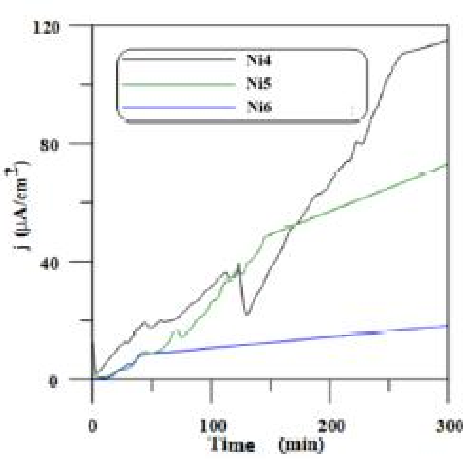
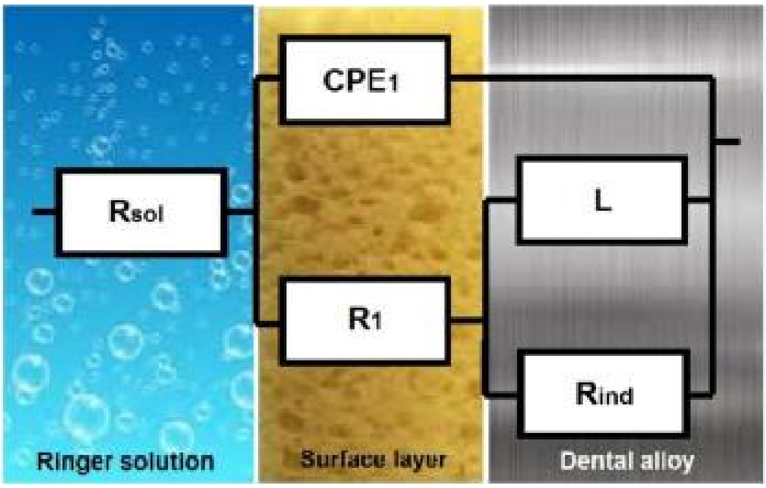
Doctorado en Ingenierías Química, Mecánica y de Fabricación





Las Palmas de Gran Canaria, abril de 2022

ANÁLISIS DEL COMPORTAMIENTO DE LA CORROSIÓN DE DIFERENTES ALEACIONES NÍQUEL-CROMO Y COBALTO-CROMO EN CONTACTO CON FLUIDOS FISIOLÓGICOS

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INFORMA,

De que la Comisión Académica del Programa de Doctorado, en su sesión de fecha .... tomó el acuerdo de dar el consentimiento para su tramitación, a la tesis doctoral titulada " Análisis del comportamiento de la corrosión de diferentes aleaciones níquel-cromo y cobalto-cromo en contacto con fluidos fisiológicos" presentada por la doctoranda Dª. Carmen Marina García Falcón y dirigida por los Doctores D. Néstor Rubén Florido Suárez y D. Tomás Gil López.

Y para que así conste, y a efectos de lo previsto en el Art. 11 del Reglamento de Estudios de Doctorado (BOULPGC 04/03/2019) de la Universidad de Las Palmas de Gran Canaria, firmo la presente en Las Palmas de Gran Canaria, a .... de ....de dos mil veintidós.

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Escuela de
Doctorado

UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA

ESCUELA DE DOCTORADO

Programa de doctorado en Ingenierías Química, Mecánica y de Fabricación

Departamento de Ingeniería Mecánica

Título de la Tesis

Análisis del comportamiento de la corrosión de diferentes aleaciones níquel-cromo y cobalto-cromo en contacto con fluidos fisiológicos.

Tesis Doctoral presentada por Dª. Carmen Marina García Falcón.

Dirigida por los Doctores D. Néstor Rubén Florido Suárez y D. Tomás Gil López.

Las Palmas de Gran Canaria, a 27 de abril de 2022.

Los Directores, **El Doctorando,**

AGRADECIMIENTOS

Dicen que una persona no puede ser feliz si no es agradecida. Yo creo firmemente en ello. Por eso, en estas líneas quiero agradecer a todos aquellos que de una manera u otra me han ayudado en el camino, familia, amigos, compañeros de investigación, trabajo y, en especial:

A Julia Mirza, por lo que me has enseñado durante estos años de doctorado.

A Tomás Gil y Néstor Florido, por ayudarme en este trabajo y en el empujón final que sin vosotros sería imposible.

