or by the use of the laser sintering technique.

Titanium is also known to be a very high biocompatible metal, with a very high corrosion resistance, used with great success as a biomaterial [1]. Despite of this, the influence of titanium on the properties of dental cobalt alloys is not well defined; only [11] mentioned this fact in the CoCr system.

The aim of the present paper was to put in evidence the titanium alloying influence on the corrosion behaviour of traditional dental CoCrMo alloys.

2. Materials and Methods

Different alloys were elaborated in an high vacuum induction melting furnace in ingots about 100g, and then centrifugal casted in cylindrical samples about Φ10 mm, as shown in figure 1. The chemical composition of the experimental alloys is given in table 1.

Table 1

Chemical composition of the experimental dental alloys, wt.%

Alloy	**Element**									
	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Co
$CoCrMoTi_{0,1}$	0,276	1,8	0,64	0,0006	0,0011	24,51	0,098	7,29	0,08	ball
$CoCrMoTi_1$	0,356	0,51	0,67	0,0010	0,0068	26,87	0,109	7,59	0,70	ball
$CoCrMoTi_3$	0,336	0,074	1,17	0,0006	0,0019	24,9	0,08	7,69	3,18	ball
$CoCrMoTi_{3,5}$	0,336	0,082	1,23	0,0006	0,0008	24,94	0,079	7,38	3,51	ball
$CoCrMoTi_4$	0,315	0,058	1,21	0,0006	0,0032	24,28	0,076	7,90	3,94	ball
$CoCrMoTi_{4,5}$	0,407	0,030	1,14	0,0006	0,0017	23,87	0,073	7,61	4,60	ball
$CoCrMoTi_5$	0,334	0,025	1,18	0,0006	0,0062	22,45	0,069	7,96	4,96	ball

In order to put in evidence the titanium influence on the corrosion behaviour of the experimental alloys two different investigations were carried out on the cast sample: structural analysis and corrosion resistance tests. Structural analysis was performed by means of a Reichert microscope, equipped with ImagePro software for image processing and scanning electron analysis on Phylips microscope.

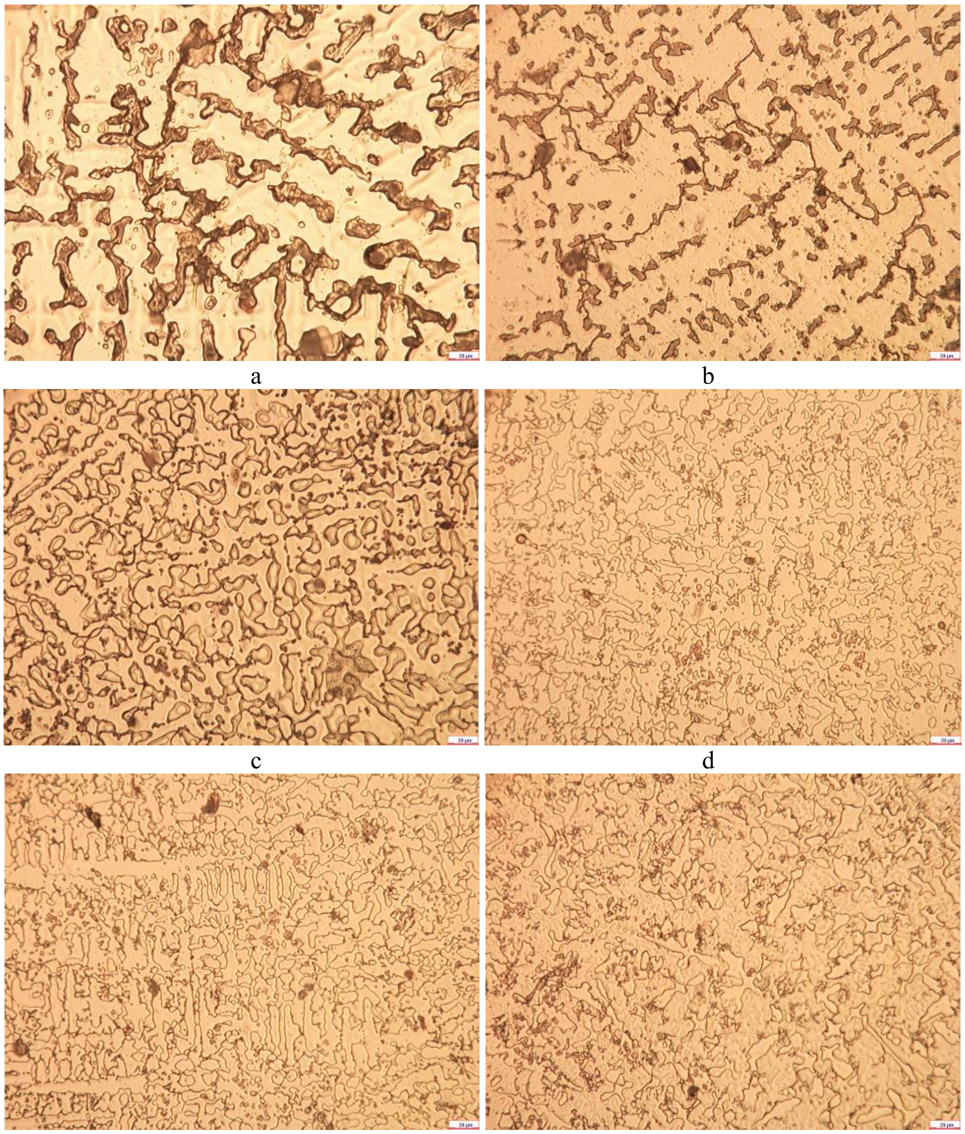
Fig. 1. Macroscopic aspect of experimental cobalt alloys samples after centrifugal casting

