In vitro Studies Regarding the Corrosion Resistance of NiCr and CoCr Types Dental Alloys

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Prosthetic treatment of reduced partial edentation supposes the introduction of a foreign object into the patient's oral cavity, which implies an increased attention regarding the compatibility and the corrosion resistance of the used materials with the biologic environment. The aim of this study was to compare the corrosion resistance of six commercial samples of dental alloys from different suppliers (three types of nickel-chromium and three types of cobalt-chromium alloys) in artificial saliva Fusayama-Meyer with different pH: 2, 5 and 7, at room temperature (25±1°C). The samples were tested electrochemically to determine their resistance to corrosion. The corrosion rates were obtained from the current-potential curves. The potentiodynamic curves of the dental alloys showed that dental alloys have variations of the corrosion parameters in all types of the studied artificial saliva. CCG have shown the lowest values of corrosion rate irrespective of the pH of artificial saliva.

Keywords: dental alloys, biomaterials, corrosion, artificial saliva.

It is known that the quality and performances of dental materials are beside the proper composition of dental alloy, the good mechanical properties, the corrosion resistance and the biocompatibility [1]. Dental materials interact with living tissues they come in contact with and generate local or systemic responses.

The main causes of failure metal-fused-to-ceramic restorations are given by the corrosion degradation of metals or alloys, mechanic wearing and fatigue [1-4].

Corrosion resistance is one of the important features of dental materials, because after introducing into the human body, the metallic biomaterials are subject to corrosive medium.

The corrosion behaviour of cast alloys is one of the important characteristics which respect the principle of material biological safety [5].

Cobalt-chrome alloys, due to excessive hardness (350-380 HB), have several disadvantages: scarce occlusal adjustment, opposing teeth attrition and difficult discard from the abutment.

Modern Ni-Cr alloys have main composition consisting of Ni (60-70%), Cr (15-20%) to which there are added small amounts of: Mo, Al, Mn, Be, Cu, Co, Fe.

Alloy corrosion resistance is due to the formation of a surface protective micro-layer of chromic oxide.

The corrosion resistance of six commercial dental alloys used in metal-fused-to-ceramic technology, alloys supplied by different worldwide well-known producers, into artificial saliva having different *p*H values was investigated by means of linear polarization scans.

Experimental part

Six commercial dental alloys were evaluated, namely Ni-Cr types (Argeloy NP/Argen – codified NP; Ugirex III/Ugin Dentaire – codified NCU; and Protechno-N8/Protechno – codified NCP) and CoCr types (Argeloy NP Special/Argen – codified NPS; Girobond/Amann Girrbach – codified CCG; Sheradent/Shera – codified CCS). The chemical composition of the alloys is the one given by the manufacturers.

Metallic alloys specimens were cast in circular moulds (fig. 1), with the dimensions 13x1.5 mm, and were polished in two stages: first with sandpaper with abrasion degrees between 600 and 2,000 microns and then with diamond paste. Before testing, specimens were washed with distilled water and then dried.

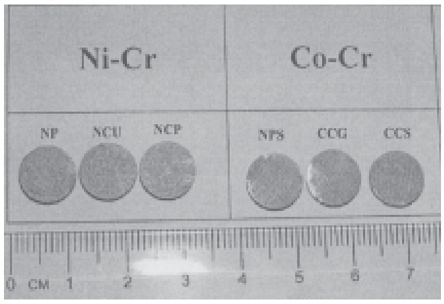

Fig. 1. Samples used for corrosion investigation

The electrochemical measurements were performed using a Potentiostat / Galvanostat (model PARSTAT 4000, produced by Princeton Applied Research), controlled by a computer and recording the results by using VersaStudio software [6]. The corrosion resistance was determined by linear polarization technique, after recording the polarization curves. The measurements were made respecting the following steps:

- measurement of the open circuit potential (E_{OC}) for 1 h;
- recording the potentiodynamic polarization curves from -0.1 V (vs OC) to +1.5 V (vs SCE), with a scanning rate of 0.33 mV/s.

