

Study of the corrosion process for some dental metal alloys under influence of the artificial saliva enriched with yeast and *Streptococcus Mutans* bacteria

E. GÂTIN^{*}, C. BERLIC, B. IORDACHE^a, P. PRIOTEASA^b

University of Bucharest, Faculty of Physics, Department of Polymer Physics, P.O. Box 11 MG, Măgurele - Bucharest, Romania

^a"Carol Davila" University of Medicine and Pharmacy, Dept. of Prostheses Technology & Dental Materials, Calea Plevnei 16, Sector 5, Bucharest, Romania

^bINC DIE ICPE-CA, Institute of Electrical Engineering-Advanced Researches, Bucharest, Romania.

Nowadays, a high interest is focussed to obtain improved fix or mobile dental prostheses. For this purpose it is used a large variety of metal alloys, making difficult to evaluate technical, biological and clinical properties of all these materials. The present study establishes the results of investigation for electrochemical behaviour of some commercial metal alloys such as: nickel alloy, Co-Cr alloy and AuAgPd. The investigation was performed using a medium of Fusayama-Meyer artificial saliva. For a complete test, sterile artificial saliva was enriched by addition of yeast extract, to attempt the development of the bacteria, in order to study the influence of *Streptococcus Mutans* in the process of corrosion on metal alloys. By studying the evolution of the open-circuit potential, its shift in negative direction was attributed to the metabolism of bacteria. Along potentiodynamic curves, high corrosion currents were observed for the potentials between -0.58 V and +0.26 V vs. ECS reference electrode. For the presence of yeast extract and bacteria as well, the Ni and Co - Cr metal alloys presented the passivity characteristics, whereas for AuAgPd alloy higher corrosion currents were observed.

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1. Introduction

The large variety of dental alloys that exists on the market presents various compositional formula and possibilities of utilisation. It is very important to know the influence of the oral bacteria on dental alloys and, as it was demonstrated in several similar industrial branches, the bio corrosion process takes action and important damages to the metal dental structure may occur [1, 2]. A good evaluation of the corrosion process is connected with a good investigation of the metal alloy biocompatibility [3]. A higher interest is noticed in non-noble alloys (Ni, Cr, Co, Ti), to avoid expensive costs and limited resources of noble alloys. The chemical nature of the metal alloy determines the composition of the superficial films with strong influence to corrosion behaviour in saliva [4, 5].

The electrochemical study of a dental alloy in artificial saliva permits the estimation of modification in alloy properties in the oral cavity, using rapid electrochemical tests as a qualitative criterion to estimate the corrosion resistance [6, 7].

An important feature of corrosion behaviour of the surgical implant of metal alloy was noticed, namely the fact that the cobalt alloys do not show the traditional active-passive transition, as they were in a passive state prior to testing [8].

The aim of this study is the investigation of electrochemical behaviour and biocompatibility of some

commercial metal alloys: nickel alloy from Minichrome, Co-Cr alloy from Wirobond and AuAgPd alloy from Midas in media of simple Fusayama-Meyer artificial saliva or enriched with *Streptococcus Mutans* bacteria

The well known metabolism of the bacteria is fermentative in anaerobic conditions at 37°C temperature, producing the lactic acid and not gaseous metabolites [9]. Our study is also offering an evaluation of the corrosion process for the above mentioned metal alloys, a process that has not been yet completely understood.

2. Materials and methods

The following materials, respecting the commercial names and chemical compositions of investigated alloys through present study, are shown in Table 1. All alloy samples were casted and subjected to heat treatment before beginning the electrochemical investigations [10, 11].

The tested sample specimens were shaped as tablet with a thickness of 4 mm and a diameter of 70 mm, casted according to the manufacturing process and finally introduced in a special epoxy resin. The active surface was metal - graphically prepared by means of fine-grained abrasive paper. At the end, the surface was polished with diamond paste with 1 µm grains, cleaned for impurities by ultrasonic waves and washed [12, 13]. Samples manufacturing process was performed at the Dental

Laboratory, Bucharest Medicine University 'Carol Davila', Faculty of Dentistry.

Table 1. Chemical compositions in weight percentages of studied alloys.