The samples were discs with 10 mm diameter and 2 mm high. Both investigations were done on the same samples. Corrosion resistance of the experimental alloys was investigated by drawing potentiodynamic curves on a potentiostat-galvanostat type AUTOLAB equipped with corrosion specified soft including module PGSTAT302N, BA and SCAN250. Two physiological solutions were selected for electrochemical experiments:

- NaCl infusion solution, which consists in NaCl 0,9% m/v, respectively sodium chloride (9g) and water for 1000 ml of infusion solution,
- Ringer solution, which consists in: potassium chloride (0,40g); calcium chloride dihydrate (0,27g); sodium chloride (6,00g); sodium lactate (3,17g); rest water up to 1000ml.

3. Results and Discussion

Structural analysis of the experimental alloys reveals heterogeneous dendritic structure, with non-metallic inclusions and chemical compounds. The microscopic images of the experimental cobalt alloys are given in figure 2. As one may remark the alloy $CoCrMoTi_{0,1}$, which is in fact the classic CoCrMo alloy, consists in dendritic segregation with large grains size. Titanium has a big important influence on the aspect of the alloy, but due to dissolving both in the primary dendrites and the matrix of the eutectic constituent, the eutectic becomes finer and the titanium carbides may increase by increasing the titanium content. Starting with the non alloyed titanium system, the alloy $CoCrMoTi_{0,1}$ shows the classic structure (usually observed by other researches [15]). By increasing the titanium content, the eutectic is not so well defined, and titanium carbides become larger. The alloy with the highest titanium content, respectively $CoCrMoTi_5$ consists in large titanium carbides in the eutectic mechanical mixture. The structure of this alloy could be compared with that obtained by [11], where there are no indications about the etching of the metallographic samples.



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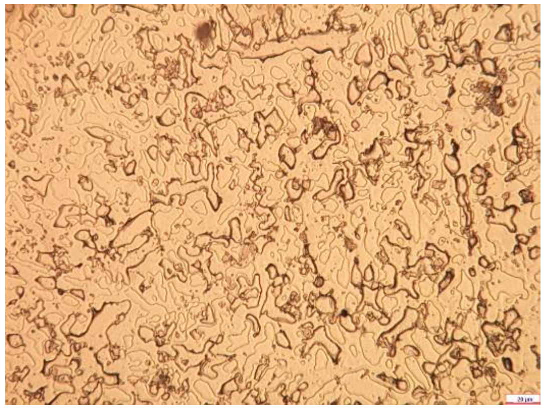

