

Comparative Study on the Corrosion of Ni-Cr and Co-Cr Alloys in the Presence of Ti6Al4V Implant Abutments

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Biocompatibility means that the materials of which fixed dental prostheses and implants are made of, should not irritate the surrounding structures, must not lead to the appearance of a inflammatory response or to a allergic reaction of the organism and may not release toxic ions. In the first part of the study we experimentally submitted a titanium implant abutment and three types of dental alloys (two NiCr alloys and one CoCr alloy) to a corrosion process, in similar conditions to the ones in the oral cavity (temperature: $37 \pm 0,5^{\circ}\text{C}$; pH values: 5.2 and 7), simulating the situation in which there is one single alloy in the oral cavity at a time. Then, we analysed the corrosion for galvanic couples made of titanium abutment – CoCr alloy and titanium abutment – NiCr alloy. According to the conducted tests, regardless of the pH value to which they have been realised, the NiCr alloys showed a better resistance to corrosion in the absence of the titanium alloy, while the CoCr alloy behaved better to corrosion in the presence of the titanium alloy.

Key words: biocompatibility, dental alloys, corrosion

The metal-ceramic fixed prosthetic restorations which reestablish the continuity of the dental arches in the case of a reduced partial edentation can have both dental and implant support. Regarding the implant support, beside the alloy of which the denture is manufactured, there also appears the implant abutment made of titanium alloy.

Biocompatibility is the ability of materials to be accepted by the organism without getting chemically or mechanically deteriorated [1]. A material is considered to be biocompatible if it does not create toxic reactions or systemic secondary effects [2]. The resistance to corrosion is one of the most important characteristics of dental materials because after their introduction into the human body, metallic biomaterials are exposed to a corrosive environment [3].

The behaviour and resistance of a metallic alloy with dental use to the corrosion process is dictated by factors such as: the chemical structure of the alloy, its surface nature, the microstructure (the presence of imperfections: structural defects or cracks), the pH of the environment in which it is applied, temperature and oxygen content [4-13].

The evolution of titanium as the main material in implantology took a big amplitude in the past years, as a result of the favorable combination between the mechanical resistance, the chemical stability and its biocompatibility [14].

The study of electrochemical properties of dental alloys is necessary since inappropriate materials may cause hypersensitivity due to metallic ions and corrosion products release [15].

The aim of our study is to analyze which type of dental alloy used for the manufacturing of fixed prosthetic restorations has a better behaviour towards the corrosion of the oral environment in case that the restoration is cemented on implant abutments.

Experimental part

For the study we took three dental alloys used in the metal-ceramic technology and implant abutments made of Ti6Al4V with a 5 medical purity level. The samples were subjected to corrosion, both individually and as galvanic couples, in order to simulate the situations in which patients have oral restorations with dental or implant support.

The samples analyzed form the corrosion resistance point of view, have been coded as follows:

A = implant prosthetic abutment made of Ti6Al4V (ADIN, Israel)

B = dental alloy made of CoCr (SHERADENT/Shera, Germany)

C = dental NiCr –B alloy (Gialloy CB-NH/BK Giuliani, Germany)

D = dental NiCr –M alloy (Magnum Clarum/Mesa, Italy)

For this experiment, the implant prosthetic abutments have been used as such, while the samples B, C, D have been casted in the dental technician's laboratory in circular shapes, with dimensions of 13x1.5 mm, have been abraded on metallographic abrasive paper (roughness 600-1200 microns) and polished with a particle suspension of $1\mu\text{m Al}_2\text{O}_3$.

The resistance to corrosion has been determined by using the linear polarization technique [3] and the help of the PARSTAT 4000 galvanostat.

For the area subjected to corrosion to be 1cm^2 , the analyzed samples have been fitted in a Teflon holder, prior to their introduction into the corrosion cell. The tests have been performed in Fusayama Meyer artificial saliva, at the temperature of the human body ($37 \pm 0.5^{\circ}\text{C}$) and at two different pH values: 5.2 and 7.

After the individual testing of the alloys, there has been selected, from the Ni-Cr class, the one with the best behavior and galvanic couples made of prosthetic abutments and metal alloys (NiCr-M and Co-Cr) have been then assembled. The samples have been prepared so that

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All authors have equal contributions to the study and the publications.

