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Electrochemical characterization of some cobalt base alloys in Ringer solution

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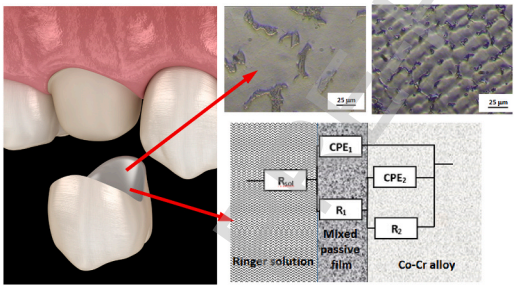
HIGHLIGHTS

- The behavior of two Co–Cr dental alloys in Ringer solution was investigated.
- Both alloys tend to passivate and this passivation tendency is very high.
- The alloys present the formation of a mixed protective layer Cr_2O_3·CoO.
- The high stability of passive film substantially improves their biocompatibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Biomaterials should be thoroughly studied in order to make sure they do not cause any harm to the human body. Considering that biocompatibility is very strict, the material must be non-toxic, and not cause any allergies or inflammation in the body. Of the different categories of metallic biomaterials, the cobalt-based alloys are among the preferred options. Applications can be found in orthopedic implants, and both cardiac and dental fields. Co–Cr alloys have been used in dentistry for porcelain-fused-to-metal (PFM) crowns due to their biocompatibility, wear resistance, long service duration, good mechanical properties, and last but not least, superior resistance to corrosion. The present investigation evaluated and compared two Co–Cr based dental alloys, studying their microstructural characterization and corrosion behavior in Ringer solution, using various techniques. Findings in this investigation revealed a high passivation tendency for the two alloys studied, with the formation of mixed protective layers Cr_2O_3·CoO with high stability on their surfaces, which substantially improves their biocompatibility in Ringer solution. The kinetic parameters of the corrosion process in the experiment indicated a two-time constants process with an anodic control, attributable to the formation of passive films on their surfaces. According to the results obtained in this investigation, the polarization resistance of the two Co–Cr alloys examined in Ringer solution reached the values of biomaterials with a high resistance to corrosion, and the passive films formed on their surface had a more than appropriate resistance to corrosion.

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1. Introduction

Biomaterials are to be used in medical applications that are in contact with living tissue. For this purpose, they should be thoroughly studied in order to make sure they do not cause any harm to the human body. Research on biomaterials represents an interdisciplinary conjugal effort and requires the collaboration of engineers, pathologists, biomedical engineers and clinicians. Considering that biocompatibility is very strict, the material must be non-toxic, and not cause any allergies or inflammation in the body [1].

The metallic biomaterials are classified into four categories based on primary application as implants: cobalt-based alloys, stainless-steels, titanium-based alloys and various others [2,3]. They present the required characteristics of excellent mechanical properties, high resistance to corrosion, and biocompatibility. In contact with body fluids, they suffer corrosion, which may be more or less accentuated, depending on certain factors: alloying elements, implant design, topography, presence of chloride and other ions, presence of biomolecules, pH, and dissolved oxygen [4]. The specific medical application determines the choice for a biomaterial. The types of corrosion in biocompatible materials have been and are being studied with responsibility by researchers in the field [5–10].

Of the different categories of metallic biomaterials presented above, the cobalt-based alloys are among the preferred options, with applications found in orthopedic implants, and both cardiac and dental fields, according to some investigations. The anticorrosive and high wear resistance properties they present are due to the crystallographic nature of cobalt [11–13]. Biomaterials are indeed very important in medical applications, helping to improve the patients' life. In the field of dentistry, composites, polymers, ceramics, and metals/alloys are biomaterials that may be used [14]. Moreover, Co–Cr alloys have been used in dentistry for porcelain-fused-to-metal (PFM) crowns due to their biocompatibility, wear resistance, long service duration, good mechanical properties, and last but not least, superior resistance to corrosion [15–18]. Non-precious alloys have the benefit of an improved elastic modulus in comparison with the precious dental alloys, which allow thinner substructures to be used in metal-ceramic restorations and result in a smaller amount of tissue destruction in the crowns' preparation [19]. Co–Cr alloys have become a typical material in dentistry. Due to the advantages they present over others regarding affordable prices, material properties and performance (worthy of comparison to other metal alloys), they have been widely used in metal-based ceramic restorations and are very suitable when a nickel-free alloy is needed [20]. In dental prostheses, whether removable or fixed, they are also commonly used, mainly because of their more than adequate corrosion properties [21–23]. In regards to the corrosion characteristics of dental implants, it is important to mention that saliva has a pH between 5.2 and 7.8, which represents a destructive atmosphere for the implant. This can cause allergies, discoloration of adjacent soft tissue, various skin rashes due to corrosion and metal ion release [24,25]. As a result, Co–Cr alloys are mostly used in dentistry when allergies to nickel are present [26]. Numerous papers have studied the behavior of biomedical cobalt-based alloys in different artificial environments [27–29]. Obviously, the corrosion attack suffered by prosthodontic restorations is due to the action of biological fluids in the formation of a passive oxide layer [30]. The study of this oxide layer, or film, is fundamental in the analysis of the alloy's stability [31–33], directly related to its resistance to corrosion, which results in the successful use of the alloy in prosthodontic restorations [34]. The metal oxide layer should present a high level of wear resistance to erosion, adherence and a small solubility and ion transfer [35].

The major alloying elements in dental cobalt alloys are chromium, molybdenum, nickel, and tungsten. Cobalt has been identified as an essential metal element in the human organism, involved in key processes such as brain function and red blood cell development, due to its relationship with vitamin B12. The chromium and molybdenum content within the alloy is important. In Ni–Cr alloys, passivation is regularly ascribed to the development of the metals' oxide layers and a high content of molybdenum and chromium oxides limit the release of metal ions [36]. Experimental investigations have shown that alloys that possess more than 20% of Cr content have higher corrosion resistance, and therefore, increased intra-oral biocompatibility. The role of chromium is mainly manifested by three factors: on corrosion resistance through Cr_2O_3, on microstructure through $Cr_{23}C_6$, and on mechanical properties by increasing the wear resistance. Additionally, the role of molybdenum is to increase the corrosion resistance, refine the grain size, and enhance the solid-solution strengthening [37,38].

