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The influence of chemical nature on the corrosion behaviour of some dental alloys in Fusayama-Meyer artificial saliva

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The paper presents the influence of chemical nature on the corrosion of dental alloys in Fusayama - Meyer artificial saliva with fluoride ions content, at human body temperature (37°C). From evolution of open-circuit potential/time and polarization curves, as well as by processing Nyquist and Bode impedance plots, it was concluded that the biocompatibility of dental alloys depends mainly on the occurence of passivating film. Better electrochemical parameters were obtained for greater Cr content in the non-noble alloy. By adding of fluoride ions, the passive film was also developed, whereas the corrosion resistance is diminished.

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1. Introduction

The large variety of dental alloys has determined numerous studies for investigation of mechanical properties, corrosion, biocompatibility etc. Corrosion in oral media may produce important alteration of metallic structure by physical-chemical and microbial attack and exerted mechanical efforts. In practice, apart of a good mechanical resistance, a dental alloy needs to be less possible toxic or allergic in its chemical composition. Most metallic materials used in dentistry contain noble metals (Au, Pt). Alternatively, much interest has attracted non-noble alloys (Ni, Cr, Co, Ti), avoiding expensive cost and limited resources. Usually, the utilization on large scale of titanium in dental technology of last years is explained through manifold advantages; it presents, in comparison with other metallic materials of this area, a great corrosion resistance and an absolute biocompatibility and missing of any toxicity, being perfect tolerate by the organism.

The chemical nature of alloy also determines the composition of the superficial films [1]. For Ni-Cr alloys, a content more than 15%Cr and minimum 6%Mo provides an oxide layer with good corrosion behavior in saliva. If the Cr and Mo content is lower, the formed oxide is not homogenous and the corrosion resistance of alloy decreases. Artificial saliva, which was utilised, has the following chemical composition (g/L): 1.5 KCl, 9 NaCl, 0.5 KSCN, 0.5 $NaH_2PO_4 \cdot H_2O$, 0.9 lactic acid; its pH was 4.6.

Medeliene and Matulionis [2] have studied the influence of morphology on corrosion properties of Ni-Cr alloy, showing that the corrosion process can be intensified at the crystal grain limits. For electrochemical characterization Bojinov [3] has applied a model of mixed electric conduction (both electronic and ionic). The defects act as either electrons donors or acceptors, contributing to electrical conductivity. Venugopolan and Lucas [4] have noticed that the noble alloys based on Ag, Au and Pd present low galvanic corrosion susceptibility in conection with titanium. On contrary, Co-Cr-Mo, Ni-Cr and Fe based alloys have a higher galvanic corrosion susceptibility, and Ni-Cr-Be alloy is considered to have the highest galvanic corrosion susceptibility with titanium contact. Cai *et al.* [5] have studied the corrosion of the dental alloys with large content of Pd in Fusayama artificial saliva; these alloys have spontaneous passivity in oral environment. Meyer and collaborators reported in al old study about the electrochemical behaviour of nickel-based casting alloy(useful for surgical implants) that the alloy with high molybdenum and manganese contents definitely show a better resistance to corrosion.

Reclaru and Meyer [6] studied the effects of fluorides om titanium and other dental alloys(Co-Cr and stainless steel).If fluoride ions are present, the dental alloys tested undergo a crevice and pitting corrosive process, as soon as the pH drops below 3.5. Venugopolan and Gaydon(2001),[7] in a review of the corrosion behaviour of surgical implant alloy observe the cobalt alloys do not show the traditional active-passive transition as they were also in a passive state prior to testing.

The electrochemical behaviour of a dental alloy in artificial saliva permits the estimation of the behaviour of the material in the oral cavity.The modification of the dental alloy properties could be determined using rapid electrochemical tests as a quqlitative criterion to estimate the corrosion resistance[8].

Generally, it is accepted that the presence of halogens in solution leads to amplification of corrosion, especially by occurence of the pitting corrosion. This study presents the results obtained about the corrosion behavior of five dental alloys in Fusayama-Meyer artificial saliva. Because in the hygiene products of oral cavity the fluoride ion is present, the study of dental alloys corrosion in the presence of F^- ions is justified, too.

