Electrochemical Behavior of Coated and Uncoated Nonprecious CoCr and NiCr Alloys in Artificial and Natural Saliva

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This article contributes to the study of the electrochemical behavior in artificial and natural saliva of coated and uncoated, with nanohydroxyapatite, of nonprecious CoCr and NiCr alloys. The procedure employed for commercial nanohydroxyapatite deposition was dip coating. Electrochemical measurements include determination of the open circuit potential (OCP), as a function of time and polarization curves. For surface analysis scanning electronic microscopy (SEM) and X-Rays diffraction (XRD) techniques were used. The dissolution of calcium from coated alloys was evaluated by inductively coupled plasma mass spectrometry (ICP-MS). The protective efficiency of the coatings has been established in both types of saliva. The CoCr alloy has a better electrochemical stability for coated and uncoated samples in both, natural and artificial saliva, when compared with the NiCr alloy. The calcium dissolution from coated alloys in natural saliva has a trend to reach a steady state after around 30 hours of immersion for NiCr and after around 48 hours for CoCr. In artificial saliva even after 168 hours a steady state trend was not visible.

1. INTRODUCTION

Dental metallic alloys such as titanium, gold, palladium, silver, CoCr based alloys and stainless steel were widely investigated in order to be used in oral environment [1-4]. Being developed for long term use in the oral cavity, an important criterion for dental alloys selection is related to their long time behavior in such cavities, especially ions release in tissues and saliva [1]. Of course, the price is a crucial factor as well, and in the developing regions of the world stainless steels [5,6] and cheapest CoCr alloys are the prevalent choices, but a combination of biocompatibility, strength, elastic modulus, corrosion and wear resistance remain suitable factors of selection for fixed prosthesis materials [7]. In the non precious family dental alloys the types based on Co, Cr, Mo and Ni are resistant to corrosion

due to a mixture of passive oxides at their surfaces with compositions depending on the type of alloy [8,9]. The types of alloys with Ni were promoted at the beginning of this century, and were considered to be cytotoxic and allergenic [10]. Some of them may cause allergic hypersensitivity with symptoms appearing not only in the mouth, but also on hands or feet due to the allergic reactions caused after the ions release. The most common allergens are nickel (25.0%), palladium (24.4%), chromium (16.7%), cobalt (15.9%) and tin (12.5%) [11]. In this context, CoCrMo alloy, as a nickel-free variety, [12] was found as an alternative. Such alloys become nowadays the most commonly used type of base metal alloys for removable, partial - denture frameworks, having a very good quality-price ratio. These types of alloys, either non treated or with modified surfaces, were intensively investigated in different ways for performance enhancement [13-15]. The assessments of the alloys are performed usually in various type of artificial saliva [16] with a composition close to the natural one. Human saliva is a complex fluid containing organic and inorganic compounds suspended in an aqueous medium. The substances are secreted by the major and minor salivary glands and the final normal pH is slightly alkaline having value around 7.4 [17]. Saliva contains glycoproteins, like mucin, digestive enzymes like lipase, amylase etc., neutral and polar lipids, and compounds, such as lactoferrins, cystatin, histatin, thiocyanate ions and immunoglobulins [18]. Lactoferrins, immunoglobulins, cystatin, histatin and thiocyanate ions give the antimicrobial properties of saliva. Despite the daily secretion of saliva, which is about 1.5 liters in humans, it is difficult to collect natural saliva and is a need to have the written patient agreement. Due to such problems there are few tests in natural saliva and this is the merit and the novel character of the present paper that the electrochemical stability test of CoCrMo and NiCr alloys were performed in both, artificial saliva and in natural fresh collected saliva.

In order to enhance electrochemical stability and diminish the ions release in environment, various thermal treatments and different depositions have been performed [19]. In order to improve alloys bioperformance, hydroxyapatite (HAp) was efficiently deposited with different procedures on metallic biomaterials as iron [20], titanium [21,22] and CoCrMo as well [23]. Cathodic deposition of HAp [24,25] was performed recently, but in the present paper the deposition procedure of commercial nanohydroxyapatite is dip coating. The performed surface analyses include scanning electronic microscopy (SEM) and X-Rays diffraction (XRD). The dissolution of calcium from coated alloys was evaluated from ICP-MS determinations and their stability was discussed taking into account their morphology, crystalline phases and corrosion rates. The protective efficiency of the coatings has been established in both the cases of saliva.