The present investigation evaluated and compared two Co–Cr based dental alloys, studying their microstructural characterization and corrosion behavior in Ringer solution, using various techniques.

2. Materials and methods

2.1. Materials and reagents

The following CoCr based dental alloys were investigated: Vera PDI (AalbaDent, USA), and Vitallium 2000 Plus (Dentsply Sirona, USA). Both alloys are nickel and beryllium-free, resulting in a biocompatible appliance for the patient. Their chemical composition, provided by the manufacturer, is presented in Table 1.

The Ringer solution employed in this study as the corrosion medium had the following composition (g/L): NaCl–6.8, KCl–0.4, $CaCl_2$–0.2, $NaCO_3H$-1, glucose–1, $MgSO_4{\cdot}7H_2O$–0.2 and $NaH_2PO_4{\cdot}H_2O$–0.14.

2.2. Microstructural characterization

The processing of the samples for microstructural examination starts with a precision cut. In order to minimize damage to the microstructure of the material and the analysis itself, the original samples were cut with a precision sectioning saw designed to cut the materials with minimal distortion (IsoMet®4000 Buehler). The use of a cutting coolant (Isocut®Plus) helped to dissipate the heat, remove the chips from the cut, and prevent any unnecessary surface damage to the sample.

The assembly of the samples was of great importance to facilitate the handling and to preserve the edge of the samples. An epoxy system (EpoThinTM) was used because the epoxy resin curing products cause low shrinkage and an acceptable physical adhesion. A release agent (silicone spray) was used to help prevent the mounts from sticking to the molds. After assembly, the specimens were wet sanded and polished with a grinding-polishing machine (Struers TegraForce-1) with 320–2500 grain SiC papers followed by a 1 μm alumina suspension. The samples were then ultrasonically cleaned in ethanol for 5 min and rinsed twice with distilled water. The experimental methods followed the ASTM E3 - 11(2017) standard for metallographic sample preparation [39].

For the microstructure analysis of the alloys, a chemical reagent containing 10 ml HNO_3-30 ml HCl-20 ml Glycerine [40] and an OLYMPUS PME 3–apparatus were utilized. Once the electrochemical treatments were performed, a microscope was used to complete a rigorous analysis of the surface's modifications.

Table 1
Components of the dental materials.

Alloys	Components, wt%				
	Co	Cr	Mo	Fe	Ni
VERA PDI	63.5	27	5.5	2	1
VITALLIUM 2000 Plus	63.4	29.0	5.2		

2.3. Electrochemical measurements

Measurements were completed using a set of three electrodes: the saturated calomel electrode/SCE as the reference electrode, platinum as the counter-electrode, and the alloy specimens as the working electrode. A potentiostat 263 A PAR/Princeton Applied Research model, connected with a lock-in amplifier PAR 5210 and with a computer with PAR Electrochemistry Power Suite software were used.

2.4. Open-Circuit Potential

Before linear potentiodynamic polarization studies were conducted using a scanning rate of 0.5 mV/s to raise the potential from −600 to +1200 mV (SCE), each alloy was tested during 24 h for open-circuit potential measurements. Electrochemical reactions took place on the metal-solution interaction when metals were submerged in the reagent [41]. Experimental information was obtained and processed using the PowerCorr software.

2.5. Potentiodynamic polarization

With a 0.25 mV/s scanning rate, linear polarization from E_{OCP} -150 mV to E_{OCP} +150 mV was conducted in order to identify the Tafel slopes (b_C, b_A) for the partial cathodic and anodic processes. To evaluate the passivation process, the polarization studies continued with measurements from −600 to +1200 mV (SCE), stepping the potential with a 0.5 mV/s scanning rate. A potentiostat was used to perform the tests, and data were processed using PowerCorr software, both from Princeton Applied Research. The results showed the potentiodynamic polarization curves and the breakdown potential.

After linear potentiodynamic tests, surface microstructures were examined with the OLYMPUS PME 3–ADL microscope.

2.6. electrochemical impedance spectroscopy

The AC/alternating current impedance spectra for the two Co–Cr dental alloys was completed at the OCP/open-circuit potential in the aerated solution. The spectra was obtained, with an amplitude of 10 mV, in the 10^{-2} to 10^{5} Hz frequency range.

To analyze the corrosion resistance of the CoCr dental materials, EIS/electrochemical impedance spectroscopy tests were performed after one-day of immersion at the open-circuit potential.

Experimental EIS results were analyzed using the software ZSimp Win-PAR, USA, in terms of obtaining the EC or equivalent circuit, to have measured data and simulated responses fit well. AC impedance data, after each experiment, was displayed as Nyquist plot and Bode (phase and |Z|) diagrams. The tests were all performed three times, and the representative results are presented.

3. Results and discussions

3.1. Initial microstructural characterization

Fig. 1 shows the microstructural characterization of the two CoCr based dental alloys.

Vitallium 2000 Plus and Vera PDI alloys both showed a dendritic microstructure. Integrated into the surface of the Vitallium 2000 Plus alloy were carbides and intermetallic compounds of σ (in a dark color), dendritically distributed in a solid solution α (in a light color). Vera PDI alloy presented some isolated carbides in its solid solution (in a light color) [42].

3.2. OCP/open-circuit potential

The open-circuit potential measurements (E_{OCP}) after 24 h are shown in Fig. 2. The curves show the potentials versus time for the different alloys studied. Table 2 summarizes the values of the open-circuit potential for the Co–Cr based dental alloys studied.