Midas (AuAgPd), Heraeus-Kultzer Company weight %	Au	Pd	Ag	Cu	Zn	Ir
	46	6	39.5	7.49	1	< 1
Wirobond (CoCr), Bego Company weight %	Co	Cr	Mo	W	Si	Ce
	61	26	6	5	1	0.5
Minichrome (NiCr), Bego Company weight %	Ni	Cr	Mo	Fe	Si	Mn
	66	20	6.5	2	2	1.5

The used electrolyte medium was Fusayama-Meyer artificial saliva, prepared as a solution with the following composition (g/L): 0.4 NaCl, 0.4 KCl, 0.8 CaCl₂, 0.69 NaH₂PO₄, 1 urea.

The pure Fusayama-Meyer artificial saliva in sterile conditions was enriched by addition of yeast extract (Difco Laboratories, Detroit, USA). This medium was then modified by addition of bacterium, *Streptococcus Mutans* ATCC 700610 (American Type Culture collection), selected because its good adherence to metal surfaces. Colonies of *Streptococcus Mutans* were separately grown, using yeast extract and an agar-agar + sucrose mixture (gelose) or 2% glutaraldehyde. The final product was filtrated and maintained in 0.2 N cocodylate tampon solution, conditions most closely to the physiological ones, without making any drying [9, 14]

In order to avoid the contamination of bacteria species with electrolyte, all utilised instruments were sterilised and the crossing of the bacteria from a medium to another was realised by keeping them in a sterilised dock.

The bacteria development was determined by absorption spectrophotometry for 550 nm wavelength, using a Metertek SP-850 spectrophotometer equipment. The analysis of the adherent bacteria colony to alloys surface was performed using a XL30 ESEM Philips scanning electron microscope.

During electrochemical experiments, the alloy samples were immersed in the electrochemical cells containing the following aqueous solution: 60mL saliva + 5g/L yeast extract + 10mL *Streptococcus Mutans* colony, respectively. It was used an electrochemical equipment, Zahmer Elektrik IM 6e, electrochemical workstation provided with Impedance Analyzer [14]. The electrochemical techniques applied were: the time evolution of the open circuit potentials, potentiostatic polarization curves and electrochemical impedance spectroscopy (EIS), carried out with data acquisition software Thales 2.01.

The cell contains the working electrode (Minichrome, Wirobond or Midas metal alloy samples), whereas the counterelectrode was a circular Pt sieve and the reference

electrode was a Saturated Calomel Electrode (SCE). The electrolyte was permanently stirred using an electromagnetic stirrer. All the experiments were carried out at a temperature of 37.0 °C ± 0.1°C (human body temperature).

3. Results

The growth of bacteria colony was followed by measuring the optical density of the system. The obtained curve, shows an exponential increase in the first part and a plateau after 4 days of incubation at a temperature of 37.0 °C ± 0.1°C (Fig. 1). According to this behaviour, it was decided to carry out the electrochemical experiments 4 days later from the moment of introduction in the enriched saliva with yeast extract, when the bacteria present a limiting optical density.

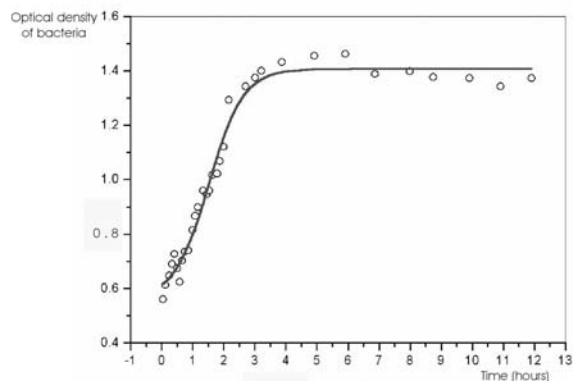


Fig. 1. The time variation of optical density showing the growth of *Streptococcus Mutans* in artificial saliva enriched with yeast extract, at 37°C.

Confirming bacteria action process, an image obtained by SEM microscopy is showing the adherence of the bacteria on Ni metal alloy surface, Fig. 2.