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Fig. 2. Optical micrographs of the experimental cobalt alloys (electrolytic etching with $HCl+HNO_3+H_2O_2$) : a- $CoCrMoTi_{0,1}$, b- $CoCrMoTi_1$, c- $CoCrMoTi_3$, d- $CoCrMoTi_{3,5}$, e- $CoCrMoTi_4$, f- $CoCrMoTi_{4,5}$, g- $CoCrMoTi_5$

The corrosion behavior in physiological media is depicted comparatively in figure 3 (for NaCl infusion solution) and figure 4 (in Ringer solution). The corrosion parameters, including the Tafel drawing slope are given in table 2 (for NaCl infusion solution) and table 3 (in Ringer solution).

a) NaCl infusion solution

This medium containing Cl-ions can normally cause pitting or localized corrosion for the different periods of immersion of the metallic materials. In our case, alloys containing titanium have similar behavior compared with the traditional alloy, without titanium. Thus, values of the corrosion current, i_{corr} are very small, being in the range of $0.295x10^{-2} \div 6x10^{-2}$ μA, in comparison with the current value of the non titanium containing alloy corrosion current, respectively 206 μA. No correlation between the titanium amount in the alloy and the corrosion current value could be established. On the other hand, one may remark that all titanium containing alloys have the value of the potential in the range of -358 ÷ -214 mV, in comparison with non titanium containing alloy having the corrosion potential about -531 mV. Titanium alloying influence on the corrosion potential of the experimental dental alloys is given in the histograms in figures 4 and 5a. So, one may remark that by increasing the titanium content the corrosion potential is moved on the right, to more electropositive values. This fact demonstrates the beneficial effect of titanium alloying on the corrosion resistance of the alloys from the system CoCrMo, which is normally used in modern dentistry. It may be noted also that the corrosion rate (as expressed either by the current density in μA/cm^2 or by the loss of thickness mm / year) is very high, namely 24 μA/cm^2, for the alloy not containing titanium (the classic alloy), in comparison with titanium containing alloys for which the experimental value is in the range 0.9 $x10^{-2} \div 5{,}2\ x10^{-2}$ µA/cm^2.

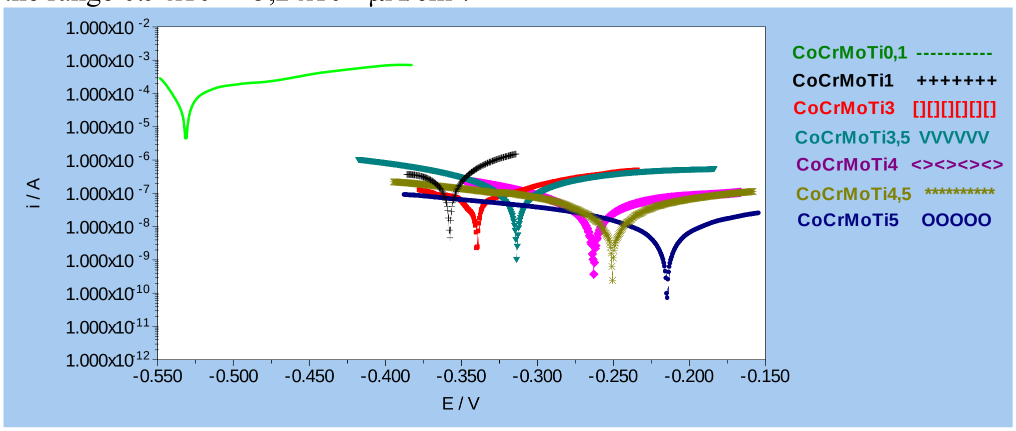


Fig. 3. Polarization curves of the experimental CoCrMoTi alloys in NaCl infusion solution

Table 2

Corrosion parameters and results concerning the Tafel drawing slope of the experimental CoCrMoTi alloys in NaCl infusion solution