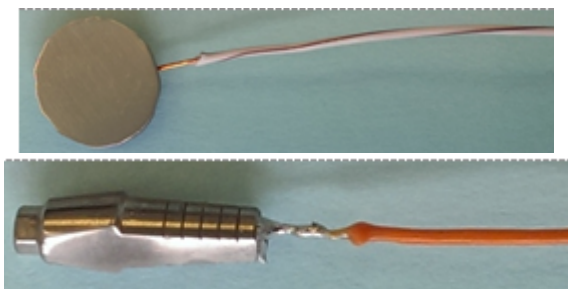


Fig.1 The samples prepared for the execution of the galvanic couple

their surface could be able to establish the largest contact possible. For the assurance of a electric contact, a electric conductor has been stucked on each alloy (fig.1), the samples were then put in contact (fig.2a), integrated and prepared on metallographic paper (fig.2b) – 600-1200 μm abrasiveness and also polished with a particle suspension of 1 μm Al_2O_3 .

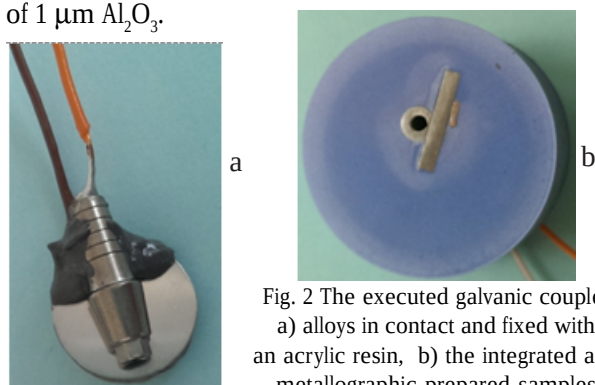


Fig. 2 The executed galvanic couple:
a) alloys in contact and fixed with an acrylic resin, b) the integrated and metallographic prepared samples

The surface of each alloy from the galvanic couple exposed into the artificial saliva, has been nearly equal by masking the bigger surface with a protective resin.

The coding of the galvanic couples is represented in table 1.

Table 1
GALVANIC COUPLES

Nr. Curr.	Galvanic couple	Coding
1	NiCr-2/Ti6Al4V	C1
2	CoCr/ Ti6Al4V	C2

Obtained results and discussions

The open circuit potential variations (E_{oc}) for the investigated alloys are showed graphically at a $\text{pH}=5.2$ in figure 3 and a $\text{pH}=7$ in figure 4, while the polarization curves are presented for $\text{pH}=5.2$ in figure 5 and $\text{pH}=7$ in figure 6.

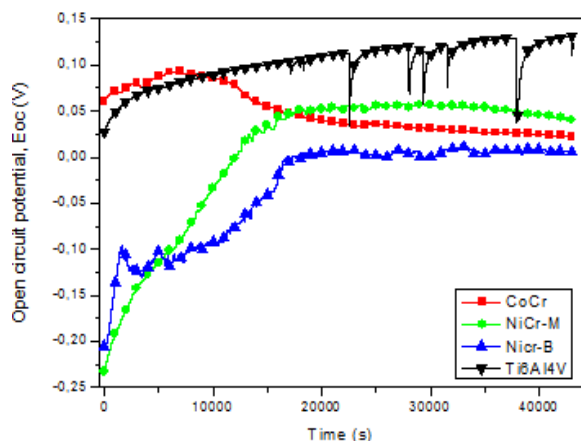


Fig. 3. The evolution of the open circuit potential (E_{oc}) for the investigated alloys at a $\text{pH}=5.2$

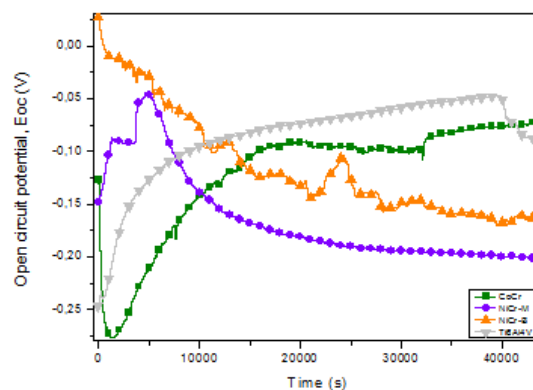


Fig. 4. The evolution of the open circuit potential (E_{oc}) for the investigated alloys at a $\text{pH}=7$