The test cell used in the measurements consists of three electrodes: a saturated calomel electrode (SCE) used as reference electrode, a platinum electrode as counter

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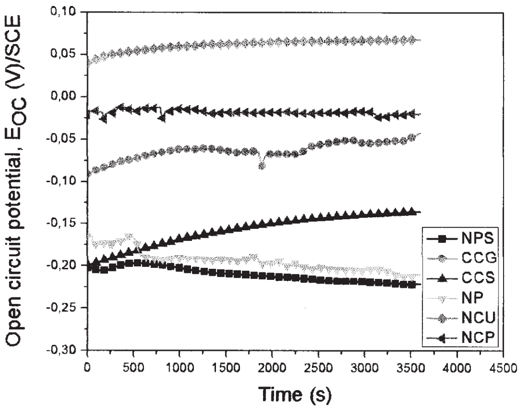

Fig. 2. Variation of open circuit potential of the alloys vs. time in artificial saliva, *p*H=2

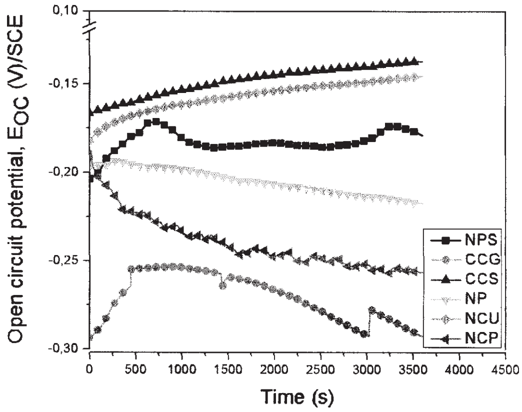

Fig. 3. Variation of open circuit potential of the alloys vs. time in artificial saliva, *p*H=5

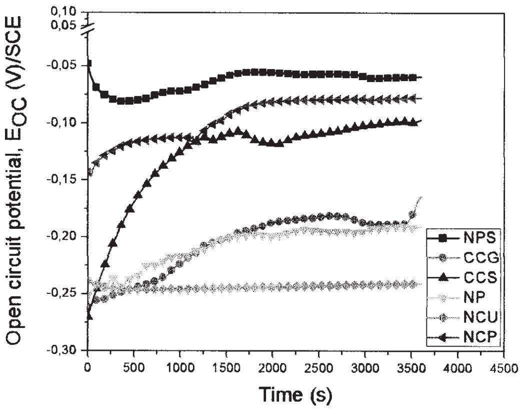

Fig. 4. Variation of open circuit potential of the alloys vs. time in artificial saliva, *p*H=7

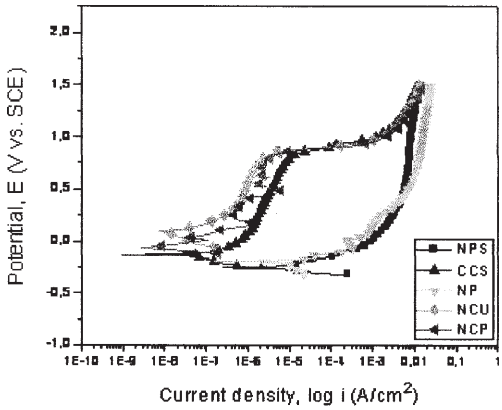

Fig. 5. Potentiodynamic polarization curves of the alloys in artificial saliva, *p*H=2

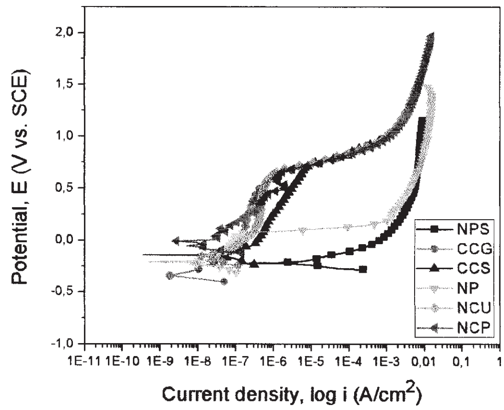

Fig. 6 - Potentiodynamic polarization curves of the alloys in artificial saliva, *p*H=5

electrode and the working electrode consisted in the analysed samples placed on a Teflon base and having the working surface of 1 cm^2.