2. Materials and methods

The selected dental alloys in this study belong to Ni-Cr and Co-Cr non-noble alloys (stainless alloys); for comparison, the AuAgPd noble alloy was also investigated. The names and chemical compositions of the alloys which have been used as working electrodes are shown in Table 1.

Table 1. The chemical composition of investigated dental alloys, in mass percentages.

Name of dental alloy	Element (%w)															
	Ni	Cr	Co	Mo	Nb	Fe	W	Si	Ce	Mn	Au	Pd	Ag	Cu	Zn	Ir	other
wiron	65	22.5	-	9.5	1	-	-	1.5	-	-	-	-	-	-	-	-	
mini-chrome	66	20	-	6.5	-	2	-	2	-	1.5	-	-	-	-	-	-	
niadur	59	27	-	12	-	-	-	1.5	-		-	-	-	-	-	-	Al, C
wiro-bond	-	26	61	6	-	-	5	1	0.5	-	-	-	-	-	-	-	
AuAgPd	-	-	-	-	-	-	-	-	-	-	46	6	39.5	7.49	1	<1	

The specimens as working electrode, in disk shape, have diameter in the range 0.7-1.1 cm, being mounted in epoxydic resin. Their surface were mechanically polished with emery paper of different grades (until 1200); then, were washed throughly with distilled water and dried with ethanol. A saturated calomel electrode SCE and a Pt sieve were used as reference electrode and counterelectrode, respectively. The experimental techniques used in the present investigation were electrochemical techniques: evolution in time of the open-circuit potentials, chronoamperometry, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). They were conducted by Zahner Electrik IM 6e (Germany) workstation.

To ensure similar conditions with the oral cavity, the corrosion studies were done at 37°C constant temperature (human body temperature), maintained permanently with a Memmert thermostat. The Fusayama-Meyer artificial saliva was freshly prepared as a solution with composition (g/L): NaCl-0.4; KCl-0.4; $CaCl_2$-0.8; NaH_2PO_4-0.69; urea-1; an admixture of F^- ions 0.11%w (added as NaF) was performed in some cases. All solutions were prepared from analytical grade reagents (Merck).

3. Results and discussion

The study of dental alloys corrosion in artificial saliva was carried out using a unitary procedure, by measuring:

a)- the open-circuit potential (OCP) for 10 minutes, to notice the corrosion tendency of the alloy;

b)- polarisation at constant potential of 0.2V/SCE for 5 minutes, during an oxide film formation on the alloy surface;

c)- the electrochemical impedance at 0.2 V/SCE electrode potential, by varying the frequency of alternative current between 10^5 Hz and 10^{-2} Hz, with an amplitude of 5 mV sinusoidal signal;

Some examples showing the evolution in time of open-circuit potential for studied alloys are shown in Fig. 1.