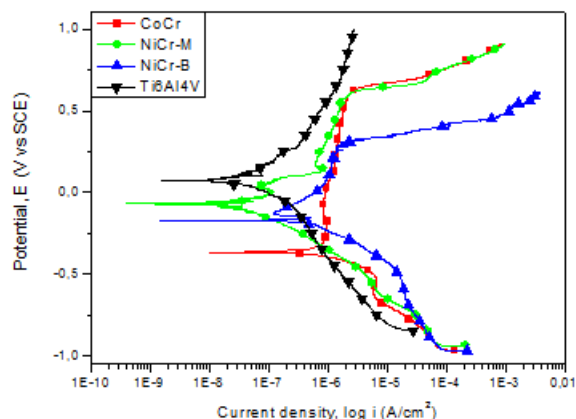


Fig.5. The potentiodynamic curves of the investigated alloys at a $\text{pH}=5.2$

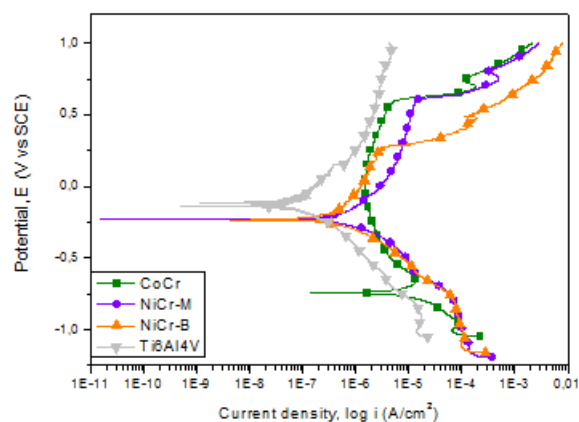


Fig.6. The potentiodynamic curves of the investigated alloys at a $\text{pH}=7$

From the polarization curves, parameters of the chemical corrosion process have been determined: the open circuit potential (E_{oc}), the corrosion potential (E_{cor}), the density of the corrosion current (i_{cor}) and the corrosion rate (CR), which are illustrated in table 2.

The corrosion rate has been calculated with the following formula:

$$CR = K_i \frac{i_{cor}}{\rho} EW$$

where:

CR – corrosion rate

$K_i = 3.27 \times 10^{-3}$

ρ – material density

i_{cor} – density of the corrosion current

EW – equivalent weight [3]

Table 2
THE MAIN PARAMETERS OF THE CORROSION PROCESS FOR THE INVESTIGATED ALLOYS

Alloy	E_{oc} [mV]		E_{cor} [mV]		i_{cor} [A/cm ²]		CR [μm/an]	
	pH=5,2	pH=7	pH=5,2	pH=7	pH=5,2	pH=7	pH=5,2	pH=7
NiCr-M	40.02	-201.889	-77.084	-231.238	70.731x10 ⁻⁹	681.395 x10 ⁻⁹	0.751	7.235
NiCr-B	5.75	-164.778	-159.828	-231.199	213.306x10 ⁻⁹	425.256 x10 ⁻⁹	2.133	4.254
Co-Cr	21.316	-72.842	-359.662	-741.283	864.477x10 ⁻⁹	15.516 x10 ⁻⁶	8.916	160.04
Ti6Al4V	144.075	-88.101	78.028	-128.128	80.61x10 ⁻⁹	129.043 x10 ⁻⁹	0.731	1.170

The electrochemical measurements have shown that the Ti6Al4V alloy has the most electropositive value of the open circuit potential (E_{oc}) in the artificial saliva (114 mV), pointing out a good behaviour to corrosion by forming a protective and adherent layer on the surface of the alloy. The next value is the one of the NiCr-M alloy (40.02 mV), followed by the CoCr alloy and then by the NiCr-B alloy that has the lowest electro positivity value, which means that it also presents the lowest resistance to corrosion.

It is known that a low corrosion current density (i_{cor}) indicates a good resistance to corrosion. According to this criterion, we can observe that the Ti6Al4V alloy has the smallest corrosion current intensity, followed by the NiCr-M alloy with pretty close current values (a difference of just 10 nA/cm²) and then by the next two investigated alloys. The CoCr alloy has the highest value of i_{cor} , which also indicates that from all analysed alloys this is the one that owns the lowest resistance to corrosion.