2. EXPERIMENTAL PART

2.1 Metal substrate preparation

Two different alloys were used as substrates and tested. First type, NiCr alloy (Ventura Truebond CCB), with chemical composition: Ni 59.3%, Cr 24.0%, Mo 10 %, Fe 1.5%, Mn 1.5%, Ta 1.5%, Si 1.2% and Nb 1%, was provided by Madespa S.A. Toledo, Spain. The second tested alloy, CoCr alloy (Ni free - Vera PDI hard) was provided by AalbaDent, United States. Chemical

composition was Co 63.5%, Cr 27.0%, Mo 5.5%, Fe 2.0%, Si, and Mn. For the preparation of substrates, all the samples were wet grinded with SiC paper of 350, 800 and 1200 grits. After polishing the samples were cleaned with ethanol in an ultrasound bath for 5 minutes, rinsed with distilled water and dried at room temperature.

2.2 Preparation of the electrolyte solutions

Collection of natural saliva and preparation of artificial saliva

Natural saliva was collected from patients without dental restorations and with a good oral health. The target group for saliva collection was advised not to drink, eat or smoke before collection. All collection procedures were made with the agreement of patients, respecting the medical ethics rules. Collected saliva was kept at 5°C and filtered. The pH of natural saliva was 7.9.

Electrochemical tests were performed in artificial saliva, also. Chemical composition of artificial saliva is presented in Table 1. Chemicals were provided by Sigma Aldrich. The pH of artificial saliva was less aggressive compared with the natural one, being closer to a neutral value of 6.8.

Table 1. Chemical composition of artificial saliva

Substance	NaCl	Na_2HPO_4	K_2HPO_4	$KHCO_3$	$MgCl_2$	$CaCl_2$	Citric acid
g/L	0.584	0.340	0.340	1.5	0.014	0.166	0.029

2.3 Preparation of the HAp coating and preparation of the coated samples

Commercial nanopowder of HAp provided by Sigma Aldrich was used for the preparation of the coating. A quantity of 10 g of hydrodroxyapatite was mixed with 120 mL of distilled water and used immediately.

Metallic samples were dip-coated with HAp for 30 minutes under continuous stirring. The coated samples were thermal treated at 400°C for 1 hour (heat rate = 5°C/min). The thermal treatment was performed in order to strengthen the bonds between the metallic substrate and the apatite.

2.4 Characterization of the coated samples

The morphology of the coated samples was investigated using a scanning electron microscope (SEM) Quanta Inspect F (1.2 nm resolution). The XRD measurements were performed with PANalytical Empyrean and the data processing was carried out using HighScore Plus Software.

In order to study the electrochemical behavior of the coated and uncoated samples, some electrochemical tests were performed. All the experiments were carried out using an electrochemical cell with three electrodes; working electrode (NiCr or CoCr samples), reference electrode (Ag/AgCl)

and counter electrode (platinum). The experiments were performed with a Voltalab PGZ 301 potentiostat/ galvanostat controlled by a computer equipped with Volta Master 4 Software.

Electrochemical measurements included determination of the open circuit potential, as a function of time and polarization curves (Tafel plots). The open circuit potential was measured for 1 hour. The polarization curves were recorded between ±300mV vs. OCP with a scan rate of 2mV/s. The exposed surface of the samples in electrolyte solution was 1cm^2.

The dissolution of the coating was analyzed with Inductively Coupled Mass Spectrometer ICP-MS, ELAN DRC-e, Perkin Elmer model as in a previous study [26]. The coated samples were held in artificial and natural saliva for different periods of time (0, 24, 48, 72 and 168 hours). In order to determine Ca^{2+} ions, an internal standard (a multi-element solution reference standard of 10 mg/ml), was used.

