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COMPARATIVE STUDIES ON THE CORROSION RESISTANCE OF Ti6Al4V AND NiCr ALLOYS IN ARTIFICIAL SALIVA

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Această lucrare prezintă un studiu al comportării la coroziune a aliajelor Ti6Al4V şi Ni-Cr imersate în salivă artificială cu şi fără bacterii de FdMn44. Aceste două aliaje au fost selectate întrucât sunt cele mai utilizate în stomatologie. Comportarea la coroziune a fost pusă în evidentă prin determinarea potenţialului circuitului deschis şi prin metoda polarizării potentiodinamice. Cercetările efectuate au arătat că aliajul Ti6Al4V are potenţiale de circuit deschis E_{oc} *cu valori mai electropozitive comparativ cu cele ale aliajului NiCr, indiferent de natura electrolitului. De asemenea, s-a demonstrat că aliajul NiCr imersat în salivă cu bacterii este susceptibil la coroziune pitting.*

A comparative study of corrosion resistance of Ti6Al4V and NiCr alloys immersed in saliva solution with and without Fd Mn 44 bacteria is presented. These two alloys were selected because they are the most popular materials used in dental applications. The corrosion behaviour was put in evidence by open circuit potential vs. time measurements and potentiodynamic polarization method. The open circuit potential (E_{oc}*) revealed that the Ti6Al4V alloy was more noble compared to the NiCr in artificial saliva with and without bacteria solution. The NiCr alloys immersed in saliva with bacteria was high susceptible to pitting corrosion.*

Keywords: NiCr and Ti6Al4V dental alloys, corrosion resistance, Fusayama Meyer saliva

1. Introduction

On the dental market there are a variety of dental alloys used for many purposes such as endodontic instruments for the dental restorations (including metallic brackets, arch wires, bands, crowns, fixed bridgework, springs, ligature wires and removable partial dentures, etc.) [1, 2]. The dental alloys work in oral

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environment for many months or years and for this reason it is necessary to have good anticorrosive properties. The corrosion parameters and corrosion products are responsible for limiting the biocompatibility of dental metallic materials, and can produce undesirable reactions in implant-adjacent tissues. In oral environment, materials are subjected to a continuous degradation process through physical-chemical attacks and mechanical pressure. The stress can be mechanical or bacterial, with permanent action. Moreover, the alloys change their colour shade due to corrosion and can generate physiological phenomena [3]. Since nickel is a known allergen, it is important for patients to know the evolution of nickel in the development of optimal quality of alloys used in dentistry. Corrosion properties of nickel–chromium alloys depend on their bulk composition [4, 5], microstructure and development of protective surface oxides [6, 7]. Alloys with 16–27% Cr, 6–17% Mo, and Be display homogeneous protective surface oxides, low corrosion rates, large passivation ranges, and resistance to pitting/crevice corrosion in electrochemical corrosion tests [4, 7–9]. Be containing alloys exhibit higher corrosion rates, smaller passivation ranges, and increased susceptibility to pitting/crevice corrosion as compared to non-Be containing alloys [5, 8, 9], which results from a NiBe eutectic formed in the microstructure of NiCrBe alloys that leads to the development of non-homogeneous Cr surface oxides which are less corrosion resistant [8].

The corrosion behaviour of dental alloys in the oral environment is vital to their biocompatibility. Alloy properties may be affected by many factors including microflower processes which may, in turn, alter alloy surface oxides and corrosion properties. The purpose of this study was to evaluate the effects of a microflower process on the microstructure, surface oxide composition, and corrosion behaviour of two commercial alloys of NiCr and Ti6Al4V alloys. This information will advance the understanding of clinical performance and the health benefit–risks of these alloys. Therefore, the aim of the present study was to comparatively investigate the influence of corrosive environments on Ti6Al4V and NiCr alloys. The alloys were comparatively investigated in terms of corrosion resistance in saliva solution with and without Fd Mn 44 bacteria (found in yogurt, dairy products) [10]. The Ti6Al4V and NiCr alloys were chosen because there are the most used alloys in dental applications in Romania due their low cost.