A Ernesto, por toda la ayuda que me has brindado durante estos años de doctorado.

A mi padre, a mi madre y hermano, por su constante apoyo, día y noche. A mi madre, decirte que ojalá tuviese tu forma de ser, me habría ayudado mucho en acortar el camino, la admiro. Ya la quisiera yo tener.

A mis amigos de Estados Unidos, que también a su manera me han ayudado en esta tesis. Siempre ahí, siempre en contacto dispuestos a ayudar. Son ya más de 30 años.

A mis hijos Marina y Diego, el motivo y el motor de este doctorado. Todo esto ha sido por vosotros, nunca lo olvidéis. Por vosotros he sacrificado muchas cosas, incluido el terminar antes este doctorado del que habéis formado parte desde un principio. Sois lo que más quiero, recordadlo siempre.

A un ángel que me encontré en el difícil camino, cuando pensé no existían. Ya sabe quién es y que le estoy eternamente agradecida por su ayuda.

ÍNDICE

1. INTRODUCCIÓN

En este primer apartado, se presentan los objetivos de la tesis titulada —**Análisis del comportamiento de la corrosión de diferentes aleaciones níquel-cromo y cobalto-cromo en contacto con fluidos fisiológicos**. También se especifican las publicaciones científicas derivadas de esta investigación.

Al presentarse esta tesis doctoral por la modalidad de compendio de publicaciones, la justificación de la unidad temática se realiza a través de los distintos artículos, donde se destaca la relación entre ellos y se describe el trabajo realizado.

1.1. OBJETIVOS

Los biomateriales se utilizan hoy fundamentalmente en el campo de la medicina, donde para su aplicación en las personas se requiere que sean biocompatibles con el organismo humano y que sean capaces de realizar aquellas funciones para las que se utilizan. El objetivo principal de esta tesis es estudiar el comportamiento de la corrosión de diferentes aleaciones dentales que incluyen níquel-cromo y cobalto-cromo en su composición en contacto con fluidos fisiológicos a través de distintas técnicas de estudio de corrosión que permiten su análisis, así como su comparación con fines biomédicos.

La resistencia a la corrosión de una aleación es la característica más importante para su seguridad biológica, ya que muchos de los problemas de biocompatibilidad son consecuencia del proceso de corrosión del material.

El objetivo principal se alcanza a través de los siguientes objetivos específicos:

1. La caracterización electroquímica de las aleaciones de cobalto. Se realiza el estudio de varias aleaciones dentales con cobalto en su composición (cobalt base alloys) en disolución Ringer. Esta simula los fluidos fisiológicos. Se publican los resultados y conclusiones obtenidas tras someter los materiales a las diferentes pruebas electroquímicas de estudio de la corrosión, tanto en corriente continua como alterna.

2. El estudio de la corrosión de aleaciones de níquel. De igual forma, partiendo de varias aleaciones dentales comercialmente usadas con níquel en su composición (nickel base alloys), se realiza el estudio en disolución Ringer. Los resultados y conclusiones a los que se llegaron tras las diversas pruebas realizadas son publicados a nivel internacional.

3. El análisis y comparación de las aleaciones de níquel y cobalto, de forma conjunta. En disolución Ringer se llevan a cabo las distintas técnicas para el estudio de la corrosión de las diversas aleaciones, analizándose conjuntamente, evaluando, comparando y publicándose a nivel internacional los resultados y conclusiones de esta investigación.

1.2. PUBLICACIONES

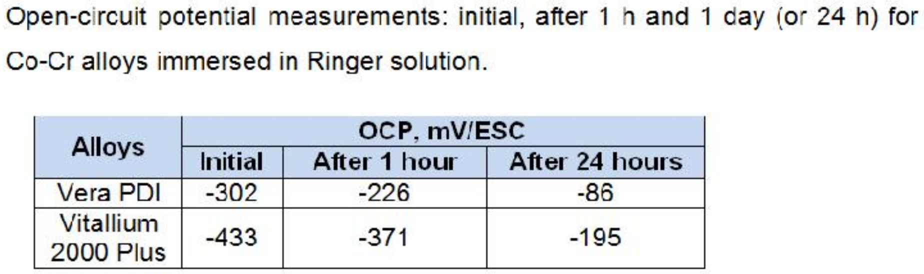
Las publicaciones científicas que se derivan de esta tesis doctoral son las que se presentan a continuación. Todas ellas han sido publicadas en revistas indexadas en el Journal Citations Reports, cumpliendo el requisito exigido para la presentación de esta tesis de que al menos una de ellas deberá haber sido publicada en una revista cuyo índice de impacto la sitúe dentro de la primera mitad en orden decreciente de índice de impacto. En este caso, las publicaciones de esta investigación cumplen el requisito. A continuación se presenta el resumen de cada publicación, siendo la primera autora o autora principal de las mismas.