3. RESULTS AND DISCUSSION

3.1 Characterization of the coated samples

Chemical composition of the HAp coating was studied with X-Ray Diffraction Spectroscopy. Fig.1 shows XRD spectra of HAp nanopowder, as received. In Fig. 1 it can be observed the existence of HAp, as single crystalline phase according to JCPDS 010-6314.
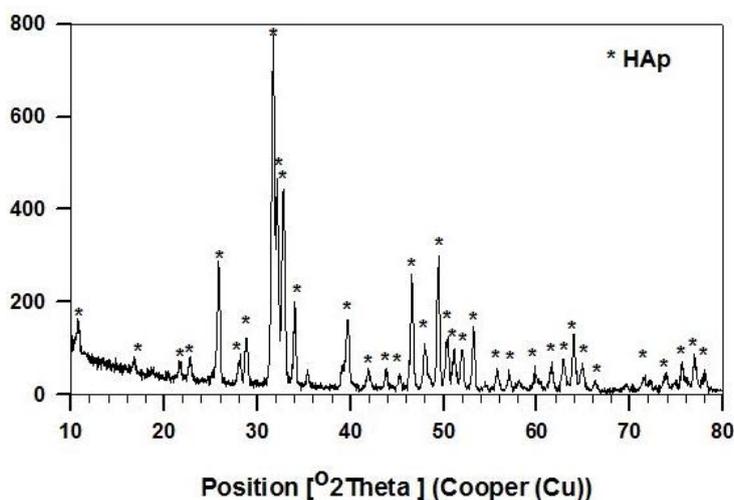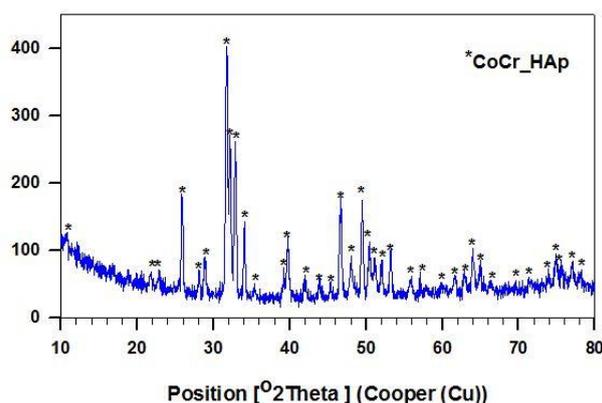

Figure 1. XRD analysis of HAp powder

According to Fig. 2 and 3, the XRD analysis of coated samples of NiCr and CoCr after thermal treatment does not indicate modifications of the composition regarding detection limit of the used equipment. The crystalline phase, deposited on metallic samples is hydroxyapatite (HAp) (JCPDS 010-6314). This proves that the thermal treatment promotes the deposition.
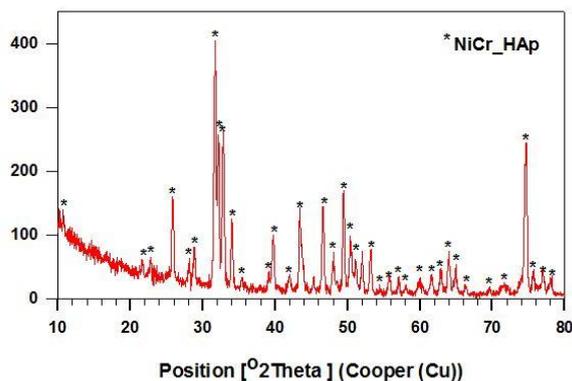
Figure 2. XRD analysis of NiCr alloy coated with HAp after thermal treatment


Figure 3. XRD analysis of CoCr alloys coated with HAp after thermal treatment

In Fig. 4 are presented the SEM images of HAp powder for coated NiCr and CoCr alloy.

The morphology of hydroxyapatite powder (Fig. 4a) consists of spherical particles with different dimensions [27]. For the coated NiCr (Fig. 4b) and coated CoCr (Fig. 4c) it can be noticed that the deposited apatite phase have the same morphology, and the particles present the same size range of granulometry as for the HAp powder.