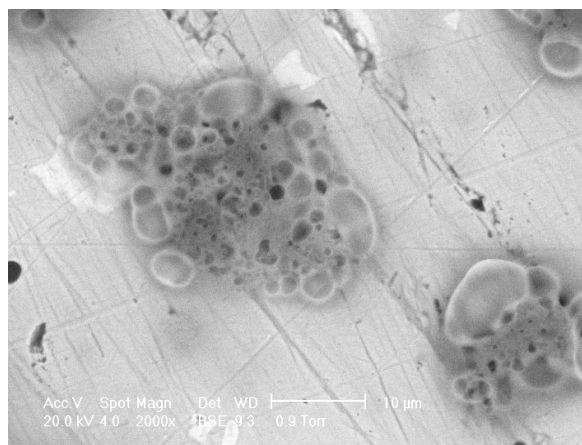


Fig. 2. Pure colony of *Streptococcus Mutans* adhered on Ni-Cr alloy.

By studying the time evolution of the open-circuit potential values, it was noticed a shift of the open-circuit potential also in negative direction, attributed to the metabolism of bacteria. In artificial saliva and saliva with yeast addition, for the noble and Co – Cr metal alloy it was noticed the same trend of passivity, but Ni-Cr metal alloy presented a rapid tendency to passivity, the electrode potential being stabilised without appearing a corrosion tendency. Ph values for each solution were as follows: 4.93 for artificial saliva; 5.91 for artificial saliva and yeast added; 8.22 for artificial saliva, yeast and bacteria added.

Ph values were measured to the end of the evaluation for each sample during open circuit potential curves investigation method. Evaluation time for each sample was of 3 hours. The addition of bacteria shifts the open-circuit potential from 75-125 mV positive potentials towards the negative values of -200mV, V/SCE (Fig. 3).

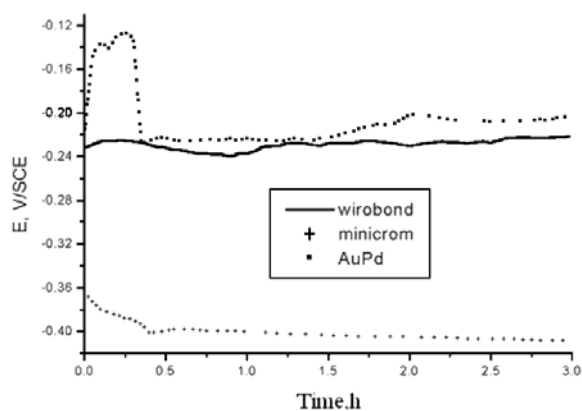


Fig. 3. Time variation of the open-circuit potential for the studied metal alloys samples in the presence of *Streptococcus Mutans*.

The differences in the corrosion behaviour were also pointed out by recording the polarization curves (Fig. 4). The polarization curves make possible to determine the rate of electrochemical reaction which takes place in the studied process. In this way, it is possible to establish the corrosion current, polarization resistance or the pitting potential. We noticed that the variation of corrosion currents is significant for the electrode potentials between -580 and +260 mV, in good agreement with the results published previously [6, 7, 8] during determinations of electrode potentials in oral cavity.

The results show that, in the presence of both yeast extract and bacteria, the Minichrome and Wirobond alloys exhibited the passivity characteristics, whereas Midas alloy (AuAgPd) produced higher currents on the anodic branch of polarization curves. In the same time, the Midas metallic material oxidation in the presence of bacteria takes place too early, at less positive potentials. It was noticed an anodic peak to +0.17 V/SCE potential which appears due to its Ag content oxidation, with formation of compounds Ag_2O and AgCO_3 (this compound resulting from a reaction with dissolved CO_2), respectively.

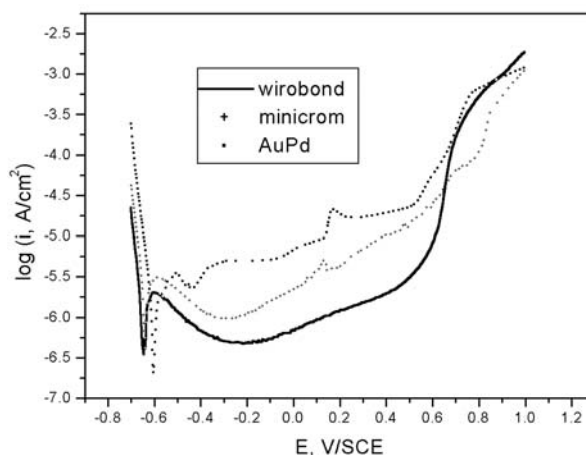


Fig. 4. Comparison between polarization curves for each of the studied alloy in artificial saliva, in the presence of *Streptococcus Mutans*.