Alloy	Corrosion parameters					Tafel slope		
	Ecorr [mV]	i corr x 10^{-2} [µA]	Rp [Ohm]	I corr x 10^{-2} [µA/cm^2]	Corrosion rate [µm/an]	bc [V/dec]	ba [V/dec]	corrosion character
CoCrMoTi$_{0,1}$	-531	20600	3,57 x 10^0	2423	2815	0,012	0,014	cathodic
CoCrMoTi$_1$	-358	2,214	6,536 x 10^2	5,271	0,612	0,006	0,006	mixed
CoCrMoTi$_3$	-339	1,325	4,417 x 10^3	4,733	0,550	0,017	0,008	anodic
CoCrMoTi$_{3,5}$	-314	6,083	2,112 x 10^4	2,433	0,283	0,050	0,060	cathodic
CoCrMoTi$_4$	-263	1,521	6,933 x 10^4	2,535	0,029	0,045	0,054	cathodic
CoCrMoTi$_{4,5}$	-251	1,068	9,845 x 10^4	0,889	0,010	0,048	0,050	cathodic
CoCrMoTi$_5$	-214	0,295	3,408 x 10^5	0,569	0,066	0,048	0,048	mixed

b) Ringer solution

In the infusion solution, respectively in Ringer solution, the experimental alloys show an easily differentiated behavior. On the one hand, titanium containing alloys have a similar behavior with a distinct field of corrosion potential values, respectively -216 ÷ -298 mV, compared to the potential of non titanium containing alloy, respectively -341mV. The same shift towards more electropositive potential with increasing content of titanium in CoCrMo metallic matrix may be observed in Ringer solution.

It can be concluded that titanium alloying of the CoCrMo system is beneficial for increasing the corrosion resistance in simulated environments.

Ringer solution proved to be less aggressive than the NaCl infusion solution. This fact is reflected both by the shift of the corrosion potential towards more electropositive values and by the absolute value of the corrosion current that is lower for Ringer solution. The same influence of titanium on the corrosion rate in Ringer solution is observed, as illustrated in the histogram in Figure 6b. It may be noted also that the corrosion rate (as expressed either by the current density in μA/cm^2 or by the loss of thickness mm / year) is very high for the alloy with no titanium (the classic alloy), namely 0.4112 μA/cm^2, in comparison with titanium containing alloys for which the experimental value is in the range 0.3 x10^{-2} ÷ 5.8 x10^{-2} μA/cm^2.

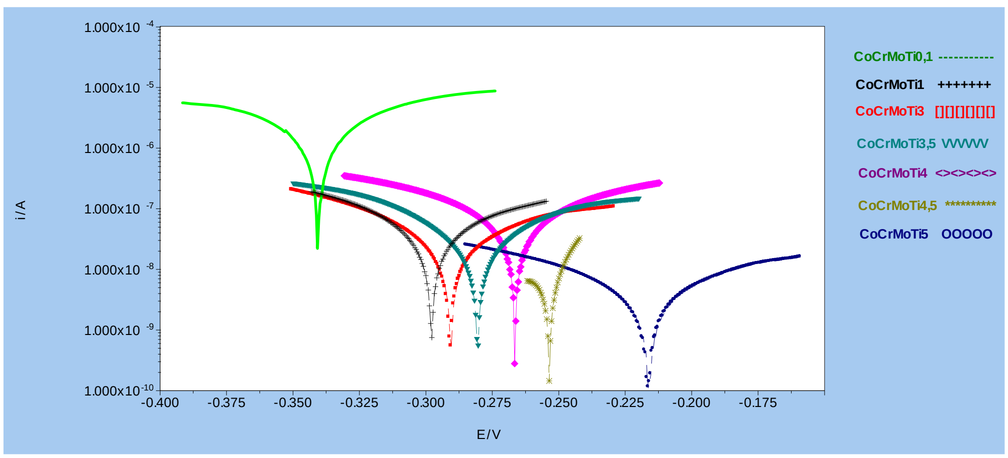


Fig. 4. Polarization curves of the experimental CoCrMoTi alloys in Ringer solution

Table 3

Corrosion parameters and results concerning Tafel drawing slope of the experimental CoCrMoTi alloys in Ringer solution