Garcia-Falcon, C.M.; Gil-Lopez, T.; Verdu-Vazquez, A.; Mirza-Rosca, J.C. Electrochemical characterization of some cobalt base alloys in Ringer solution. Mater. Chem. Phys. **2021**, *260*, 124164.

Este artículo científico se centra en las aleaciones de cobalto. Para su uso como biomateriales es necesario un estudio a fondo que asegure que las aleaciones no causen daño al cuerpo humano. Teniendo en cuenta que la biocompatibilidad es muy estricta, el material no debe ser tóxico ni producir en el cuerpo alergias o inflamación. De las diferentes categorías de biomateriales metálicos, las aleaciones a base de cobalto se encuentran entre las opciones preferidas. Sus aplicaciones se pueden encontrar en los campos cardíaco y dental. Las aleaciones de Co-Cr se han utilizado en odontología para las coronas de porcelana fundida sobre metal (PFM) debido a su biocompatibilidad, resistencia al desgaste, larga duración, buenas propiedades mecánicas y, por último, pero no menos importante, debido a su superior resistencia a la corrosión. Esta investigación evaluó y comparó dos aleaciones dentales a base de Co-Cr (Vera PDI y Vitallium 2000 Plus), estudiando su caracterización microestructural así como su comportamiento frente a la corrosión en disolución Ringer, utilizando diversas técnicas.

Los hallazgos de esta investigación revelaron una alta tendencia a la pasivación de las dos aleaciones estudiadas, con la formación de capas protectoras mixtas $Cr_2O_3 \cdot CoO$ con una alta estabilidad, lo que mejora sustancialmente su biocompatibilidad en disolución Ringer. Los parámetros cinéticos del proceso de corrosión en el experimento indicaron un proceso con un control anódico, atribuible a la formación de películas pasivas en sus superficies. De acuerdo con los resultados obtenidos en esta investigación, la resistencia a la polarización de las dos aleaciones de Co-Cr examinadas en disolución Ringer alcanzó valores de biomateriales con alta resistencia a la corrosión y las películas pasivas formadas en sus superficies mostraron una resistencia más que adecuada.

A continuación se incluyen algunas de las tablas y figuras publicadas en el artículo, a modo de muestra.



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

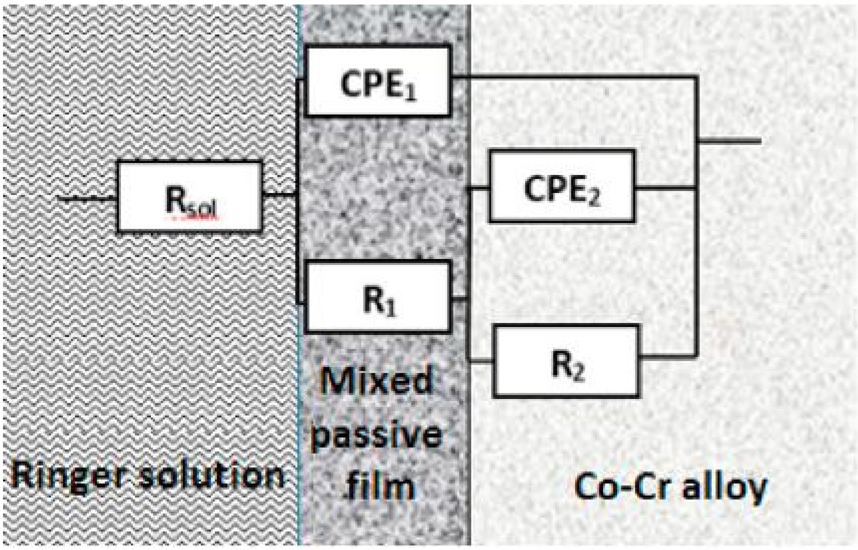
Alloys	OCP, mV/ESC		
	Initial	After 1 hour	After 24 hours
Vera PDI	-302	-226	-86
Vitallium 2000 Plus	-433	-371	-195