3.2 Electrochemical stability in artificial and natural saliva

In Fig. 5a are presented the measurements for (Fig. 5a) and the Tafel plots (Fig. 5b) for the uncoated samples of NiCr and CoCr alloys. The OCP measurements in artificial saliva show the stability of the studied system for the whole period of the measurement. In case of CoCr alloys the potential (E_{ocp}) is stable from the beginning and it is maintained for the whole interval, but NiCr alloys in natural saliva indicate a stability of the potential after 45 minutes, probably due to existence of the passivation-repasivation of the oxide film present on the surface of the metal.
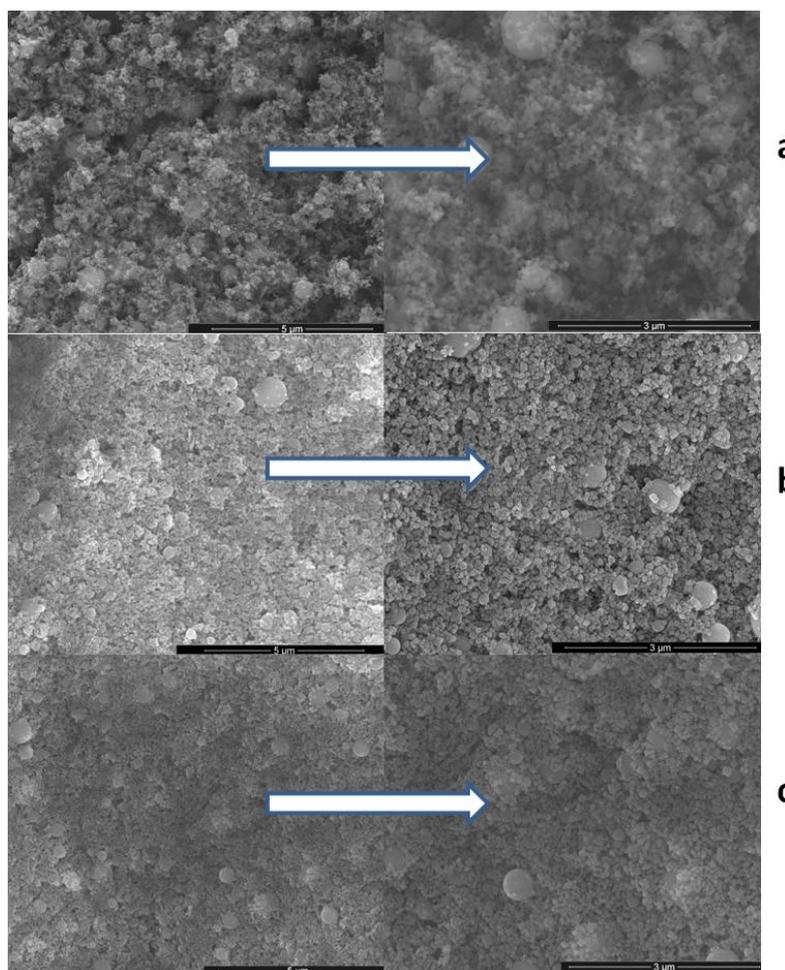
Figure 4. SEM images of HAp powder (a), coated NiCr alloy with HAp (b) and coated CoCr alloy with HAp (c)

The corrosion parameters (V_{corr} - corrosion rate, I_{corr} - corrosion current density, R_p - polarization resistance, B_{anodic} - anodic slope, $B_{cathodic}$ - cathodic slope) were calculated from Tafel plots (Fig. 5b). It can be noticed that in artificial saliva NiCr alloy present more negative value for corrosion potential (Table 2) compared to corrosion potential of CoCr alloy. Electrochemical behavior in natural saliva indicates a small corrosion current in case of CoCr alloy.

Regarding the open circuit potential of coated samples (Fig. 6a) in artificial and natural saliva it can be mentioned that the stability of potential is reached almost from the beginning of the measurement and it is maintained. The coated samples present smaller values for corrosion potential E_{ocp} and for current in both types of saliva compared with uncoated alloys (Table 2 and 3). The protective efficiency (Pi) [28] of the coating was calculated with Eq. (1) and the obtained values are presented in Table 2 and 3.