Alloy	Corrosion parameters					Tafel slope		
	Ecorr [mV]	i corr x 10^{-3} [μA]	Rp [Ohm]	I corr [μA/cm^2]	Corrosion rate [μm/an]	bc [V/dec]	ba [V/dec]	Corrosion character
CoCrMoTi$_{0,1}$	-341	320,7	2,742 x 10^2	4,112 x 10^{-1}	4,776	0,014	0,014	mixed
CoCrMoTi$_1$	-298	7,953	1,128 x 10^4	6,627 x 10^{-3}	7,697 x 10^{-2}	0,014	0,014	mixed
CoCrMoTi$_3$	-291	7,330	2,446 x 10^4	1,309 x 10^{-2}	0,152	0,018	0,023	cathodic
CoCrMoTi$_{3,5}$	-281	8,990	2,333 x 10^4	2,497 x 10^{-2}	0,29	0,021	0,023	cathodic
CoCrMoTi$_4$	-266	14,64	9,656 x 10^3	5,857 x 10^{-2}	0,68	0,018	0,018	mixed
CoCrMoTi$_{4,5}$	-254	0,950	6,984 x 10^3	1,056 x 10^{-2}	0,123	0,004	0,004	mixed
CoCrMoTi$_5$	-217	1,657	3,174 x 10^5	3,453 x 10^{-3}	4,01 x 10^{-2}	0,033	0,037	cathodic

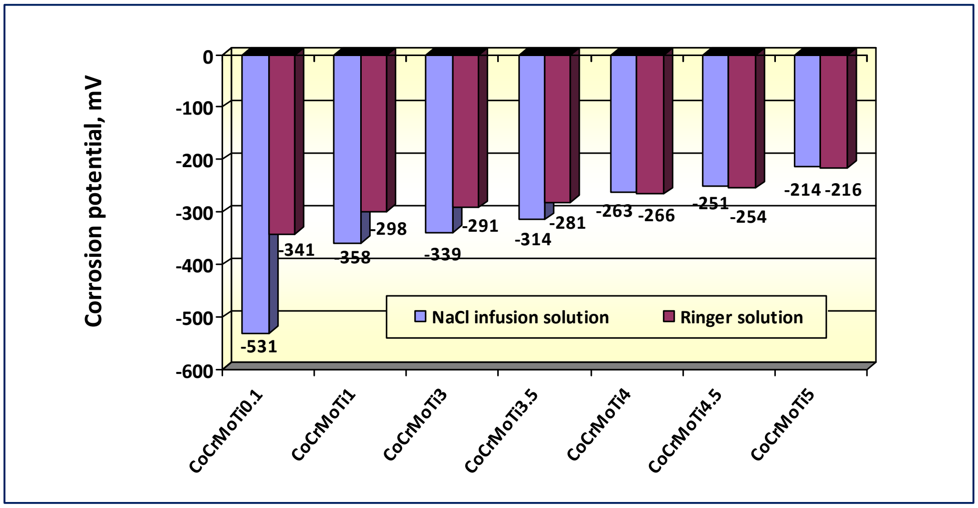
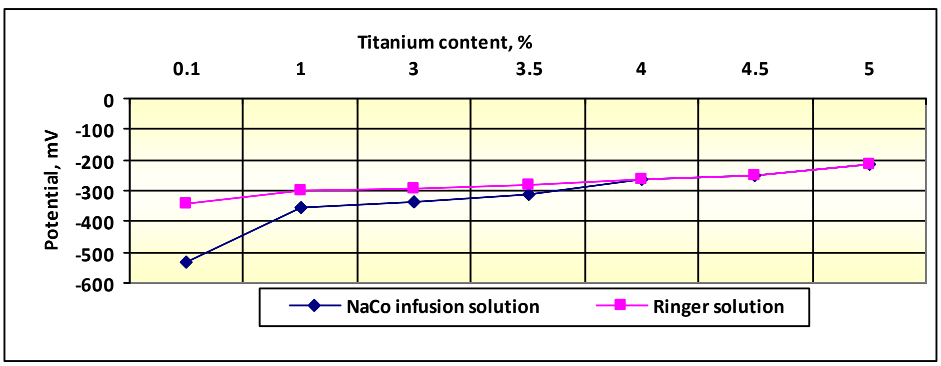


Fig. 5. Values of corrosion potentials in physiological media of the experimental CoCrMoTi dental alloys