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

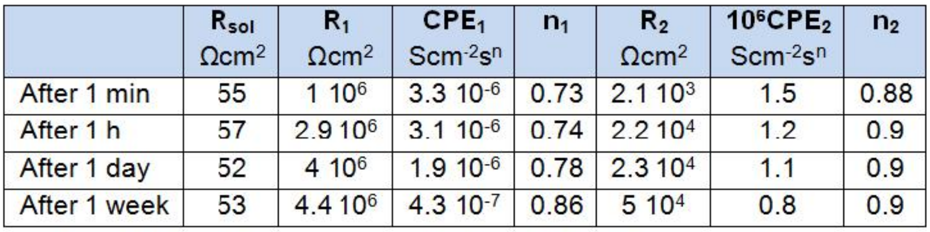
VITALLIUM 2000 PLUS	**E_{corr}** mV/SCE	**i_{corr}** µA/cm^2	b_A mV/ div	b_C mV/ div	**R_p** Ω cm^2	**Corrosion rate** µA/year
After 1 min immersion	-685	0.43	111	63	4.16 10^4	0.455
After 1 h immersion	-680	0.37	160	84	6.5 10^4	0.392
After 1 day immersion	-455	0.24	162	82	9.7 10^4	0.254
After 1 week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

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** µA/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

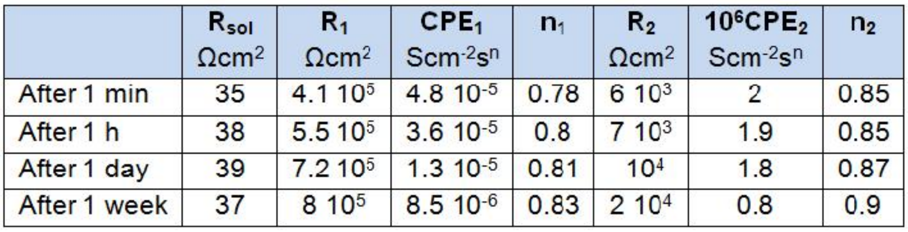


Fitted EIS parameters of the Vitallium 2000 Plus alloy in Ringer solution.



	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
After 1 min	55	$1\ 10^6$	$3.3\ 10^{-6}$	0.73	$2.1\ 10^3$	1.5	0.88
After 1 h	57	$2.9\ 10^6$	$3.1\ 10^{-6}$	0.74	$2.2\ 10^4$	1.2	0.9
After 1 day	52	$4\ 10^6$	$1.9\ 10^{-6}$	0.78	$2.3\ 10^4$	1.1	0.9
After 1 week	53	$4.4\ 10^6$	$4.3\ 10^{-7}$	0.86	$5\ 10^4$	0.8	0.9

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
After 1 min	35	$4.1\ 10^5$	$4.8\ 10^{-5}$	0.78	$6\ 10^3$	2	0.85
After 1 h	38	$5.5\ 10^5$	$3.6\ 10^{-5}$	0.8	$7\ 10^3$	1.9	0.85
After 1 day	39	$7.2\ 10^5$	$1.3\ 10^{-5}$	0.81	10^4	1.8	0.87
After 1 week	37	$8\ 10^5$	$8.5\ 10^{-6}$	0.83	$2\ 10^4$	0.8	0.9

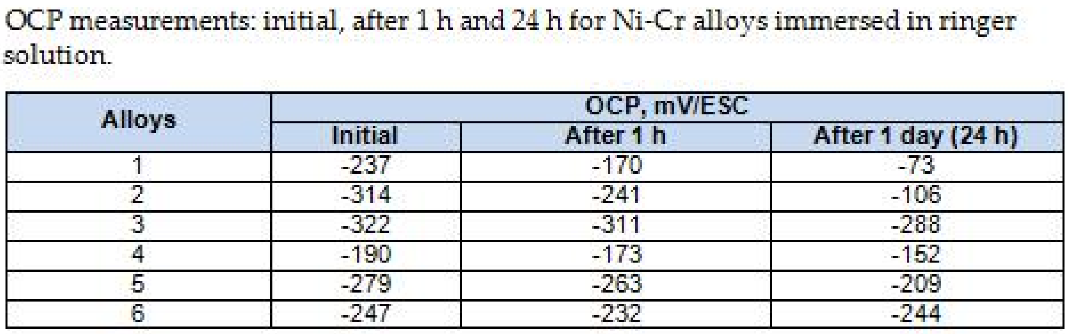
Este trabajo fue publicado en el mes de febrero del año 2021 en la revista Materials Chemistry and Physics (ISSN: 0254-0584, JCR-2020, Impact factor: 4.094, Q2 in the Category of Materials Science).