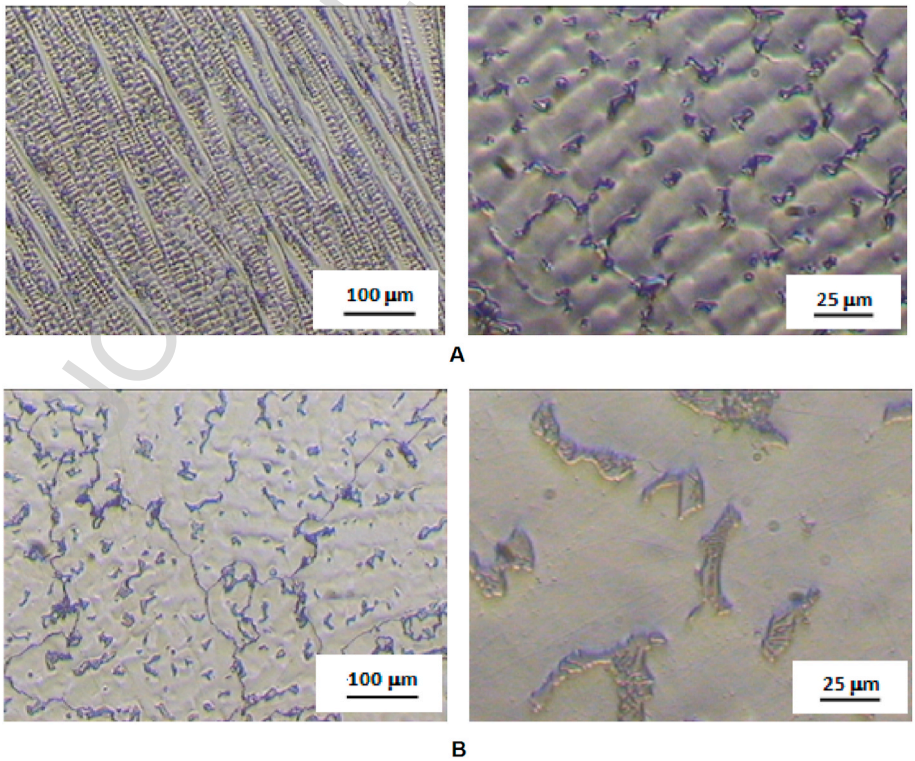

Fig. 1. Metallography analysis: (A)- Vitallium 2000 Plus alloy, (B)- Vera PDI alloy.

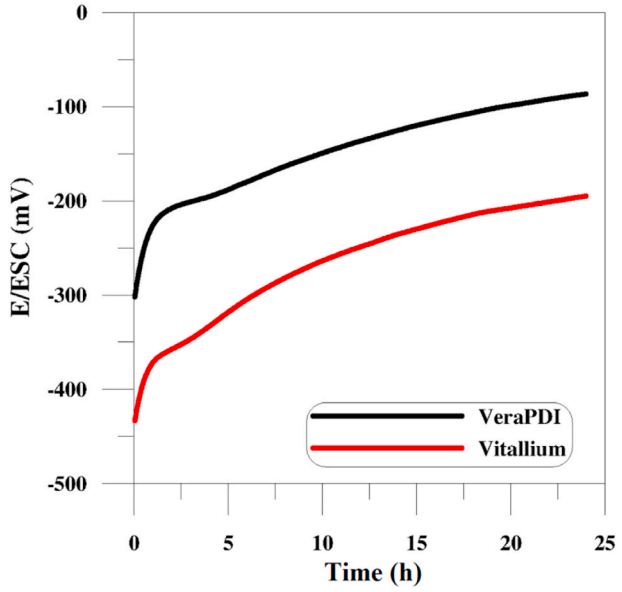

Fig. 2. Open-circuit potential variation versus time immersion in Ringer Solution for Vera PDI and Vitallium 2000 Plus.

Table 2
Open-circuit potential measurements: initial, after 1 h and 1 day (or 24 h) for Co–Cr alloys immersed in Ringer solution.

Alloys	OCP, mV/ESC		
	Initial	After 1 h	After 24 h
Vera PDI	−302	−226	−86
Vitallium 2000 Plus	−433	−371	−195

The variation of the corrosion potential was similar in both the Vera PDI and Vitallium 2000 Plus alloys. The potential increased suddenly after the first hour of immersion due to the passivation of the two alloys. The continued shift of potential to noble values indicated, for both alloys, that there were changes in the passive layer. During the 24-h test, potentials dropped to overcome potential over-achievement. The potential increase was roughly the same for both alloys. After 24 h of immersion, the potential of the Vera PDI alloy reached the value of −86 mV, and the Vitallium 2000 Plus alloy was more than 100 mV less, with a value of −195 mV. Thus, the maintenance of alloys in Ringer solution for 24-h revealed that the passivation tendency was high for Vera PDI and Vitallium 2000 Plus alloys, from a qualitative point of view.

3.3. Potentiodynamic polarization results

The potentiodynamic polarization curves for the Vitallium 2000 Plus alloy are displayed in Figs. 3 and 4.

With increasing immersion time, the values of E_{corr} shifted in a positive direction. This suggested that the material became nobler as a result of the passive layer formed on its surface.

Results displayed in Table 3 showed that the values of i_{corr} decreased with immersion time. These values were in agreement with OCP results, indicating an improved corrosion resistance of the material. Moreover, E_{corr}, i_{corr}, and the anodic-cathodic Tafel slopes (b_A and b_C), were estimated in the range of ±150 mV vs OCP.

The values of the polarization resistance (R_p) were calculated by the Stern-Geary equation [43]:

$$R_p = \frac{b_A \cdot \leq b_C}{2.3 i_{corr}(b_A + b_C)}$$

This equation shows that the polarization resistance (R_p) and the corrosion current are inversely proportional. Thus a high polarization resistance implies a low corrosion current.