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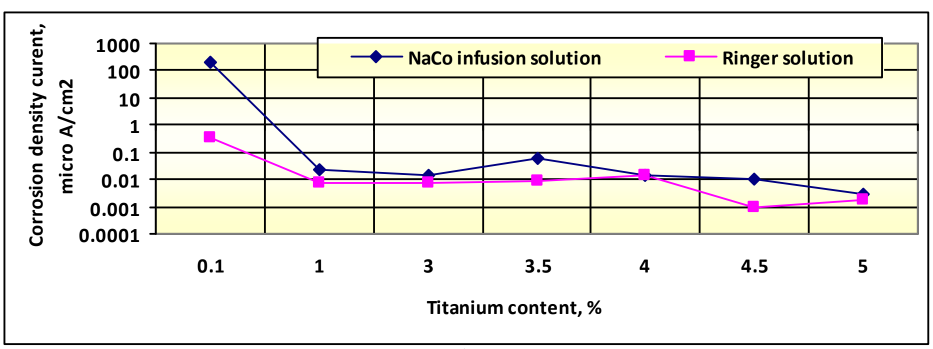

b

Fig. 6. Titanium influence in the experimental CoCrMoTi dental alloys, on corrosion potential (a) and on density of corrosion curent (b) in physiological media

The morphological aspects of the corrosion points are similar for all investigated alloys, as depicted in the SEM micrographs in Figure 7. It is to be noted that the corrosion pit has generally a form of open hemisphere, which can provide repassivasion geometric conditions, namely stabilization pit increase.

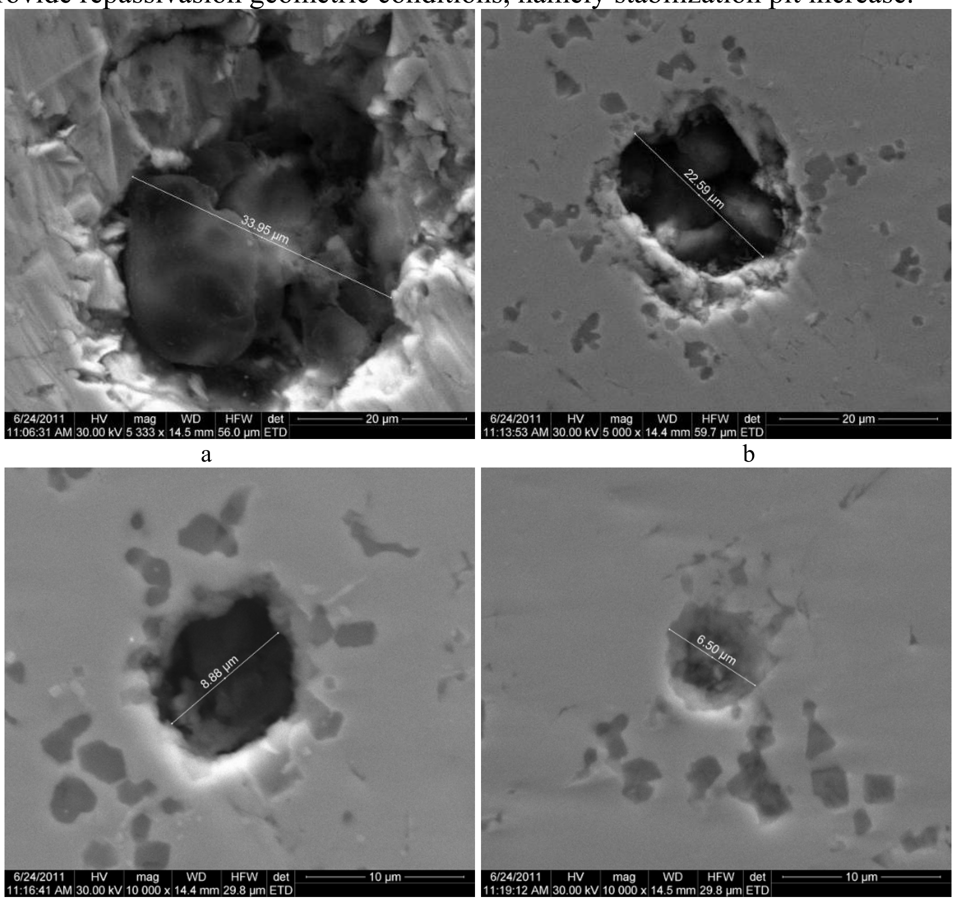

Fig.7. SEM Images of corrosion pits in the experimental CoCrMoTi alloys:
a- Alloy with 0,1%Ti, NaCl solution; b- alloy with 3%Ti, NaCl solution;
c- alloy with 4%Ti, Ringer solution; d- alloy with 5% Ti, Ringer solution