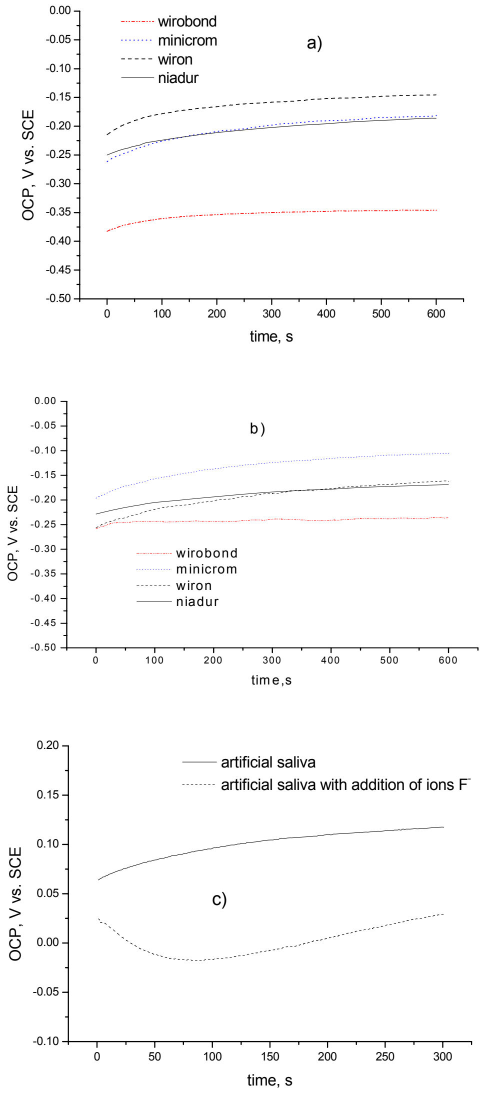


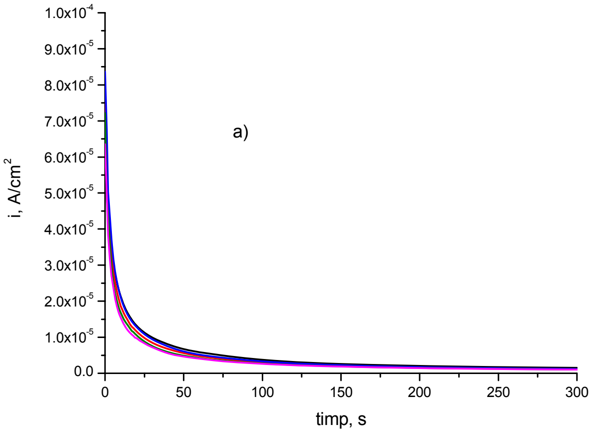
Fig. 1. The potential variation in open circuit for alloys with content Cr in saliva without F^-(a) and with F^- (b) and also for the alloy AuAgPd in the both solutions (c);37 °C.

The curves from Fig. 1 show for all dental alloys a shift in the negative direction of the open circuit potential (especially in the first 10 minutes after immersion), that is an indication of a passive film formation. Refering to the values of OCP (Table 2), the wirobond and niadur alloys have the greatest tendency of oxidation, opposite to behaviour of AuAgPd alloy, which is a noble metallic material (with a positive OCP value). However, for this last alloy immersed in artificial saliva with fluoride ions content, it appears an initial corrosion process followed by a passivity state.

Table 1. Values of the open-circuit potentials (OCP after 10 min) of dental alloy in artificial saliva (37^0).

Dental alloy	OCP,V in saliva	OCP,V in saliva+ F^- ions (0.06-0.1%wt)
wiron	-0.159	-0.162
minichrome	-0.161	-0.106
wirobond	-0.346	-0.236
niadur	-0.186	-0.169
AuPd	+0.110	-0.005

The following step of experiment consisted in the maintaining of electrode at +0.2 V/SCE constant potential for 5 minutes and measuring the evolution of current in time (chronoamperometry). In the cases of non-noble alloys this electrode potential corresponds to a passive region on the polarization curve, except for AuAgPd alloy (the noblest alloy) where the passive plateau is not recorded, being only a continuous increase of current. Examples of the obtained chronoamperograms are presented in Figure 2.