Regarding the corrosion rate, we can see very close values of the Ti6Al4V and NiCr-M alloys in the artificial saliva, with a pH=5.2 (about 0.7 μm/year). The next alloy that has a better behaviour to corrosion, reported to the investigated materials, is NiCr-B and the one with the biggest corrosion rate is the CoCr alloy.

Pursuant to these criteria, the best behavior to corrosion in the Fusayama Meyer artificial saliva, at a pH=5.2 and a temperature of 37±0.5°C is owned by the Ti6Al4V alloy, followed by the NiCr-M alloy, while the poorest corrosion behavior belongs to the CoCr alloy.

The variations of the open circuit potential (E_{oc}) at a pH=5.2 for the analysed galvanic systems are illustrated in figure 7 and at the pH=7 in figure 8.

The polarization curves for the studied galvanic systems at a pH=5.2 are illustrated in figure 9 and at a pH=7 in figure 10.

The parameters of the corrosion process for the galvanic couples are shown in table 3.

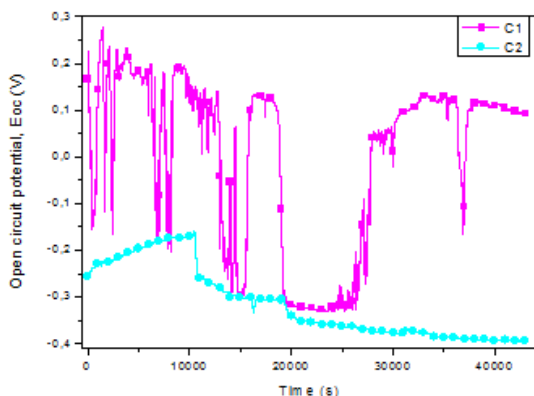


Fig. 7 The evolution of the open circuit potential (E_{oc}) for the galvanic systems at a pH=5.2

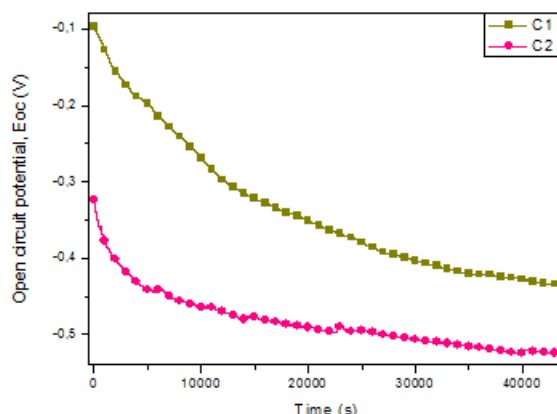


Fig. 8. The evolution of the open circuit potential (E_{oc}) for the galvanic systems at a pH=7

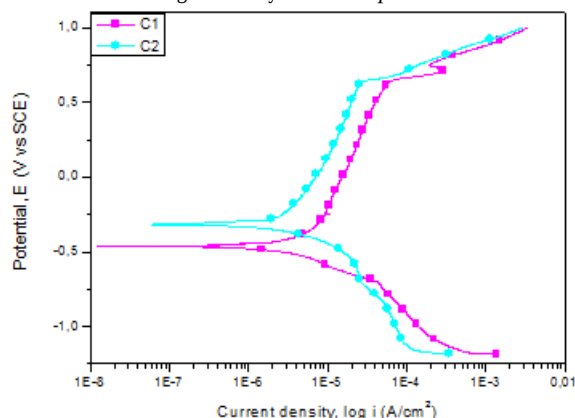


Fig. 9. The potentiodynamic curves of the galvanic systems at a pH=5.2

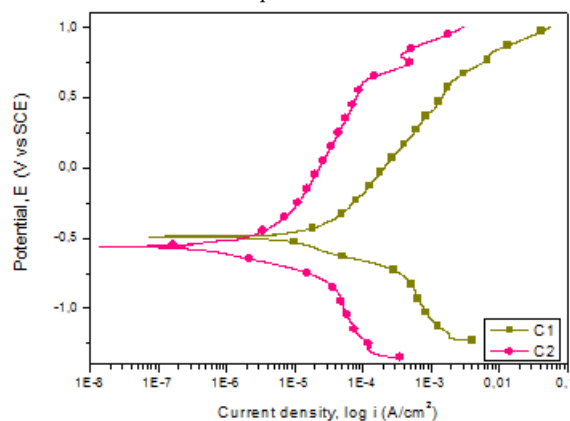


Fig. 10. The potentiodynamic curves of the galvanic systems at a pH=7

For a more precise comparison regarding the corrosion behavior of the galvanic system and of the alloys they are made of, the potentiodynamic curves have been overlaid.