For confirmation of the above results, the electrochemical impedance measurements were performed as well. In Fig. 5 are presented the Nyquist plots for all three metal alloys.

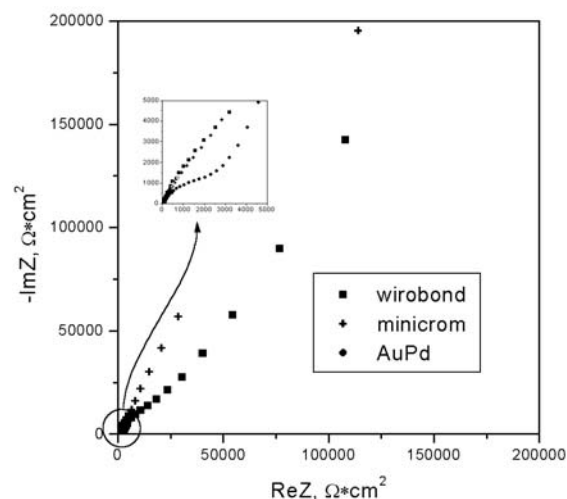


Fig. 5. Comparison between Nyquist diagrams for each of studied alloy in the presence of *Streptococcus Mutans*.

The fact that Midas alloy has the weakest corrosion resistance (illustrated by the smallest semicircle diameter) is the main observation noticed by analyzing the EIS spectra. To interpret the results, a simulation using an equivalent electrical circuit containing serial and parallel components was made [15, 16]. The obtained values for electrolyte resistance (R_0) and oxide layer resistance (R_1) are presented in Table 2.

Table 2. The values of electrolyte resistance (R_0) and oxide layer resistance (R_1) obtained by simulation of alloy/electrolyte interface in the cases of successively experiments in 60 mL saliva, 60 mL saliva + 5 g/L yeast extract and 60 mL saliva + 5 g/L yeast extract+10 mL *Streptococcus Mutans* colony.

		R_0 (Ω)	R_1 (Ω)
AuAgPd (Midas)	Artificial saliva	-	243.5
	Artificial saliva + yeast extract	-	1064
	Artificial saliva + yeast extract + bacteria	-	1447
Ni-Cr (Minichrome)	Artificial saliva	48.45	1.020×10^6
	Artificial saliva + yeast extract	39.92	0.647×10^6
	Artificial saliva + yeast extract + bacteria	88.31	0.262×10^6
Co-Cr (Wirobond)	Artificial saliva	35.63	1.520×10^6
	Artificial saliva + yeast extract	54.57	0.635×10^6
	Artificial saliva + yeast extract + bacteria	53.70	8838

4. Conclusions

The modification that appears in the case of open-circuit potential investigation method (it shifts towards the negative values with about 300 mV) is generally due to the increase of local pH, proving the influence of bacteria metabolism. We consider that only the measurements for open circuit potential variation are not enough for appreciating the degree of corrosion resistance;

The obtained results using polarization curves confirm a particular behaviour of each alloy, depending on its nature. Ni-Cr alloy has a corrosion rate with values much lower than those acceptable for saliva media in the presence of bacteria. Although the corrosion currents on anodic branches indicate relatively low corrosion rates for noble alloy (Midas), the data show a modification of a noble alloy behaviour in the bacteria presence, comparing to its behaviour at identically electrode potentials existing in human oral cavity.

Studying these three metal alloys, our investigation study confirmed that very important modifications take place at alloy/saliva solution interface, a phenomenon that directly influences the corrosion process. However, it is worth to mention that the bacteria consumes the dissolved products in saliva medium and produces, in the same time, new metabolites that remain attached to bio film deposit. So, the results evidenced that a more complex bacteria influence to corrosion behaviour exists for all studied dental alloys and a mechanism of this influence is difficult to be elaborated. A high interest for these corrosion phenomena is still requested in order to improve biocompatibility of dental prosthetic restoration works.

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*Corresponding author: edgatin@netscape.net