2. Experimental part

The chemical compositions of the studied alloys (NiCr and Ti6Al4V) are presented in Table 1, the compositions as given by the manufactures. These alloys were delivered under the form of pills, in order to be casted easily to obtain dental fixed or mobile prostheses. The alloys were flame-cast using a 50/50 oxygen–propane gas mixture into cylinders (0.2 cm diameter ×1 cm length) and discs (1cm diameter×0.5 cm thickness) by a private dental laboratory (Lawrence Tehnodent SRL) [11]. The cast specimens were wet-polished using silicon carbide abrasive sandpaper up to 1500 grit to simulate clinical procedures [7], then ultrasonically cleaned for 4 min in acetone, ethanol, and de-ionized water to remove surface contaminants.

Two discs of each alloy were mounted in Bakelite, wet-polished on metallographic polishing tables, cleaned with acetone and distilled water and then air dried. Microstructures were observed by optical microscopy (OM) after grinding, mechanical polishing and etching, using an Olympus PME3 optical microscope. The surface of the NiCr alloys was etched with 2 ml HF, 10 ml HNO_3 and 88 ml water, and Ti6Al4V with 10 ml HF and 90 ml water, for approximately 15 s. The corrosion resistance was evaluated by means of electrochemical tests using a Galvanostat/Potentiostat AMEL R1/4MMSKT. All data were processed with Corrasist software. A conventional three-electrode cell was used, with a saturated AgCl electrode (SCE) as reference, a platinum one as counter electrode, and the sample (1 cm^2) as working electrode. Electrochemical tests were performed on triplicate cylindrical specimens of each alloy in Fusayama Meyer saliva solution (composition: 0.4 g l^{-1} NaCl, 0.9 g l^{-1} KCl, 1 g l^{-1} uree, 0.69 g l^{-1} NaH_2PO_4, 0.795 g l^{-1} $CaCl*2H_2O$) [7, 12, 13] at room temperature (20°C ± 0.5 °C) in a environment with and without Fd Mn 44 bacteria. The pH was measured using a pHmeter Hanna 221.

Before testing all samples were immersed in solution at room temperature for 10 min or 12 hours. The open circuit potential (EOC) was measured during the following 1 h and the global polarization curves from -1 V to +1 V (vs. SCE) was plotted. The linear polarization curves (± 20 mV vs. EOC) were acquired for determining the polarization resistance Rp [14, 15]. From the polarization curves (± 150 mV vs. E_{OC}), the Tafel slope and the corrosion current density (i_{corr}) were determined. For all the measurements the scanning rate was 0.4 mV/s. The following electrochemical parameters were determined: corrosion potential (E, i=0), corrosion current density (i_{corr}), polarization resistance (R_p), and corrosion rate (CR).

Table 1

Chemical composition of studied alloys in weight %
(the compositions as given by the manufactures)

Alloys	Chemical composition (wt. %)							
	Ni	Cr	Mn	Si	Al	Cu	V	Ti
NiCr	53.6	14.5	19.4	1.5	1.5	9.5	-	-
Ti6Al4V	-	-	-	-	6	-	4	balanced

3. Results and discussions

3.1. Microstructures

The microstructures of the NiCr and Ti6Al4V alloys, obtained by optical microscopy after chemical attack, are presented in Figs. 1 and 2, respectively. One may observe that NiCr alloy are characterized by a solid solution array in dendritic disposition of as-cast state (primary phase) and an interdendritic phase (secondary) regularly distributed. The as-cast structure is pre-dominantly dendritic and it is known that in this structure the dendrites have different metal concentrations in the interdendritic spaces. This is due to solidification process, where dendrites solidify firstly and, consequently, are resistant to different chemical and electrochemical attacks.

The microstructure of the Ti6Al4V alloy is represented by equiaxed grains of primary α-phase, as well as β-transformed structure with α-phase lamellas (Fig.2).

3.2. Corrosion behaviour

3.2.1. Open circuit potential measurement

The nature of the metal-electrolyte interface varies in time and consequently the open circuit potential (E_{OC}) is no longer a characteristic of the metal. It is well known that E_{oc} depends on the experimental conditions, such as the electrolyte composition, temperature and oxygen content, and on the surface state of the metal [16]. The values of E_{oc} allow the comparison with the nobility of the investigated samples. The open circuit potentials of the investigated samples in saliva solution with and without bacteria are shown in Figs. 3-5.