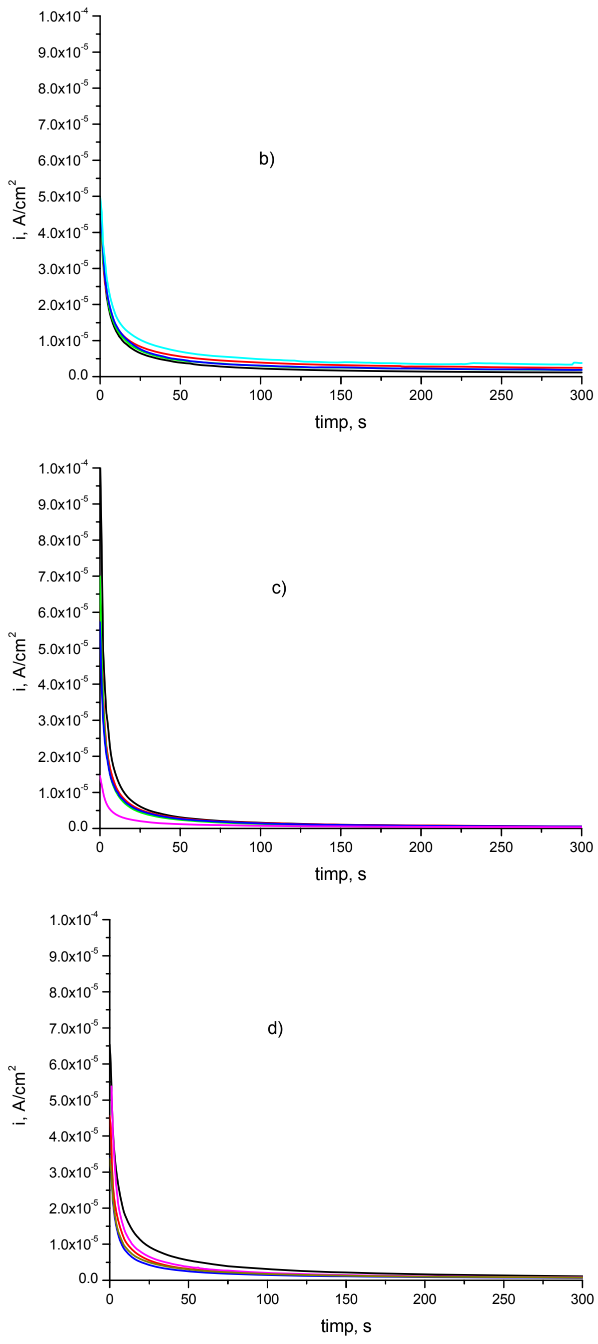


Fig. 2. Chronoamperograms for non-noble alloys polarised at +0.2 V/SCE in artificial saliva, 37^0C: a) wiron; b)minichrome; c) wirobond; d) niadur.

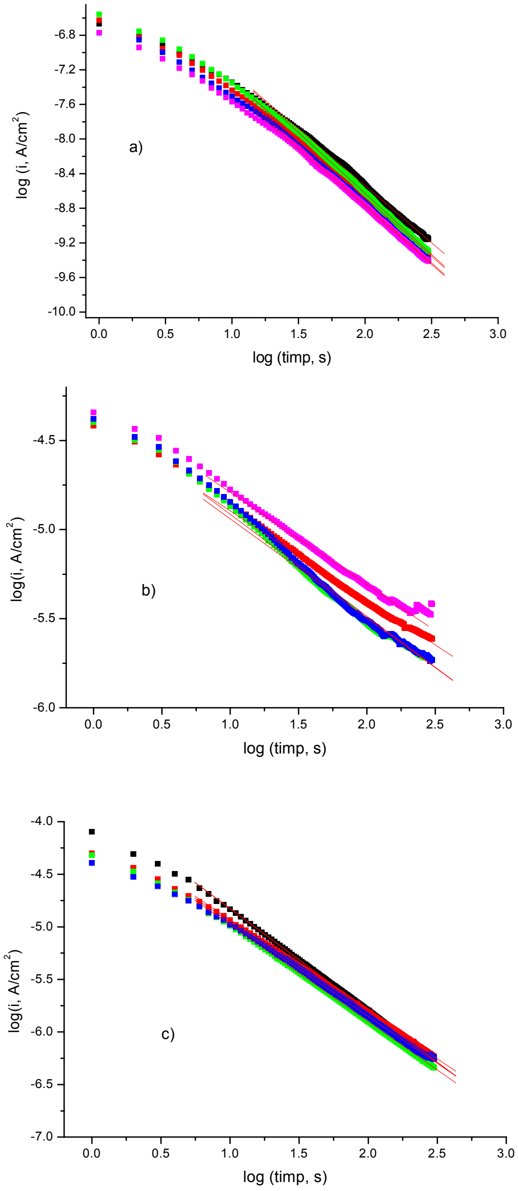
The repeated five curves in identical conditions are shown in each figure, demonstrating the reproducibility.