Table 3
THE MAIN PARAMETERS OF THE CORROSION PROCESS FOR THE GALVANIC SYSTEMS

Galvanic couple	E_{oc} [mV]		E_{cor} [mV]		i_{cor} [A/cm ²]	
	pH=5.2	pH=7	pH=5.2	pH=7	pH=5.2	pH=7
C1	93.622	-434.909	-464.039	-491.119	6.442×10^{-6}	2.448×10^{-5}
C2	-394.807	-524.927	-316.999	-562.732	3.735×10^{-6}	1.132×10^{-5}

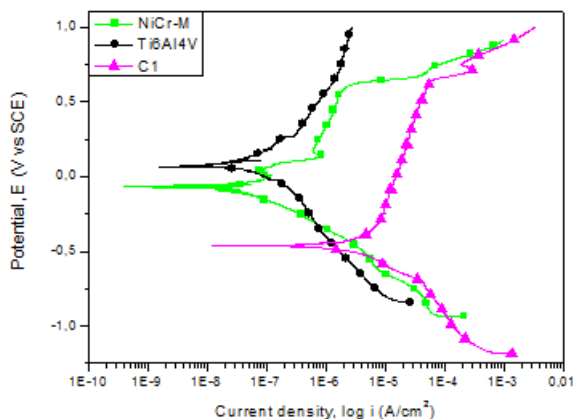


Fig. 11. The potentiodynamic curves of the galvanic system C1 and of the component alloys at a pH=5.2

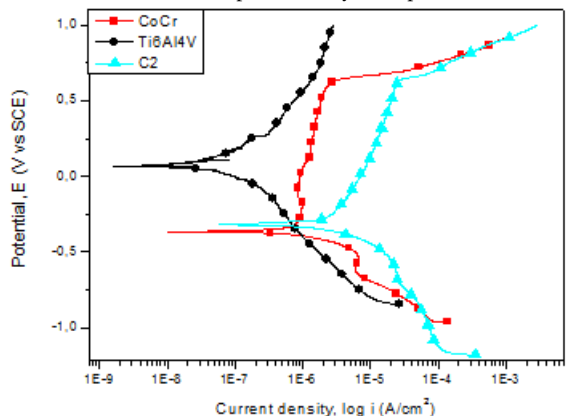


Fig. 12. The potentiodynamic curves of the galvanic system C2 and of the component alloys at a pH=5.2

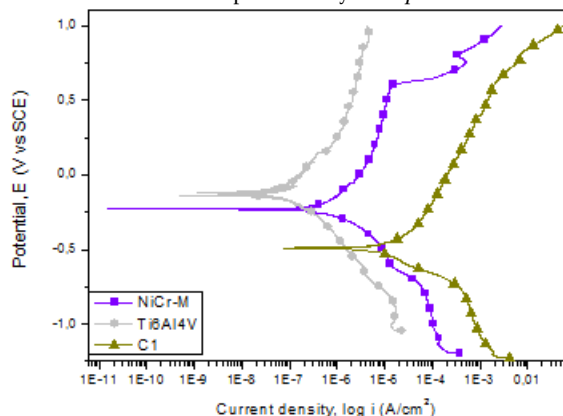


Fig. 13. The potentiodynamic curves of the galvanic system C1 and of the component alloys at a pH=7

In the case of galvanic systems, the main parameters of the corrosion process for the evaluation are: the open circuit potential (E_{oc}), the corrosion potential (E_{cor}) and the corrosion current density (i_{cor}).

So, the most electropositive value of the open circuit potential is registered for the couple C1.