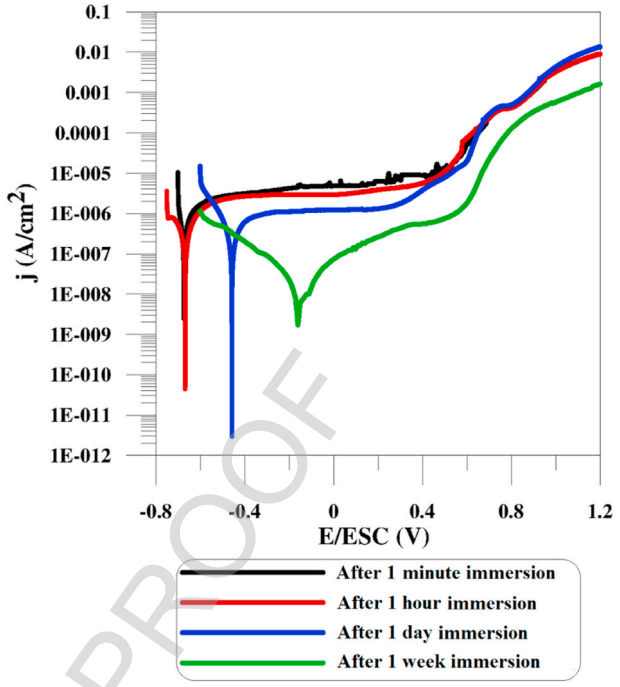

Fig. 3. Polarization curves for Vitallium 2000 Plus dental alloy at different immersion times in Ringer solution.

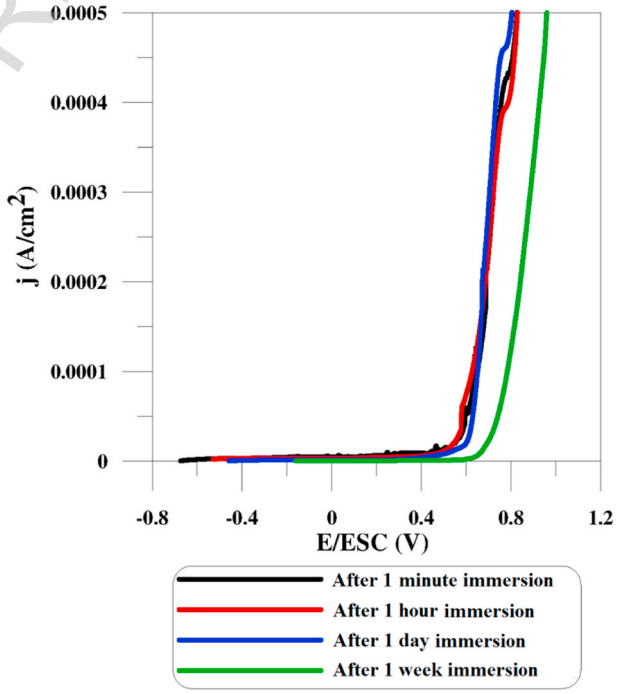

Fig. 4. Potentiodynamic anodic polarization curves for Vitallium 2000 Plus at different immersion times in Ringer solution.

The corrosion rate (μm/year) was obtained from the corrosion current density through Faraday's law. However, being proportional, either of them could be used to explain the corrosion behavior of the Co–Cr alloys studied.

The Vitallium 2000 Plus alloy, after 1-min immersion in Ringer solution, showed a low corrosion current, and it was clearly under an

Table 3
Electrochemical parameters of the Vitallium 2000 Plus dental alloy at different immersion times in Ringer solution.

VITALLIUM 2000 PLUS	E_{corr} mV/SCE	i_{corr} μA/cm^2	b_A mV/div	b_C mV/div	R_p Ω cm^2	Corrosion rate μm/year
After 1 min immersion	−685	0.43	111	63	4.16 10^4	0.455
After 1 h immersion	−680	0.37	160	84	6.5 10^4	0.392
After 1 day immersion	−455	0.24	162	82	9.7 10^4	0.254
After 1 week immersion	−182	0.1	141	125	3 10^5	0.106

anodic control (the anodic slope b_A was higher than the cathodic slope b_C, which meant that the material was subjected to passivity) [44].

To evaluate the passivation process, potentiodynamic polarization measurements from −600 mV to +1200 mV (SCE) were performed (see Fig. 4).

The pitting potential (see Table 4) had a fairly high anodic value, being over 500 mV, giving it high electrochemical stability.

The positive effect of surface passivation, due to the immersion time of the dental material in Ringer solution, was the decrease in the corrosion current, and the displacement of the breakdown potential to more anodic values. After 7 days of immersion it was about 650 mV. Under these conditions, the Vitallium 2000 Plus alloy had a wide passive range and low passivity currents between 2 and 7 μA/cm^2.

The potentiodynamic polarization curves for the Vera PDI alloy are displayed in Figs. 5 and 6.

The corrosion potential slightly changed with immersion time while corrosion current values were reduced, indicating a thicker and more compact passive film on the surface of the material.

The values of the electrochemical parameters of the corrosion process for the Vera PDI alloy after immersion in Ringer solution are shown in Table 5.

The Vera PDI alloy had significant corrosion resistance in the Ringer solution. The data presented in Table 5 showed a small corrosion rate at the initial moment that decreased during the immersion time of this alloy in Ringer solution, reaching a value of 0.15 μA/cm^2 after one week. The higher value of b_A vs b_C indicated an anodic control of the corrosion process caused by the passive film on their surface. The breakdown potential (see Table 6) increased over time, reaching more than 600 mV after the 7 days of immersion. Thus, the Vera PDI alloy had a wide range of passivation and low passivation currents.

The standard DIN 13912 (1996) establishes an equivalent number of resistance to pitting corrosion for steels by means of which the resistance to this type of corrosion can be evaluated. In this investigation, we are dealing with alloys containing chromium (which allow the formation of passive layers), and can use the PREN index (see Table 7) when we accompany it with other corrosion studies (for example, linear polarization). Very little difference is observed, confirming a similar behavior to pitting corrosion.

Table 4
Pitting corrosion parameters of the Vitallium 2000 Plus dental alloy at different immersion times in Ringer solution.