The average size of the corrosion points depends on the alloying manner. In the case of titanium alloyed alloys, due to the abundance of titanium carbides, the corrosion pit may be generated by such agglomeration of precipitates, having the wall with many definite compounds traces. The diameter of the biggest corrosion pit measured in the titanium containing alloys may vary between 23 - 6,5 µm. Figure 8 depicts the titanium influence on the average diameter of the corrosion pits in the two investigated physiological media. One may remark that titanium has a beneficial influence on the corrosion in physiological media. Indeed, the higher the titanium content, the smaller the average size of corrosion pits.

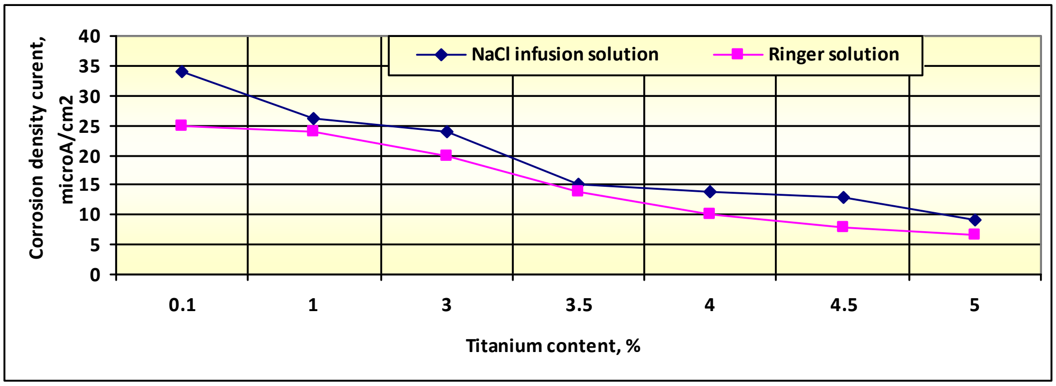

Fig. 8. Titanium influence on the medium diameter size of corrosion pits in the experimental CoCrMoTi alloys, according to potentiodynamic tests in NaCl infusion and Ringer solutions

The obtained results could be compared with those from the literature, considering either the physiological conditions [4,13,16,17], methods of investigations [14,17,18], or even types of corrosion which are met in dentistry [12].

4. Conclusions

Our experiments could reveal the following considerations:

- Alloying with titanium of CoCrMo dental alloys could be made in the same manner as the elaboration process of commercial alloys;
- The structure of CoCrMoTi alloys consists in a mixture of solid solution and eutectic with dendritic segregation;
- Titanium has a beneficial effect on the corrosion resistance of CoCrMo alloys as revealed by the tests in physiological conditions, in NaCl infusion solution and Ringer solution, respectively.
- Titanium may shift the corrosion potential to more electropositive values, respectively for NaCl infusion solution in the range of (-358 ÷ -214 mV) in comparison with -531mV for alloy with no titanium content and for Ringer solution in the range of (-216 ÷ -298 mV) in comparison with -341mV for alloy with no titanium content.
- Titanium may diminish the corrosion density current of the experimental CoCrMoTi alloys tested in physiological conditions. The corrosion density current in an alloy with no titanium content is very high (about 24 μA/cm^2 in NaCl infusion solution and 0.4 μA/cm^2 in

Ringer solution) in comparison with the corrosion density current of alloys with titanium (which are placed in the range of 0.9 ÷ 5,2.10^{-2} μA/cm^2 for NaCl infusion solution and 0.3 ÷ 5,8.10^{-2} μA/cm^2 for Ringer solution).

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