Garcia-Falcon, C.M.; Gil-Lopez, T.; Verdu-Vazquez, A.; Mirza-Rosca, J.C. Corrosion behavior in Ringer solution of several commercially used metal alloys. Anti-Corrosion Methods Mater. **2021**, *68*, 324–330.

Esta investigación se centra en las aleaciones de níquel. El propósito es analizar el comportamiento de corrosión de seis aleaciones a base de Ni (specimens 1-6), comercialmente utilizadas, que están presentes y se usan comúnmente como biomateriales metálicos, en disolución Ringer. Los especímenes para las pruebas se recibieron en forma de lingotes cilíndricos que fueron cortados para obtener cinco muestras por aleación, cilíndricas de 2 mm de altura, y proceder a su estudio. Las técnicas utilizadas en esta investigación fueron las de potencial de circuito abierto, estudios de polarización potenciodinámica y espectroscopía de impedancia electroquímica. Los hallazgos del estudio revelaron la tendencia a la pasivación de los diferentes especímenes. Además, cuando se compararon los materiales, se descubrió que el factor decisivo para una alta resistencia a la corrosión fue la concentración de cromo. Sin embargo, con un contenido de cromo similar, la mayor concentración de molibdeno aumentó la resistencia.

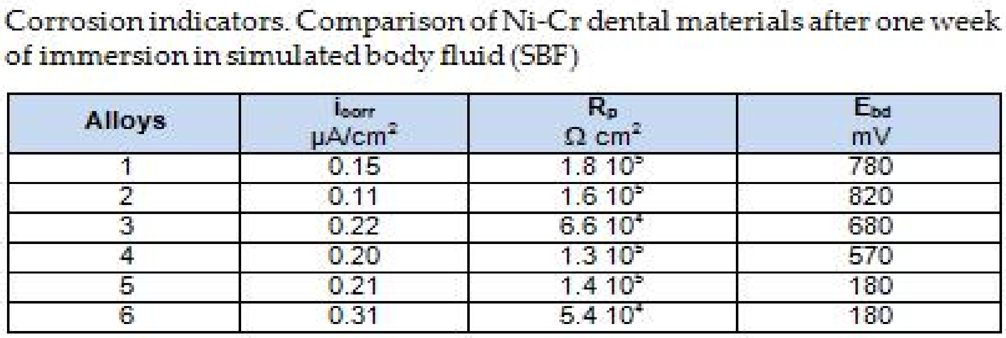
De acuerdo con los resultados obtenidos en esta investigación, la seguridad biológica de los materiales dentales estudiados en disolución Ringer se consideró muy alta para las muestras 1 y 2, y adecuada para las demás muestras de la investigación. La investigación existente sobre biomateriales dentales a base de Ni es muy escasa, y no se ha encontrado ninguna para estos materiales dentales utilizados comercialmente en disolución Ringer.

A continuación se incluyen algunas de las tablas y figuras publicadas en el artículo, a modo de muestra.