VITALLIUM 2000 PLUS	i_{pass} μA/cm^2	E_{bd} mV
After 1 min immersion	6.3	530
After 1 h immersion	4.5	550
After 1 day immersion	3.16	600
After 1 week immersion	2.1	650

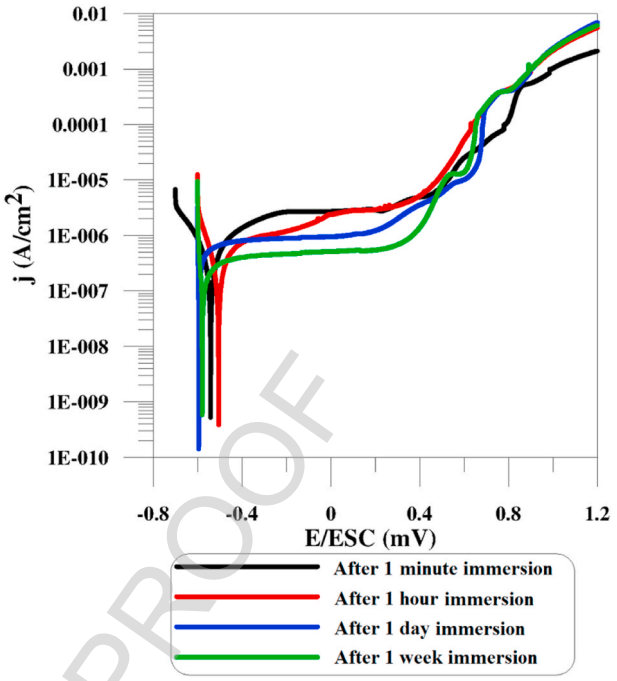

Fig. 5. Polarization curves for Vera PDI dental alloy at different immersion times in Ringer solution.

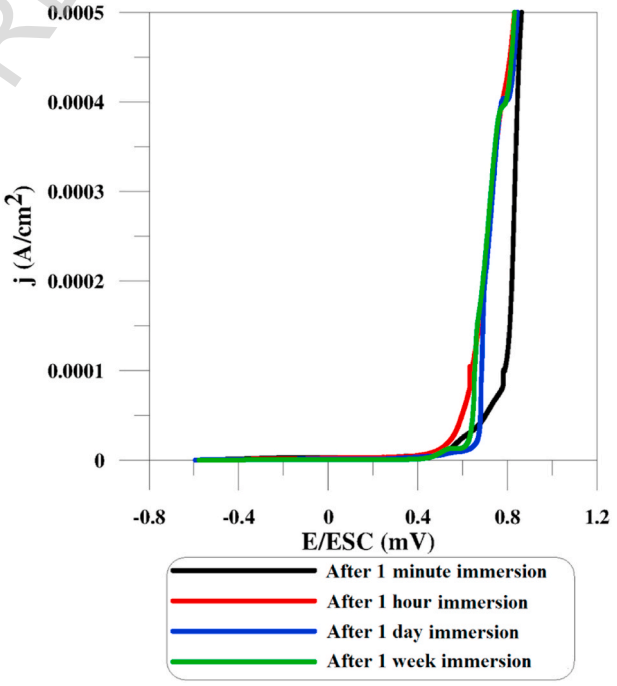

Fig. 6. Potentiodynamic anodic polarization curves at different immersion times in Ringer solution for Vera PDI dental alloy.

3.4. Final microstructural characterization

Microstructures of the Vitallium 2000 Plus and Vera PDI alloys, after the linear potentiodynamic tests, are shown in Fig. 7. The analysis of the surface micrographs, after electrochemical measurements, showed a generalized corrosion process in the Co–Cr based dental alloys studied. Vera PDI and Vitallium 2000 Plus alloys passivated over time. After linear potentiodynamic polarization at 1200 mV, it was found that the entire surface of both alloys presented a homogeneous attack, with

Table 5
Electrochemical parameters of the Vera PDI dental alloy at different immersion times in Ringer solution.

VERA PDI	E_{corr} mV/SCE	i_{corr} μA/cm^2	b_A mV/div	b_C mV/div	R_p Ω cm^2	Corrosion rate μm/year
After 1 min immersion	−685	0.36	177	85	6.9 10^4	0.450
After 1 h immersion	−680	0.27	178	80	8.9 10^4	0.337
After 1 day immersion	−455	0.24	173	72	9.4 10^4	0.300
After 1 week immersion	−182	0.15	164	103	1.75 10^5	0.187

Table 6
Pitting corrosion parameters of the Vera PDI dental alloy at different immersion times in Ringer solution.

VERA PDI	j_{pass} μA/cm^2	E_{bd} mV
After 1 min immersion	5	480
After 1 h immersion	2.1	410
After 1 day immersion	2.2	650
After 1 week immersion	1.9	640

Table 7
PREN index values for the studied alloys.

Alloy	PREN
VERA PDI	45
VITALLIUM 2000 Plus	46

adherent corrosion products formed. After removal of the sediment, the generalized corrosion that developed on the surface of Vera PDI and Vitallium 2000 Plus alloys was confirmed (areas a, b).

3.5. Electrochemical impedance spectroscopy

Representative EIS data of the Vitallium 2000 Plus alloy after various dipping times in Ringer solution are presented in Fig. 8. The results from the fits to the relevant equivalent circuit model, the theoretical spectra, appear as lines, while the experimental measurements are shown as individual points.

The equivalent circuit model used in the study for the spectral data of the Co–Cr based dental alloys is presented in Fig. 9.

In the model, the ohmic resistance of the electrolyte was designated R_{sol}, the resistance of the passive film was designated R_1, the charge transfer resistance (R_{ct}) was designated R_2, the passive film capacitance was represented CPE_1 and the double layer capacitance was represented as CPE_2. The EC model resembles the one suggested by M. Meticos-Hukovic et alia [45] for Co–Cr alloys immersed in Hank's solution.

The most important corrosion indicators from the substrate-electrolyte system were provided by the equivalent circuit (EC), which was comprised of different arrangements of capacitors, circuit elements, and resistances. It was imperative to have an adequate model of the reactions that occurred at the electrodes for the interpretation of the system's electrochemical behavior from EIS spectra. The electrochemical cell was represented by an EC as it displayed impedance to a sinusoidal excitation [46].