Corrosion tests were carried out in artificial Fusayama-Meyer saliva (with composition of 0.4 $g \cdot L^{-1}$ NaCl, 0.9 $g \cdot L^{-1}$ KCl, 1 $g \cdot L^{-1}$ urea, 0.69 $g \cdot L^{-1}$ NaH_2PO_4, 0.795 $g \cdot L^{-1}$ $CaCl_2 \cdot H_2O$) at room temperature (25±1°C), according to standard ASTM G15-97a. Since the *p*H of the oral cavity can decrease below 5.0 following a meal, more aggressively acidic conditions in the oral cavity were also simulated by decreasing the *p*H (7, 5 and 2).

Results and discussions

The evolution of potential recorded under open circuit conditions (E_{oc}) for the samples of the two types of studied NiCr and CoCr alloys versus time in different *p*H artificial saliva are presented in figures 2-4.

As a general tendency, the potential slightly increased as the samples were immersed in the Fusayama's solution and then stabilized after 30 min, except for the NP and NPS samples at *p*H=2 and NCP and CCG samples at *p*H=5 that the potential decreased versus time.

The curves for NiCr alloys showed that the NCU alloy has the greatest electronegative value of the open circuit potential (E_{oc}) in artificial saliva with *p*H=7, indicating the weakest noble character, whereas in the case of artificial saliva with *p*H=2 the same NCU alloy has the noblest character as for E_{oc}.

Taking into account the same evaluation criterion for the CoCr alloys, in artificial saliva with *p*H=5, CCG alloy has the weakest noble character and in artificial solution with *p*H=2 the same CCG alloy stands out.

The polarization curves for the studied dental alloys are presented in figures 5-7. The current density is correlated with the corrosion rate. A high current density (the ratio current / surface) at the corresponding potential indicated a high corrosion rate of the alloy.

The comparison of the polarization curves shows a similar shape for all the curves with exceptions for each type of solution.

The following parameters were determined from the polarization curves, parameters which characterise the corrosion resistance of the analysed samples and was calculated the corrosion rate (CR):

-open circuit potential (E_{oc})
-corrosion potential (E_{corr})
-corrosion current density (i_{corr})

The main parameters of the electrochemical corrosion process are listed in table 1.

The corrosion rates are calculated (according to ASTM G102-89, 2004) using the equation:

$$CR = K_i \cdot \frac{i_{corr}}{\rho} \cdot EW$$

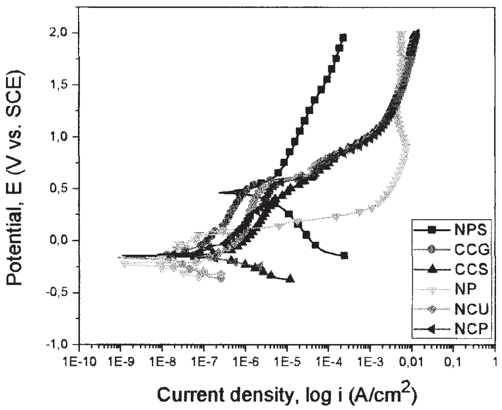

Fig. 7 - Potentiodynamic polarization curves of the alloys in artificial saliva, *p*H=7

Table 1
SUMMARY OF THE ELECTROCHEMICAL PARAMETERS OF THE CORROSION PROCESS EVALUATED FROM THE OCP AND POLARIZATION MEASUREMENTS

Alloy		NP	NCU	NCP	NPS	CCG	CCS
E_{oc} [mV]	pH=2	-209.78	66.56	-19.39	-221.21	-34.76	-128.96
	pH=5	-218.06	-144.30	-25.65	-181.79	-304.17	-135.18
	pH=7	-191.39	-241.14	-78.11	-59.28	-164.57	-97.19
E_{corr} [mV]	pH=2	-198.03	77.21	-37.10	-258.99	-40.51	-137.03
	pH=5	-231.58	-147.23	-57.15	-157.80	-322	-139.39
	pH=7	-221.83	-223.42	-131.50	-81.67	-166.10	-134.26
i_{corr} [A/cm^2]	pH=2	3.61×10^{-6}	1.59×10^{-8}	0.91×10^{-8}	3.65×10^{-6}	1.54×10^{-8}	4.21×10^{-8}
	pH=5	1.61×10^{-8}	1.83×10^{-8}	1.18×10^{-8}	2.08×10^{-6}	0.92×10^{-8}	3.83×10^{-8}
	pH=7	5.77×10^{-9}	2.45×10^{-8}	6.18×10^{-8}	3.69×10^{-8}	1.05×10^{-8}	5.12×10^{-8}
CR [mm/year]	pH=2	3.88×10^{-2}	1.69×10^{-4}	0.98×10^{-4}	3.76×10^{-2}	1.57×10^{-4}	4.32×10^{-4}
	pH=5	1.73×10^{-4}	1.95×10^{-4}	1.27×10^{-4}	2.14×10^{-2}	0.94×10^{-4}	3.93×10^{-4}
	pH=7	0.62×10^{-4}	2.61×10^{-4}	6.66×10^{-4}	3.80×10^{-4}	1.07×10^{-4}	5.26×10^{-4}

where:

CR – corrosion rate (mm/year)
K_i – 3.27x10^{-3} (μm/ mA·cm·year)
ρ – density (g/cm^3)
i_{corr} – corrosion current density (μA/cm^2)
EW – equivalence weight (g)

For the CoCr tested alloys the best behaviour to corrosion was for CCG alloy in saliva with *p*H=2 (-40.51 mV), and also the highest electronegative value of E_{corr}, was for CCG alloy (-322 mV) in artificial saliva with *p*H=5.

The NP alloy has a lower resistance to corrosion compared to the other NiCr alloys in artificial saliva with *p*H=2 and *p*H=5, having better corrosion resistance in artificial saliva with neutral *p*H. For CoCr alloys in artificial saliva with *p*H=2 and *p*H=5 but as well as in neutral *p*H saliva, the lowest corrosion current density is recorded by CCG alloy and, therefore, this alloy showed the best behaviour to corrosion.

By comparing the corrosion rate for NiCr alloys, the values are close for all samples in artificial saliva with *p*H=5. Corrosion rate changes in neutral saliva, as expected, decreasing for NP alloy but increasing for NCU and NCP alloys which indicates a better behaviour to corrosion in neutral environment, confirmed as well from the assessment of the other corrosion parameters.

Behaviour and corrosion resistance of a metal alloy with dental destination is given by factors such as: alloy chemical composition, its surface nature, micro-structure (presence of structural and crevice type imperfections), *p*H of the environment, temperature, oxygen content [1-4, 7-11].

The corrosion behaviour of dental alloys based on CoCr and NiCr mainly depend on the percentage of Cr and Mo of the alloy [12]. In commercially available alloys, the percentage of Cr and Mo varies between 11-25%, respectively between 0 and 10 wt% [13].

In the last years, there have been introduced sub-classes of CoCr or NiCr based alloys with Pd (25% wt), in adequate quantity in order to be considered noble alloys. Unique for this type of noble alloys is the fact that they evolved from a class already existing of common alloys [14]. Unfortunately, little information is available regarding the properties of these specific alloys [14], which combine the properties of Pd [15-19], common alloys [13, 20] and features derived from previous attempts to enrich dental materials with Pd [21].

Conclusions

Alloys corrosion resistance was assessed based on several evaluation criteria.

The study demonstrated the importance of the content of different components in dental alloys related with the importance of the *p*H of the medium.

Comparing the results of the tested alloys, they showed that NiCr alloys have higher electropositive values for open circuit potential than those of CoCr alloys in artificial saliva with acidic *p*H. For CoCr alloys it was obvious that open circuit potential values in artificial saliva with *p*H=7 are more electropositive as compared to those in NiCr alloys, thus emphasising their nobler character.

Taking into consideration the value of corrosion potential (E_{corr}), it is considered that metals with more electropositive E_{corr} potential have a better corrosion behaviour. According to this criterion, for the NiCr type alloys, NCU has the best behaviour to corrosion in artificial saliva with *p*H=2 and NCP alloy has the best behaviour in saliva with *p*H=5.

It is recognised that a lower corrosion current density indicates a better corrosion resistance. Thus, if we take into consideration this criteria, we can notice that NiCr alloys have the values of corrosion current density roughly equal in saliva with *p*H=5, and in the acidic one the values are little different for NCU and NCP alloys remaining within the same order of magnitude, compared to NP alloy whose value increases to three order of magnitude. When dipped into artificial saliva with neutral pH the i_{corr} values increase in the case of NCU and NCP alloys and decreases in the case of NP alloy reaching the lowest value (5.77 $nA\cdot cm^{-2}$).

Dental alloys have variations of the corrosion parameters in all types of the studied artificial saliva. CCG have shown the lowest values of corrosion rate irrespective of the artificial saliva *p*H.

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