The measurements revealed that the Ti6Al4V alloy was more noble compared to the NiCr in artificial saliva with and without bacteria solution after 10 min immersion. After 12 h immersion in saliva without bacteria, it can be seen that NiCr alloys have a more electropositive open circuit potential than the Ti6Al4V alloy. This behaviour suggests that protective passive films are formed rapidly on surface of the NiCr alloys and act as a barrier for metal dissolution, reducing the corrosion rate. Also, this increase is related to the thickness of the oxide film, this improving its corrosion protection ability.

The NiCr alloys tested in saliva solution after 10 min immersion did not have the same tendency of spontaneous formation of the passive films as Ti6Al4V alloy. The curves profiles show potential fluctuations, indicating that NiCr alloy is sensible to localized corrosion (pitting or crevice). The same tendency of NiCr alloy was also observed after 12 h immersion.

One may observe that NiCr alloy proved to have better corrosion behaviour in saliva with Fd Mn 44 bacteria compared to Ti6Al4V alloy.

Moreover, fluctuations of the potential of Ti6Al4V alloy immersed in saliva with bacteria were observed, indicating the presence of a pitting corrosion process.

After the OPC test, it can be seen that both alloys exhibited good corrosion resistance in saliva with bacteria environment than the samples investigated in saliva without bacteria.

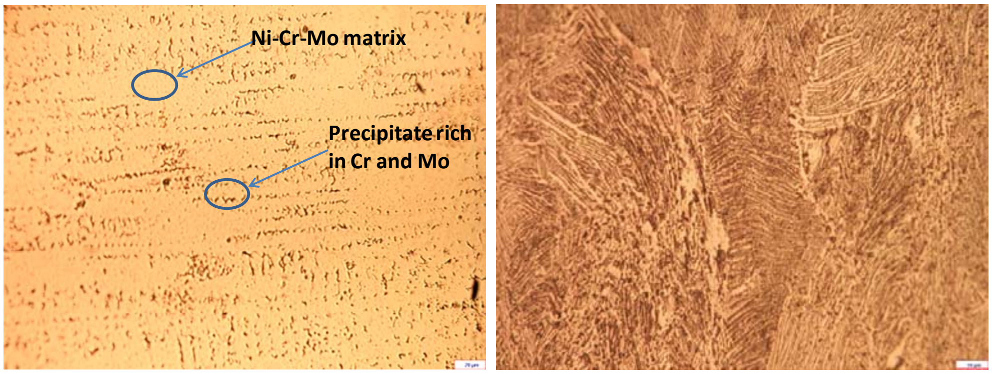

Fig. 1 Fig. 2

Fig. 1. Optical micrographs of the experimental NiCr alloys (electrolytic etching with $HF+HNO_3+H_2O$); Fig. 2. Optical micrographs of the experimental Ti6Al4V alloys (electrolytic etching with $HF+H_2O$)

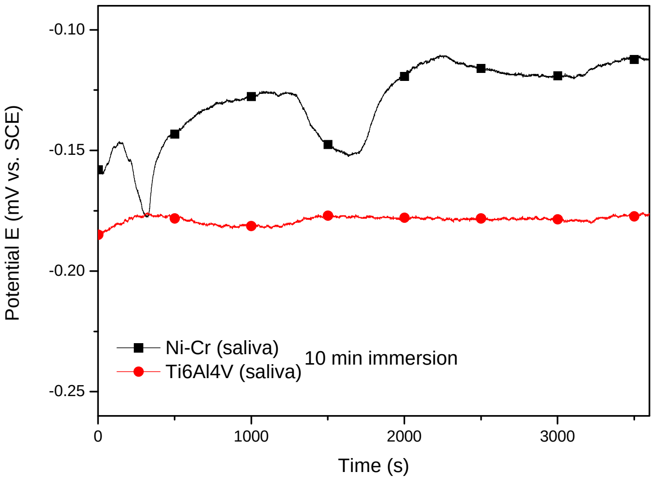

Fig. 3. Open circuit potential vs. time curves of the Ti6Al4V and NiCr alloys in saliva solution after 10 min immersion

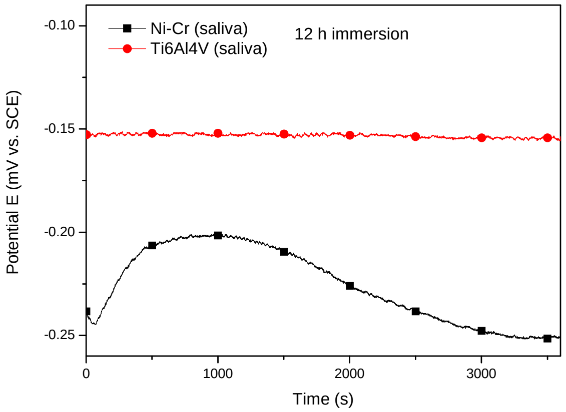

Fig. 4. Open circuit potential vs. time curves of the Ti6Al4V and NiCr alloys in saliva solution after 12h immersion