Using the chronoamperometric data at anodic polarization (+0.2V/SCE), we have tried to verify the validity of equation for repassivation rate (used in the current density term):

$$i = A\,t^{-n}$$

where i- current density, t- time, A and n being constant parameters; generally, the n exponent has a value n = 0.5 - 1.

Obviously, by processing the chronoamperometric data in double logarithmic coordinates, log i- log t, a linear relationship is expected from which the values of parameters in repassivation current expression (1) may be obtained. Fig. 3 and Table 3 show these dependences for studied non-noble alloys and the corresponding values for *n* exponent.



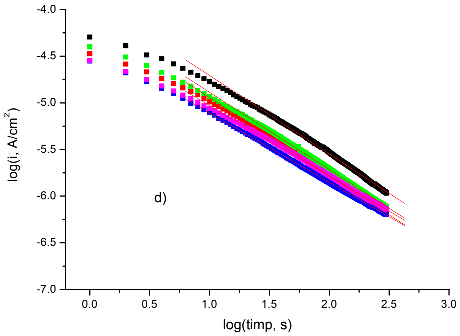


Fig. 3. The log i - log t plots for non-noble alloys at +0.2 V/SCE: a) wiron; b) minichrome; c) wirobond; d) niadur

Table 3. Values of repassivation exponent deduced from chronoamperometry measurements

Table 3. Values of repassivation exponent deduced from chronoamperometry measurements.

Alloy	*Repassivation exponent, n*	*Standard deviation*
wiron	0.861	0.022
minicrom	0.537	0.033
wirobond	0.918	0.041
niadur	0.819	0.036

While the n-value is very closed to the upper limit (n=1) for wiron, wirobond and niadur alloys, the minichrome alloy has a very low value of n exponent, near to the lower limit of the interval. According to these results we can suppose that the oxide layer formation is more difficult for minichrome, in spite of the existence of chromium in its composition.

In our experiments, the next step consisted in performing electrochemical impedance spectroscopy (EIS), by continuing the polarization of oxide covered electrodes, a specific techniques for identification the growing of oxide films of the experimented alloys.

Electrochemical impedance spectroscopy

On the surfaces of the alloys was formed the oxide film by polarization at constant potential. The properties resulted were investigated using electrochemical impedance spectroscopy.

Impedance spectra were recorded at the same potential used to obtain the films (0.2 V/SCE)