Regarding the E_{cor} the couple C2 has the most electropositive value and a better behavior to corrosion due

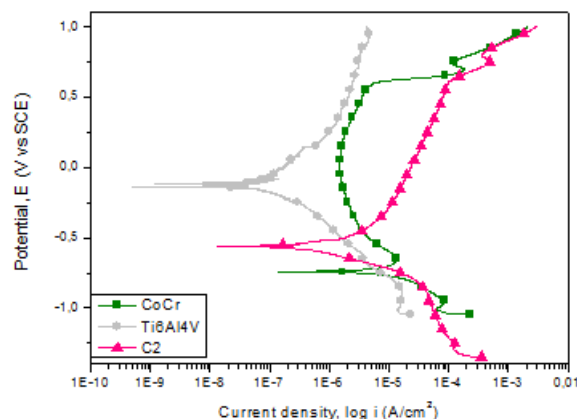


Fig.14. The potentiodynamic curves of the galvanic system C2 and of the component alloys at a pH=7

to it. Also, comparing the E_{cor} values of the alloys which made-up the galvanic systems, we note:

(i) Couple 1 – its E_{cor} value is more electronegative and this explains the fact that it has a poorer behaviour of the system compared to the one of the component alloys;

(ii) Couple 2 – its E_{cor} value is situated between the two values corresponding to the component alloys; it has a more electropositive value than the CoCr alloy, but less electropositive than the Ti6Al4V alloy.

The entire C2 couple has the lowest density of corrosion current ($3.735 \mu\text{A}/\text{cm}^2$) and as a result, from the point of view of the corrosion, it behaves better in the artificial saliva at a pH=5.2. Both i_{cor} values of the galvanic systems are much higher (three measurement units) than the ones of the alloys they are made of.

Tests of corrosion resistance have been conducted for all investigated materials in artificial saliva at a pH=7. Comparing the corrosion potential values, the Ti alloy has the most electropositive value, as against all the other analysed alloys (-128.128 mV). Moreover, we can see that the E_{cor} values of the alloys are more electropositive in the case of the tests made at pH=5.2 than the ones realised in artificial saliva at pH=7. We are so able to say that all alloys have a better behavior towards corrosion in a saliva with pH=5.2 than in one with a more acid pH (pH=7).

As respecting the corrosion rate (CR), the Ti6Al4V has the lowest value ($1.17 \mu\text{m}/\text{year}$), followed by NiCr-B, NiCr-M and CoCr with a value significantly higher than the one calculated when using saliva with pH=5.2 as an electrolyte. This could happen due to some small defects (microscopy) on the surface of the investigated material.

Regarding the galvanic couples, the most electropositive value is registered for the C1 couple, which means that it also has a better behavior to corrosion in saliva with a pH=7. From the point of view of the corrosion current density, the best behavior to corrosion is owned by the C2 couple with a value of $1.132 \times 10^{-6} \text{ A}/\text{cm}^2$. We can observe that when using less acid artificial saliva as an electrolyte, the C2 couple has a better behaviour to corrosion than the C1 couple. Making a parallel between the values of the parameters which define the corrosion resistance of the

galvanic couples in both types of artificial saliva, we can see that they behave better in the one with $pH=7$.

Conclusions

Taking into consideration the corrosion potential value (E_{cor}), we assume that the alloys with a more electropositive E_{cor} potential react better to corrosion. According to this criteria, the Ti6Al4V alloy presents a better behavior to corrosion in artificial saliva with $pH=5.2$ and with a E_{cor} positive value of 78.028 mV. Following the Ti alloy come the rest of the alloys with negative corrosion potential values, from which NiCr-M the most electropositive value has (-77.084 mV).

We can observe that the C2 system made of CoCr/Ti6Al4V has a better behavior to corrosion than the galvanic couple made of NiCr-M/Ti6Al4V (C1), something unexpected considering the values obtained when analysing the component alloys separately.

Comparing the values of the corrosion current intensity registered at $pH=7$, we can establish that Ti6Al4V is the alloy with the lowest value, which means that it has the best behavior towards corrosion. Compared to the values of the tests conducted in a $pH=5.2$ saliva, the CoCr alloy had a spectacular increase of i_{cor} with three measurement units higher. This shows a poorer corrosion behavior of the alloy in artificial saliva with $pH=7$. This case also reveals that all alloys have bigger i_{cor} values as the ones measured in the $pH=5.2$ saliva. This highlights the poorer behavior towards corrosion of the analysed alloys in the saliva with $pH=7$.

In conclusion, according to the corrosion tests conducted at a temperature of $37\pm0.5^{\circ}C$ and two different values of salivary pH (5.2 and 7), from the analysed alloys, we recommend the following: the use of NiCr metallic support for the manufacturing of fixed prosthetic restorations with dental aggregation and the use of CoCr metallic support for metal-ceramic restorations with implant aggregation.

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