$$P_i = 100 \times \left(1 - \frac{i_{corr}}{i_{corr}^0}\right) \qquad (1)$$

where i_{corr} and i^0_{corr} are the values of corrosion current densities from polarization curves for the coated substrate and uncoated substrate.
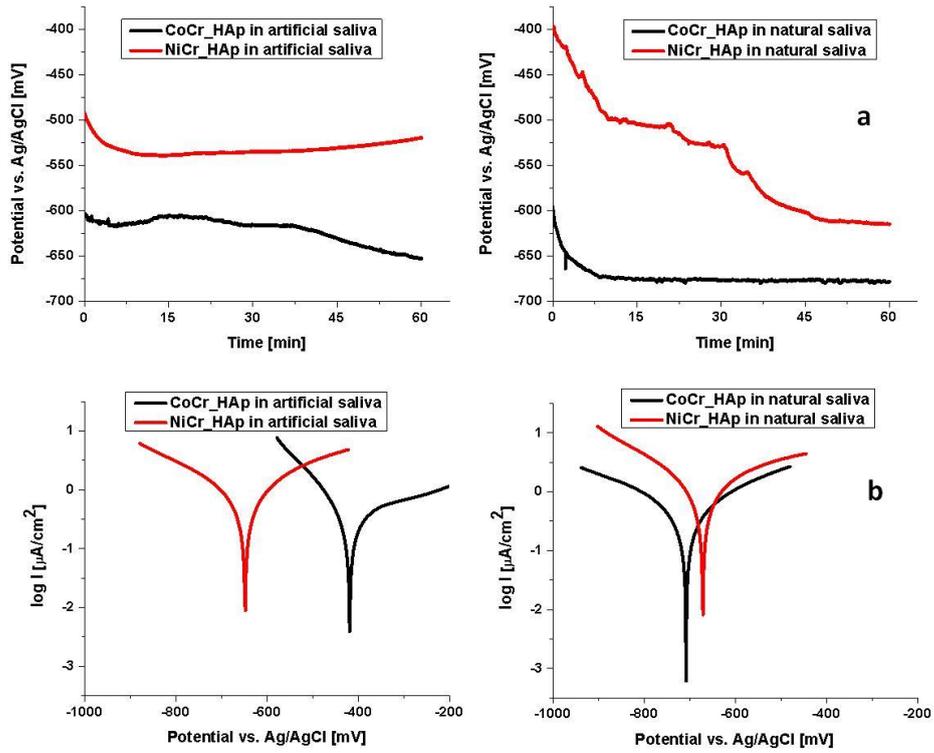
Figure 5. OCP (a) and Tafel plots (b) for NiCr and CoCr alloys in artificial (left side) and natural saliva (right side)
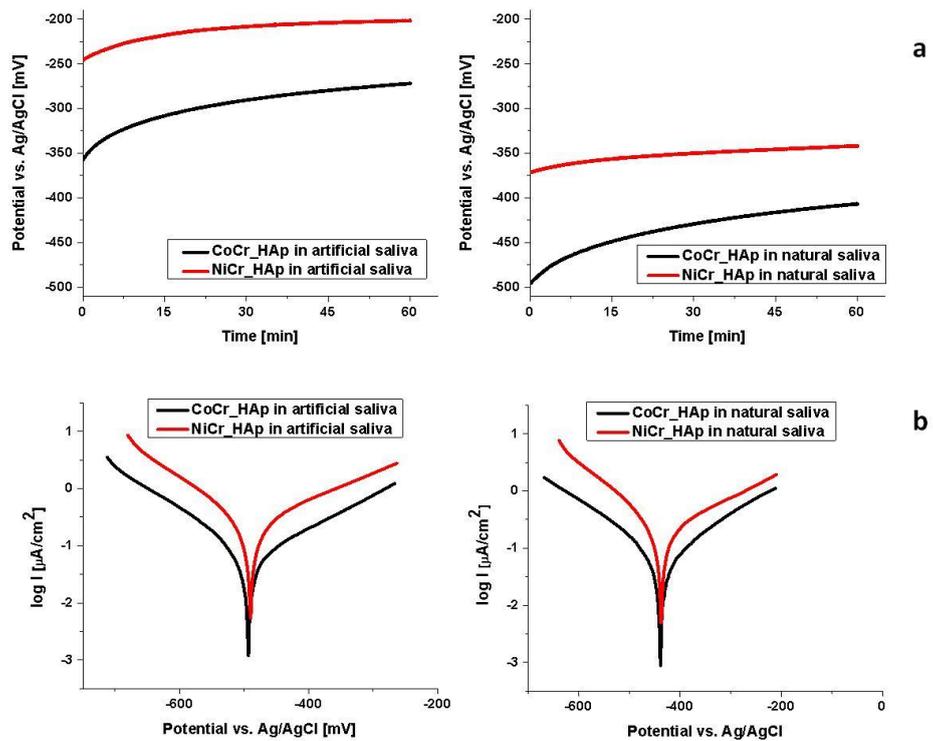
Figure 6. OCP (a) and Tafel plots (b) for coated NiCr and coated CoCr alloys in artificial (left side) and natural saliva (right side)