From the Nyquist curves that showed a capacitive arc, it was found that the impedance increased with immersion time. From the Bode graphs, which contain two-time constants, the phase magnification increased over time. After 1 week of immersion, it reached 80°. The best simulation was obtained using the equivalent circuit in Fig. 9. The parameters obtained are presented in Table 8.

Findings from the data presented in Table 8, showed that the compact layer resistance and the resistance of the passive pellicle increased with immersion time. This trend indicated an increase in the resistance to corrosion over time. The polarization resistance reached 10^6 Ω cm^2, characteristic of biomaterials with high corrosion resistance (titanium alloys) [47]. The thickness of the passive film, and its homogeneity, increased over time (CPE_2 decreased, and n_2 increased).

Representative EIS data of the Vera PDI alloy after various dipping times in Ringer solution are presented in Fig. 10. The individual points are the experimental measurements, and the lines are the simulated data or theoretical spectra that resulted from the fits to the equivalent circuit model presented in Fig. 10.

From the Nyquist impedance spectra, we found that Vera PDI alloy in Ringer solution had a capacitive behavior, and the impedance increased with immersion time. Bode spectra shape showed two-time constants and highlighted an increase in phase angle over time, moving to 80° with immersion time. The best simulation was completed using the same circuit shown in Fig. 10, and the parameters obtained are displayed in Table 9.

Corrosion resistance ($R_p = R_1 + R_2$) increased with immersion time and reached a value close to 10^6 Ω cm^2 after a week of immersion, characteristic of materials with high corrosion resistance. However, this resistance was slightly smaller than the one found for Vitallium, due to the small content of Fe and Ni in the composition of the alloy. Additionally, the passive film capacity decreased over time, indicating increased thickness, as well as homogeneity (increased n_2).

Comparing the representative EIS data after 1 day of the Vitallium 2000 Plus and Vera PDI alloys, it was discovered from the Nyquist impedance spectra obtained that both had a capacitive behavior in Ringer solution, and an increased impedance with immersion time. The Bode spectra presented two peaks in the medium frequency range, and highlighted an increase in the phase angle, approaching 80° at the immersion time, indicating the development of a passive layer on the surface of the studied CoCr alloys. In the region of high frequency, log |Z|showed a tendency to be constant and the phase angle values approached 0° as frequency increased, showing a resistant behavior due to the solution resistance, R_{sol}.

From the main parameters presented after 1 day, the Vitallium 2000 Plus alloy exhibited a higher polarization resistance (R_p) than the Vera PDI alloy, indicating higher resistance to corrosion after 1 day immersion time. The R_p, or polarization resistance, is the sum of R_1 and R_2 (R_{ct} and passive film resistance, respectively). Results displayed large determinations of R_p for the Co–Cr alloys studied. These results were a quantitative indicator of the high resistance to corrosion of the passive film formed at the surface of the CoCr dental materials studied in Ringer solution. However, Vitallium 2000 Plus presented a higher R_p after 1 day immersion time. This can be explained by the higher concentration of chromium in Vitallium 2000 Plus. The Cr metal formed a protective passive oxide layer of Cr_2O_3, according to the reaction [48,49]:

$$Cr + H_2O \rightarrow Cr_2O_3 + 6H^+ + 6e^-$$

The large amount of cobalt promoted the formation of a passive film, following the reaction:

$$Co + H_2O \rightarrow CoO + 2H^+ + 2e^-$$

This meant that on the surface of the alloys there was a mixed passive film formed, Cr_2O_3·CoO. This increased the stability of the Cr_2O_3 film, and attenuated the hydrolysis of Cr^{3+}, which took place in the *trans*-passive region, when the oxidation of chromium (III) oxide to form soluble Cr (VI) species occurred:

$$Cr_2O_3 + 5H_2O \rightarrow 2CrO_4^{2-} + 10H^+ + 6e^-$$

The spontaneous formation of the mixed passive film, and its high stability, reduced the damage by chloride ions and increased the corrosion resistance of the Co–Cr alloys, improving their

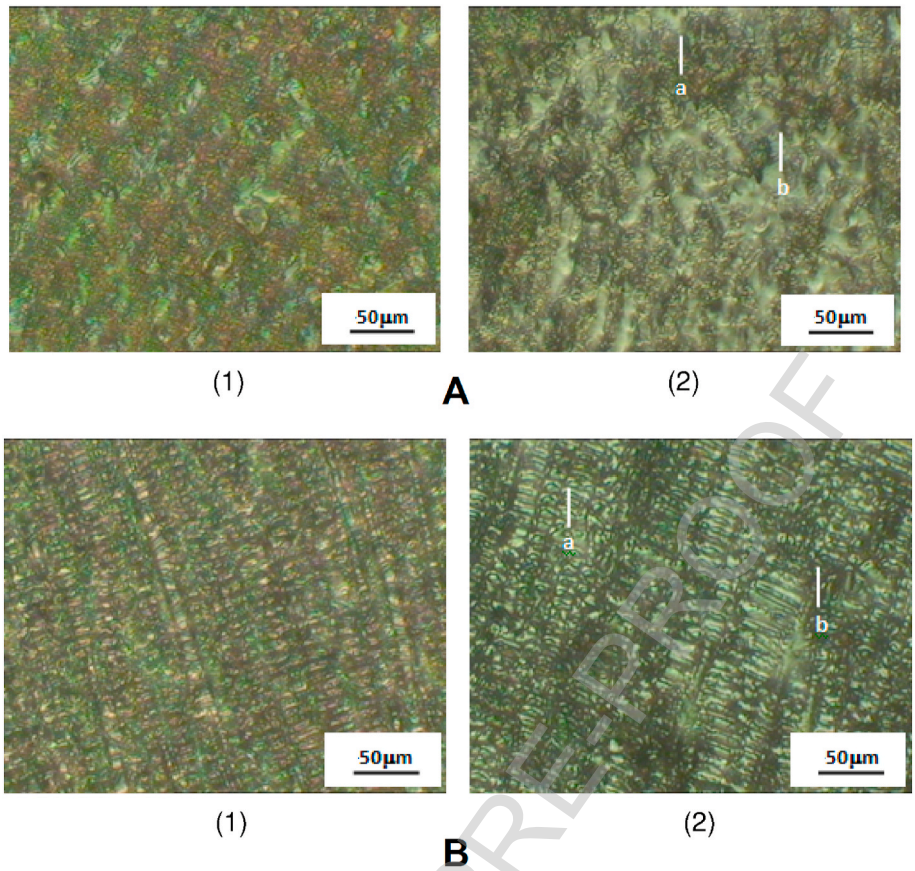

Fig. 7. Microstructures (1) after electrochemical treatment, (2) after removal of the sediment: (A)- Vera PDI alloy, (B)- Vitallium 2000 Plus alloy.