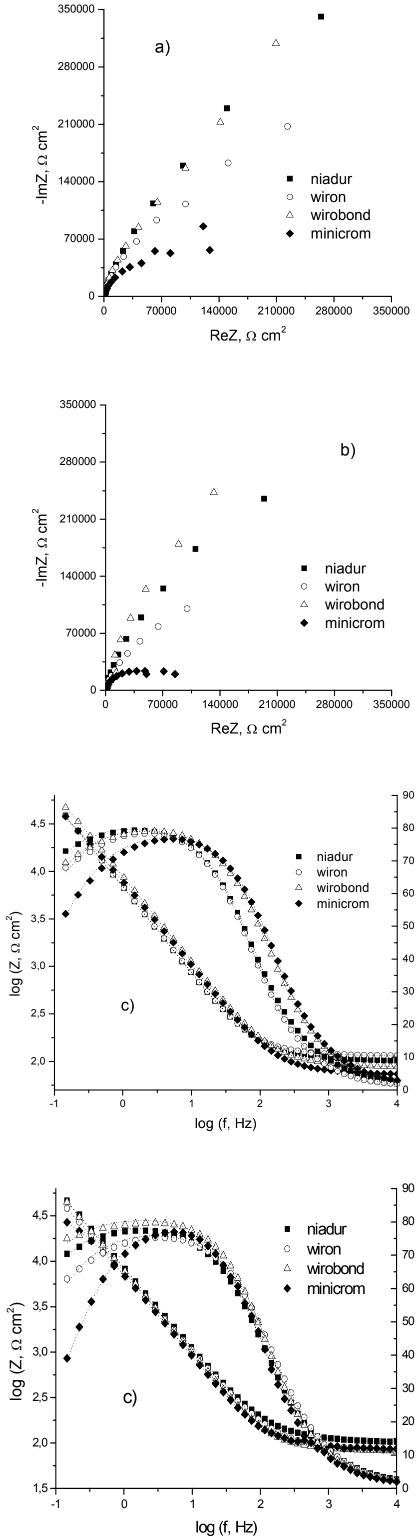


Fig. 4. The diagrams Nyquist and Bode for non noble alloys polarizated by +0.2 V/SCE in saliva without F^- a) and saliva with F^- b); t=37°C

Therefore we observe in Fig. 4, all the diagrams who have on ordinate line the imaginary part of the impedance and on real part (Nyquist diagrams) have the shape of the beginning of semicircle, which result in a capacitive behavior; the diameters will correspond the polarization resistance R_P, inversely proportional parameter with i_{coroz}. Though uncertainly of R_P determination, corrosion currents value are the same size order with the one calculated from polarization curves, and corrosion resistance will increase in following order:

minicrom < wiron < niadur ≈ wirobond.

The capacitive behavior confirmation and the dependence phase angle, φ, the frequency logarithm, (the curves with the maxim from Bode specters), where will reach the maxim values of 80°(90° being the theoretical alteration of phase for on condenser. The impedance specters for noble alloys (Fig.4) suggest an ohmic a character more pronounced of impedance (the angle phase maxim 45-60°, imaginary component more reduced .For data filtering was used a model of equivalent circuit presented in figure (Fig.5)

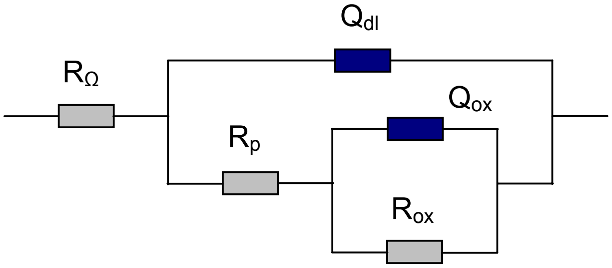


Fig. 5. The circuit equivalent for data filtering.

From the equivalent circuit components, the oxide resistances R_{OX} play an very important role, because the increased value of him directly depend of dental alloy biocompatibility.

Table 4 The oxide film resistance R_{ox} for non noble alloys.

Dental alloys	The oxide film resistance, kΩ cm^2	Standard deviation, kΩ cm^2
wiron	123.4	17.8
minicrom	88.2	7.8
wirobond	219.1	21.4
niadur	225.7	29.8

In the Table 4 will present the values of R_{0X} for them which circuit will model (filtering) the best experimental data in saliva without flour.

From the previous obtained results by polarization or by impedance spectroscopy, for the criterion case R_{ox}

it seems only two alloys are very resistant at corrosive attack of the saliva : niadur and wirobond, the wiron alloy it is an intermediary position and the minicrom alloy the least resistant.

According to the data for the resistance R_{ox} we can assume all the factors which influence the increase of oxide layer are different from the factors which are depend on oxide layer stability [9].

4. Conclusions

The paper intended to highlight the differences between biocompatibility of some unnoble dental alloys, type Ni-Cr (wiron, minicrom, niadur), respectively type Co-Cr (wirobond). A noble alloy type AuAgPd was also studied;

The biocompatibility of dental alloys is dependent on the metallic ions quantity freed by the alloy;

Although by immersion in saliva, Ni-Cr, Co-Cr and AuAgPd dental alloys develop a passive film, its behaviour is different depending on the chemical composition of the alloy. The order of corrosion resistance is: minichrome<wiron<wirobond<niadur.

The noble alloy it is obviously inferior to nonnoble alloy from the point of view of the corrosion resistance.

zFor a greater certainty of the experimental data in the presence of agressive environment given by fluorine ions further studies are necessary.

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