Table 2. Corrosion parameters of coated/ uncoated NiCr and CoCr alloys in artificial saliva

Artificial saliva pH = 6.8	NiCr_HAp	NiCr	CoCr_HAp	CoCr
E_{ocp} (mV)	-202	-519	-418	-652
R_p (Ωcm_2)	$1.21 \cdot 10^5$	$5.21 \cdot 10^4$	$3.86 \cdot 10^5$	$8.69 \cdot 10^4$
E_{corr} (mV)	-490	-647	-493	-418
I_{corr} ($\mu A/cm^2$)	0.24	0.82	0.05	0.38
B_{anodic} (mV)	217	272	175	492
$B_{cathodic}$ (mV)	-134	-266	-128	-122
V_{corr} (mm/Y)	$2.88 \cdot 10^{-3}$	$9.61 \cdot 10^{-3}$	$0.68 \cdot 10^{-3}$	$4.49 \cdot 10^{-3}$
P_i (%)	71	-	87	-

Table 3. Corrosion parameters of coated/ uncoated NiCr and CoCr alloys in natural saliva

Natural saliva pH = 7.9	NiCr_HAp	NiCr	CoCr_HAp	CoCr
E_{ocp} (mV)	-342	-615	-407	-678
R_p (Ωcm_2)	$1.42 \cdot 10^5$	$3.86 \cdot 10^4$	$4.64 \cdot 10^5$	$9.78 \cdot 10^4$
E_{corr} (mV)	-437	-670	-438	-707
I_{corr} ($\mu A/cm^2$)	0.23	1.17	0.09	0.57
B_{anodic} (mV)	242	359	200	329.5
$B_{cathodic}$ (mV)	-145	-228	-180	-353
V_{corr} (mm/Y)	$2.79 \cdot 10^{-3}$	$1.37 \cdot 10^{-2}$	$1.05 \cdot 10^{-3}$	$6.67 \cdot 10^{-3}$
P_i	81	-	84	-

Based on the experimental values from tables 2 and 3, a stability ratio in artificial and natural saliva is presented in table 4 for the coated and uncoated samples.

Table 4. The relationship between corrosion rates of the alloys in artificial and natural saliva

Type of samples	**Artificial saliva**		**Natural saliva**	
Coated	NiCr/NiCr_HAp	3.33	NiCr/NiCr_HAp	4.91
	CoCr/CoCr_HAp	6.60	CoCr/CoCr_HAp	6.35
	NiCr_HAp/CoCr_HAp	4.23	NiCr_HAp/CoCr_HAp	2.65
Uncoated	NiCr/CoCr	2.14	NiCr/CoCr	2.05

Table 4 data sustain the protective efficiency values and indicate more clearly that the coated samples have a smaller susceptibility to corrosion. We observed that the natural saliva is a more aggressive environment for the analyzed samples. Such behavior is due probably to the pH which is closer to a neutral value in artificial saliva. CoCr alloys have good corrosion resistance due to the presence of its passive oxide film [29] and phosphates coatings have enhanced the stability and

adhesion as well, reducing the ions release. The curve for uncoated substrate in artificial saliva has same trend as obtained in the simulated physiological solutions [30] and reflects the passivation of CoCr through thickening of the Cr_2O_3 oxide and formation of the mixture CoO/Co_2O_3 oxide. It is worth to mention the positive effect given by the presence of Mo in both alloys on corrosion resistance.