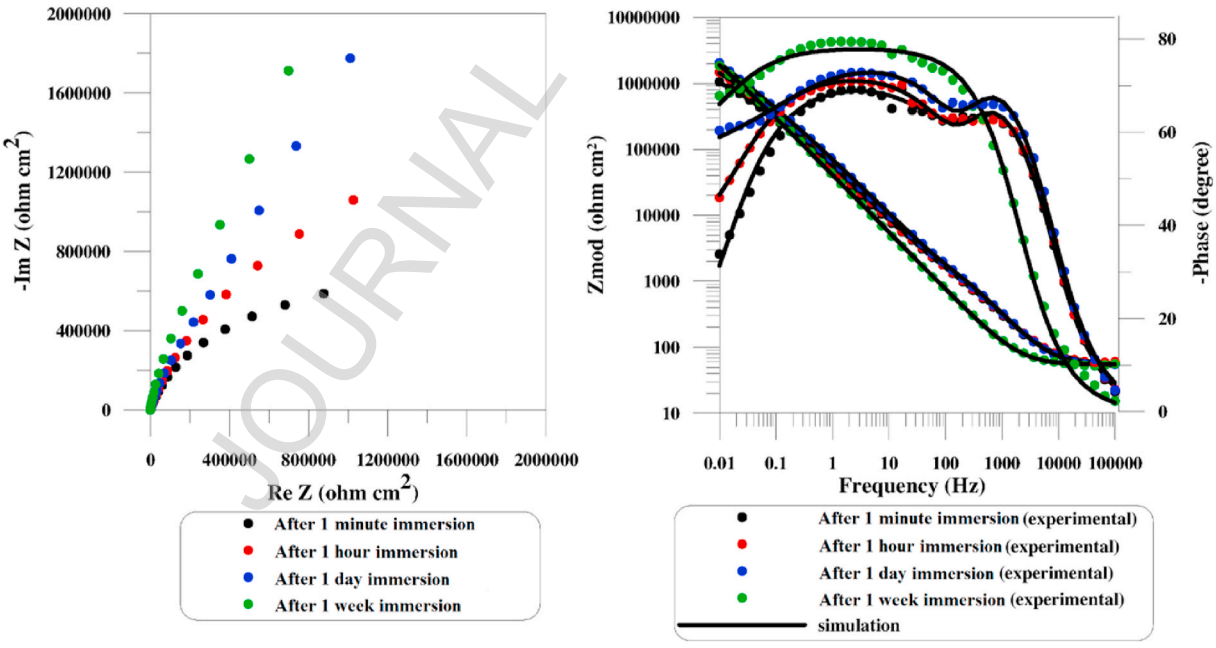

Fig. 8. Representative Nyquist and Bode spectra for Vitallium 2000 Plus alloy after 1 min, 1 h, 24 h, and 1 week of immersion in Ringer solution.

biocompatibility in contact with the gum.

In all the CoCr based dental alloys studied, the polarization resistance (R_p) in Ringer solution was high. According to ASM Handbook [50], in materials that have a high level of corrosion resistance, the R_p may reach 1 MΩ cm^2. Implants for surgery operations may have a polarization resistance of approximately 1 MΩ cm^2, showing a very low corrosion rate [51]. Furthermore, around 1 MΩ cm^2 is the polarization resistance of commercially pure titanium in acidic artificial saliva, and titanium in a phosphate-buffered saline solution [52,53]. Therefore, according to the results obtained in this investigation, the polarization

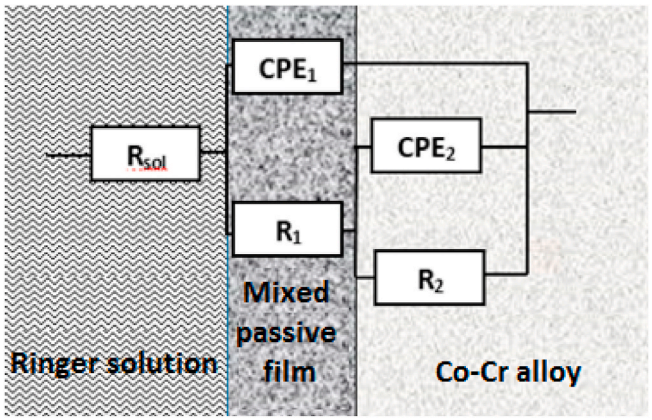

Fig. 9. The equivalent circuit used to fit the experimental impedance data.

resistance of the two Co–Cr alloys examined in Ringer solution reached the values of biomaterials with a high resistance to corrosion, and the passive films formed on their surface had a more than appropriate resistance to corrosion.

4. Conclusions

In the present investigation, the corrosion behavior of two Co–Cr based dental materials in Ringer solution was analyzed. Using microstructural analysis, OCP/Open-Circuit Potential, Potentiodynamic Polarization studies, and EIS/Electrochemical Impedance Spectroscopy technique, the following conclusions were derived:

1. Both alloys tend to spontaneously passivate, and this passivation tendency is very high. The alloys presented the formation of mixed protective layers Cr_2O_3·CoO with high stability on their surfaces, which substantially improves their biocompatibility in Ringer solution.
2. After electrochemical treatment, the alloys exhibited a uniform or general corrosion behavior, homogeneous on the surface, for areas a

Table 8
Fitted EIS parameters of the Vitallium 2000 Plus alloy in Ringer solution.