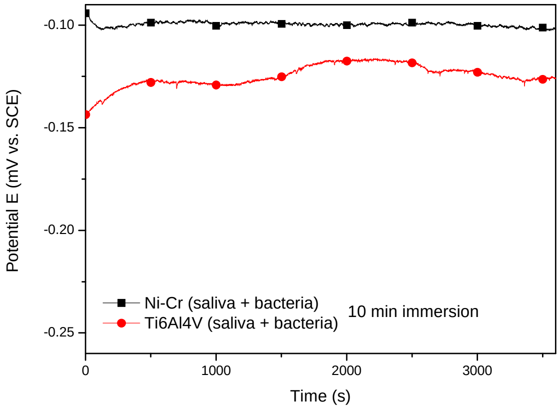

Fig. 5. Open circuit potential vs. time curves of the Ti6Al4V and NiCr alloys in saliva with bacteria solution after 10 min immersion

3.2.2. Effect of solution pH

The effect of solution pH on the open circuit potential for studied alloys in saliva with and without bacteria at 20 °C is shown in Figs. 6 – 8. Before the test, the saliva has pH of about 5.5.

The immersion of the alloys in both corrosive solutions prior to the OCP measurement renders the increase of pH from 5.5 to 10 either with or without bacteria. In the case of Ti6Al4V alloy, the effect is generally more pronounced as the immersion time increases. We noticed for Ti6AlN alloy, no pH drops associated with surface activation during 12 hours exposure electrolyte solution. This kind of behaviour suggests that the air-formed native oxide is thermodynamically resistant at chemical dissolution in electrolyte solutions. After

12 h immersion, the NiCr alloy has a lower pH of about 6.2, indicating that this alloy is susceptible to chemical dissolution in electrolyte solutions.

The pH evolution in the solutions with and without bacteria is almost the same for both alloys, pH 9.8 – 10.5, so it can be said that the effect of chlorides diminishes with pH increase. The explanation for this kind of behavior may possibly be found in the results of the study of the structure of surface film formed in corrosive solutions in the presence of chloride ions.

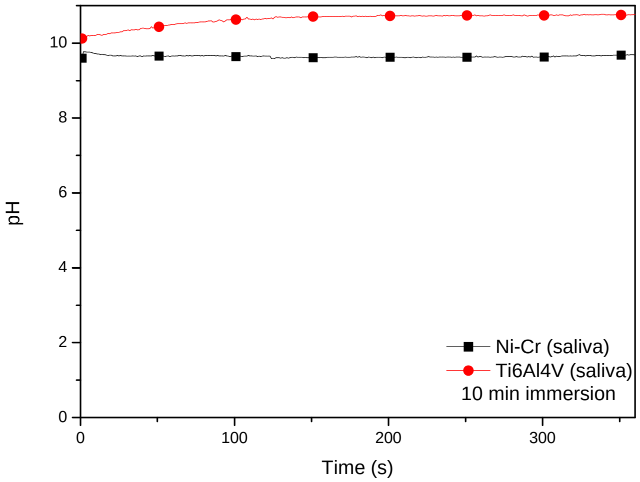

Fig. 6. pH vs. time curves of the Ti6Al4V and NiCr alloys in saliva solution after 10 min immersion

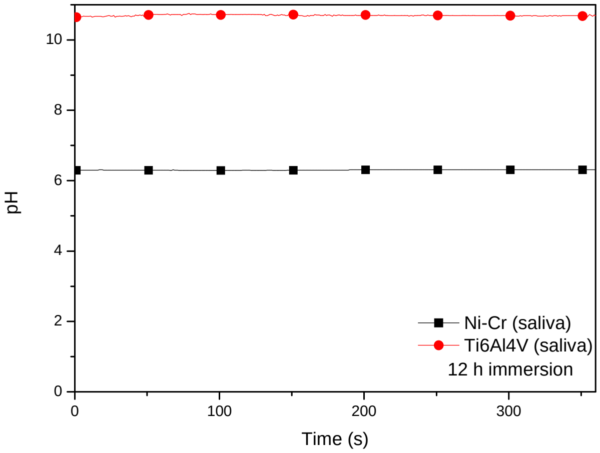

Fig. 7. pH vs. time curves of the Ti6Al4V and NiCr alloys in saliva solution after 12 h immersion