3.3 Dissolution of the coating in artificial and natural saliva

As can be seen from Fig. 7 calcium dissolution (in part per million-ppm) of coated and uncoated CoCr and NiCr alloys presents a different behavior in artificial and natural saliva. In natural saliva the steady state trend is clearly reached after around 30 hours of immersion for NiCr and after around 48 hours for CoCr. Also it is to mention that in natural saliva the dissolution process is more aggressive at the beginning, with more important values for calcium dissolution, but after a while probably due to the adsorption of the salivary compounds on the substrate, the protective function of natural saliva is more evident.
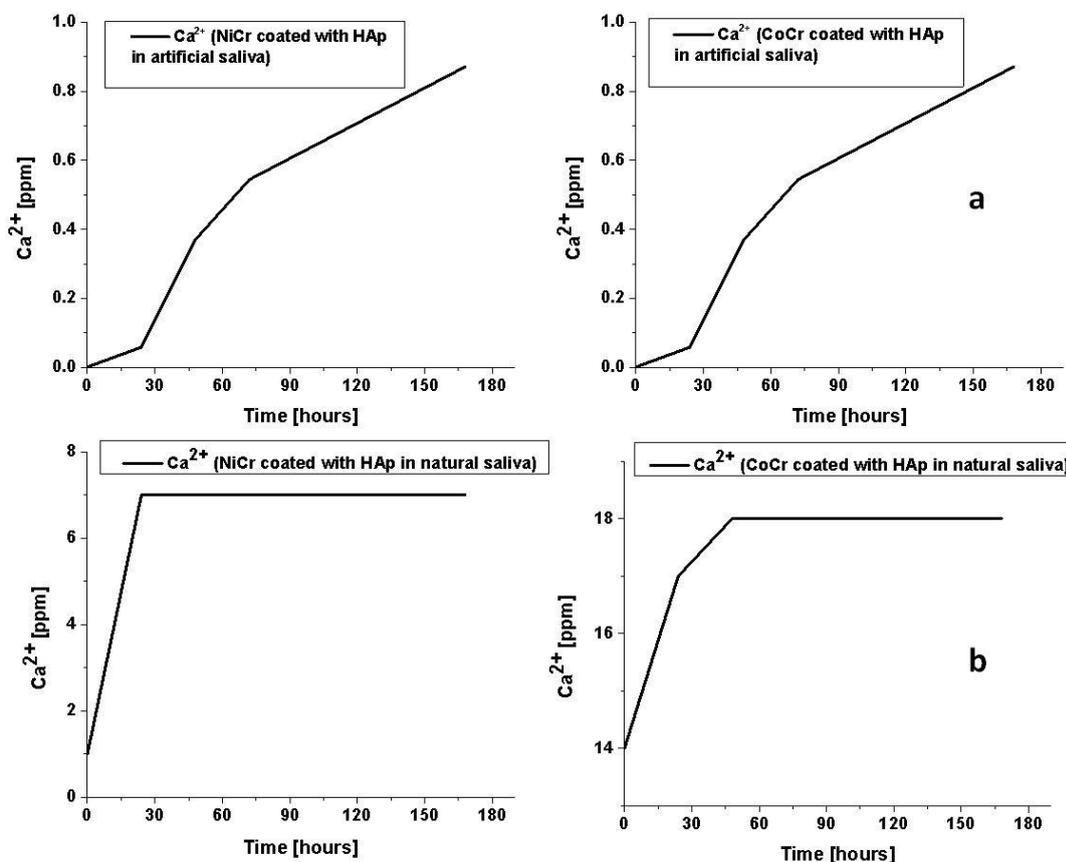

Figure 7. Ca^{2+} dissolution in artificial (a) and natural (b) saliva

4. CONCLUSIONS

Based on our experimental data we conclude that CoCr alloy has a better electrochemical stability for coated and uncoated samples in both, natural and artificial saliva, compared with NiCr alloy. Tafel plot procedures sustain the results of the open circuit method; the corrosion rates in both saliva types being relative close to each other, especially for uncoated samples of the same alloy, being smaller in artificial saliva. Regarding HAp coatings the index of their protection is close to each other for both alloys in natural saliva and smaller for CoCr alloy in artificial saliva. It is to mention that the calcium dissolution for coated non precious alloys in natural saliva has a trend to steady state clearly reached after around 30 hours of immersion for NiCr and after 48 hours for CoCr. In artificial saliva after 168 hours the steady state trend was not visible. The results are going to help the selection of alloys used in oral cavity.

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