	R_{sol} Ωcm^2	R_1 Ωcm^2	CPE_1 $Scm^{-2}s^n$	n_1	R_2 Ωcm^2	10^6CPE_2 $Scm^{-2}s^n$	n_2	χ^2
After 1 min	55	$1\ 10^6$	$3.3\ 10^{-6}$	0.73	$2.1\ 10^3$	1.5	0.88	$7\ 10^{-4}$
After 1 h	57	$2.9\ 10^6$	$3.1\ 10^{-6}$	0.74	$2.2\ 10^4$	1.2	0.9	$6\ 10^{-4}$
After 1 day	52	$4\ 10^6$	$1.9\ 10^{-6}$	0.78	$2.3\ 10^4$	1.1	0.9	$3\ 10^{-4}$
After 1 week	53	$4.4\ 10^6$	$4.3\ 10^{-7}$	0.86	$5\ 10^4$	0.8	0.9	$6\ 10^{-4}$

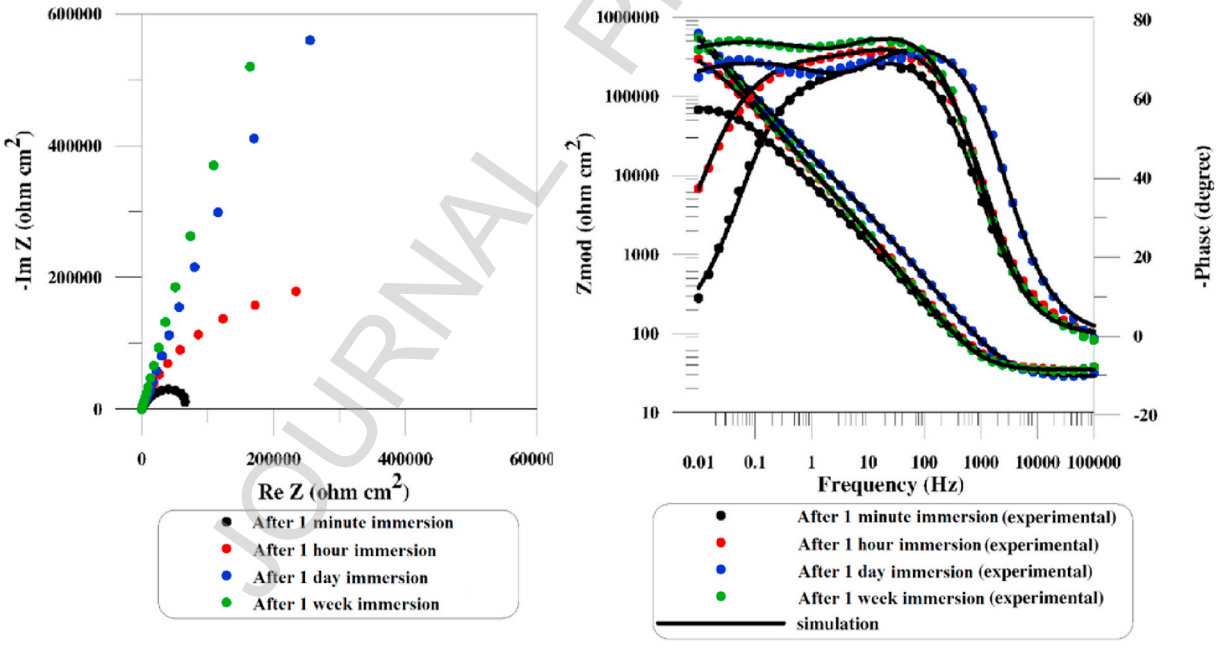

Fig. 10. Representative Nyquist and Bode spectra for Vera PDI alloy after 1 min, 1 h, 24 h, and 1 week of immersion in Ringer solution.

Table 9
Fitted EIS parameters of the Vera PDI alloy in Ringer solution.

	R_{sol} Ωcm^2	R_1 Ωcm^2	CPE_1 $Scm^{-2}s^n$	n_1	R_2 Ωcm^2	10^6CPE_2 $Scm^{-2}s^n$	n_2	χ^2
After 1 min	35	$4.1\ 10^5$	$4.8\ 10^{-5}$	0.78	$6\ 10^3$	2	0.85	$6\ 10^{-4}$
After 1 h	38	$5.5\ 10^5$	$3.6\ 10^{-5}$	0.8	$7\ 10^3$	1.9	0.85	$2\ 10^{-4}$
After 1 day	39	$7.2\ 10^5$	$1.3\ 10^{-5}$	0.81	10^4	1.8	0.87	$9\ 10^{-4}$
After 1 week	37	$8\ 10^5$	$8.5\ 10^{-6}$	0.83	$2\ 10^4$	0.8	0.9	$2\ 10^{-4}$

and b. However, due to the content of Fe and Ni, a higher degree of corrosion was found in the Vera PDI alloy. Furthermore, the kinetic parameters of the corrosion process in the experiment indicated a two-time constants process with an anodic control, attributable to the formation of passive films on their surfaces.

3. In terms of susceptibility to corrosion, both alloys had a more than adequate corrosion resistance in Ringer solution. Although, when the alloys were compared, it was discovered that the Vitallium 2000 Plus dental alloy presented a higher corrosion resistance than the Vera PDI dental alloy.
4. According to the results obtained in this investigation, the polarization resistance of the two Co–Cr alloys examined in Ringer solution reached the values of biomaterials with a high resistance to corrosion, and the passive films formed on their surface had a more than appropriate resistance to corrosion.

CRediT authorship contribution statement

C.M. Garcia-Falcon: Conceptualization, Writing - original draft, Methodology, Investigation. **T. Gil-Lopez:** Methodology, Validation, Investigation. **A. Verdu-Vazquez:** Data curation, Writing - review & editing. **J.C. Mirza-Rosca:** Software, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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