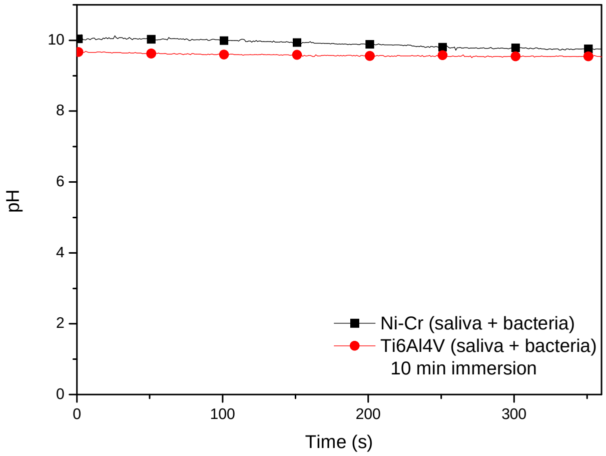

Fig. 8. pH vs. time curves of the Ti6Al4V and NiCr alloys in saliva with bacteria solution after 10 min immersion

3.3.3. Potentiodynamic polarization

In Table 2, the main electrochemical parameters of investigated samples are presented. Figs. 6-8 show the potentiodynamic polarization curves of the investigated specimens.

As it is known, high values of polarization resistance R_p are indicative of good corrosion resistance [14, 17]. Compared with the Ti6Al4V, R_p was more than two times higher for the Ni-Cr, demonstrating that the NiCr is more resistant to corrosion, independent on the nature of electrolyte.

The corrosion potentials of Ti6Al4V alloy are more electropositive than those of the NiCr alloy, independent on the nature of electrolyte, which demonstrates the effective barrier effect for the titanium alloy.

Regarding the corrosion current density (i_{corr}), in saliva without bacteria, the NiCr alloy showed a high corrosion resistance. In the case of the NiCr alloy, addition of the bacteria in saliva solution led to significantly increase of the i_{corr} values, indicating a decrease in corrosion resistance.

The Ti6Al4V alloy exhibited an improved corrosion behavior as compared to the NiCr alloy, by lowering the corrosion current density and increasing corrosion potentials, in saliva with bacteria.

The corrosion rate, understood in terms of the penetration rate of the solution into the coating, was calculated from the corrosion current by the following equation (ASTM G 102 (1999)):

$$\mathrm{CR} = \frac{\mathrm{K} \cdot \mathrm{i_{corr}} \cdot \mathrm{EW}}{\rho} \qquad [\mathrm{mm/year}] \qquad (1)$$

where: CR is corrosion rate (mil per year or mm per year depending on units of K); K = constant for converting units; i_{corr} = corrosion current density ($\mu A/cm^2$); ρ = compound density (g/cm^3); EW = compound equivalent weight (g/equivalent). EW was calculated following the way presented for compounds in ASTM G 102 (1999).

In the case of NiCr alloy, a low Cr and Mo content is causing a high corrosion rate and susceptibility to an improved bacteria deposits [18]. We conclude that the presence of larger passive range for the NiCr sample with respect to the Ti6Al4V alloy was ascribed mainly to a higher percentage of Cr and Mo, for the chemical composition of specimens.

An important parameter for Ni-Cr alloys, is the relative effectiveness of Cr and Mo content on pitting or crevice corrosion usually that can be considered equivalent with pitting resistance equivalent (PRE). It can be calculated with the empirical equation [19]:

$$\text{PRE} = \%\,\text{Cr} + 3.3\,\%\,\text{Mo}$$

A PRE value above 38, is supposed to provide good resistance to pitting corrosion in a Cl- containing solution, as is the case of artificial saliva [19]. The NiCrMo casting alloy is pitting resistant in artificial saliva when the PRE value increases up to approximately 49 [19]. For the NiCr alloy investigated in the present paper, according to the PRE equation, the PRE value is 14.5 (no Mo containing), indicating that it is high susceptible to pitting corrosion. This result is in concordance with those obtained after the OPC measurements.

Table 2

Electrochemical parameters of studied alloys in different environments
(E_{oc} – open circuit potential; R_p – polarization resistance; $E_{corr,\ i=0}$ – corrosion potential at i=0; i_{corr} – corrosion current density; CR – corrosion rate)

Alloy	Electrolyte	E_{OC} (mV)	R_p (Ω)	E_{corr} (mV)	i_{corr} (γA)	CR (mpy)
Ti6Al4V	saliva (after 10 min)	-107.65	11629	-136.65	7.824	9.095
	saliva (after 12h)	-251.19	7915	-277.82	17.646	48.908
	saliva+ bacteria (after 10 min)	-108.88	24507	-129.31	6.482	3.035
NiCr	saliva (after 10 min)	-176.36	57864	-162.46	0.765	0.868
	saliva (after 12h)	-156.42	49650	-177.93	10.444	4.222
	saliva+ bacteria (after 10 min)	-124.22	60721	-127.47	34.162	0.699

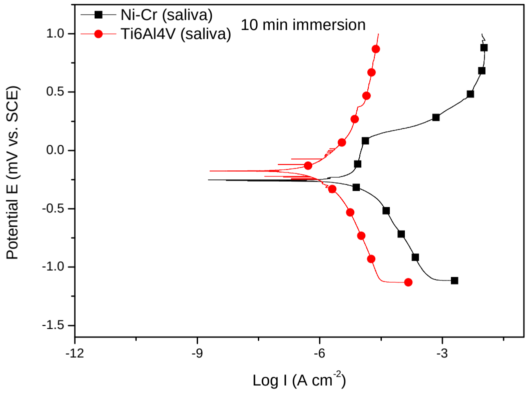

Fig. 9. Polarization curves of the Ti6Al4V and NiCr alloys in saliva solution after 10 min immersion

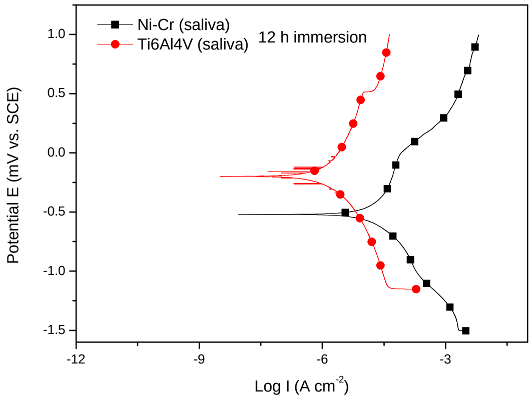

Fig. 10. Polarization curves of the Ti6Al4V and NiCr alloys in saliva solution after 12 h immersion

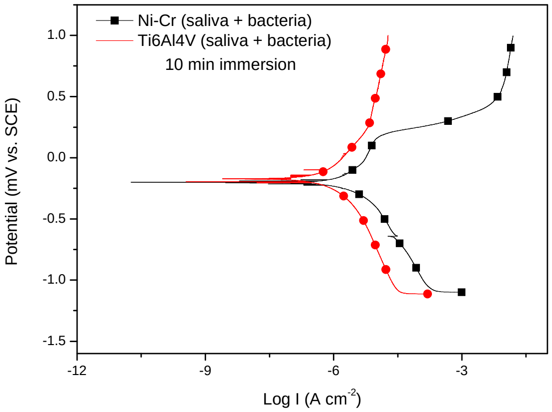

Fig. 11. Polarization curves of the Ti6Al4V and NiCr alloys in saliva with bacteria solution after 10 min immersion

4. Conclusions

The corrosion resistance of Ti6Al4V and NiCr alloys immersed in saliva solution with and without Fd Mn 44 bacteria was investigated.

Corrosive behaviour was appreciated by means of an electrochemical test. The coatings were also characterized with respect to evolution of pH in time.

OPC measurements showed that NiCr alloy was susceptible to pitting corrosion, independent on the type of corrosive solution. The E_{oc} values of the Ti6Al4V alloys immersed in saliva with or without bacteria were shifted in the noble direction compared to the NiCr alloy, indicating a better protection of Ti6Al4V alloy.

The potentiodynamic polarization tests revealed better corrosion resistance of Ti6Al4V alloy, as compared to NiCr, independent on the nature of electrolyte.

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