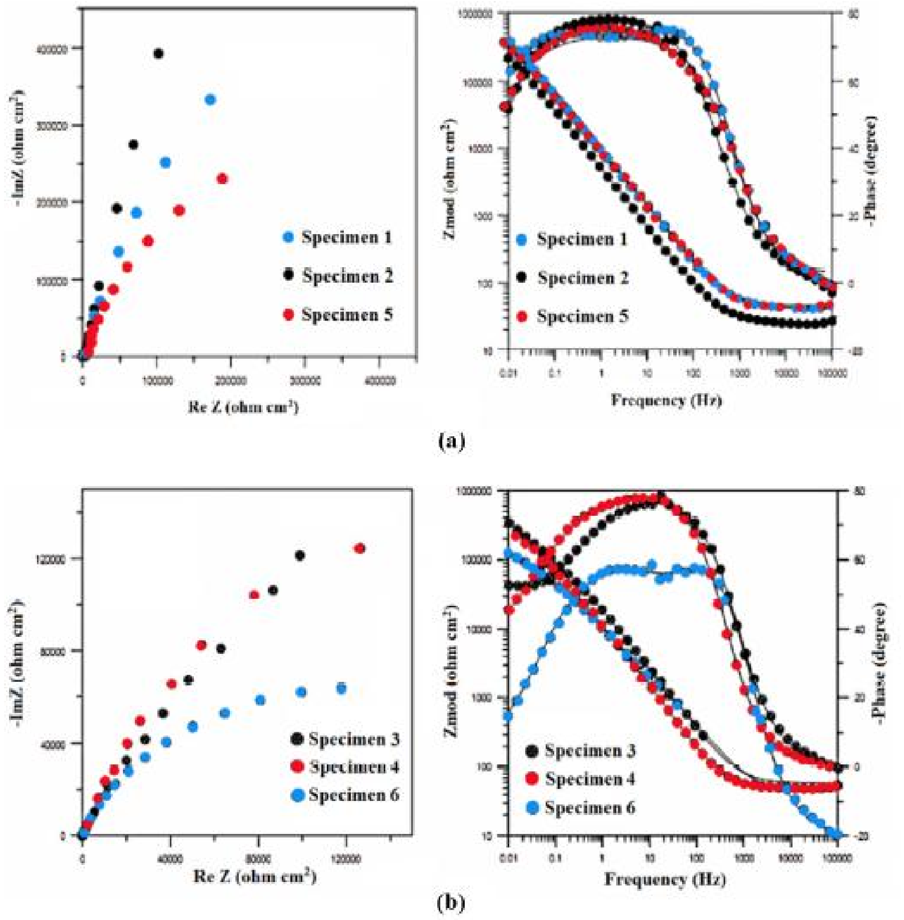
OCP measurements: initial, after 1 h and 24 h for Ni-Cr alloys immersed in ringer solution.

Alloys	OCP, mV/ESC		
	Initial	After 1 h	After 1 day (24 h)
1	-237	-170	-73
2	-314	-241	-106
3	-322	-311	-288
4	-190	-173	-152
5	-279	-263	-209
6	-247	-232	-244



Corrosion indicators. Comparison of Ni-Cr dental materials after one week of immersion in simulated body fluid (SBF)

Alloys	i_{corr} μA/cm^2	R_p Ω cm^2	E_{bd} mV
1	0.15	1.8 10^5	780
2	0.11	1.6 10^5	820
3	0.22	6.6 10^4	680
4	0.20	1.3 10^5	570
5	0.21	1.4 10^5	180
6	0.31	5.4 10^4	180



Representative Nyquist and Bode spectra after one day of immersion in Ringer solution

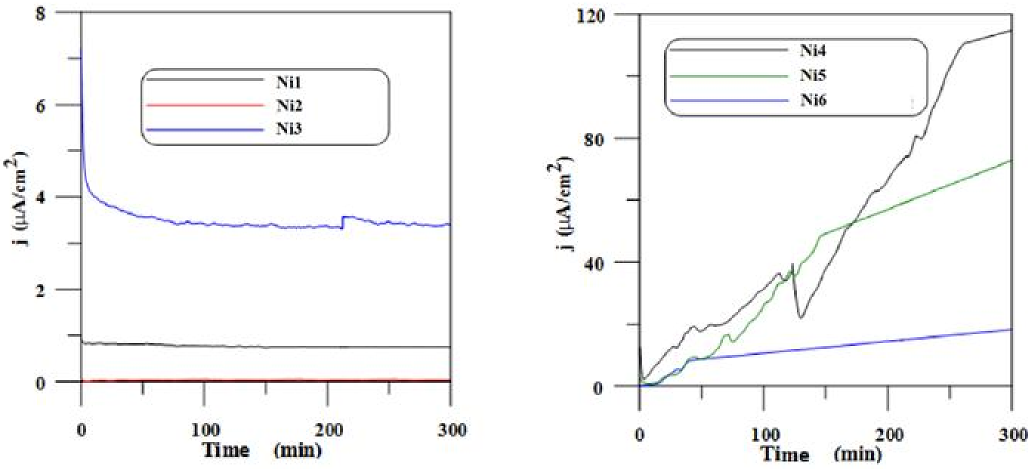
Este trabajo fue publicado en el mes de agosto del año 2021 en la revista Anti-Corrosion Methods and Materials (ISSN: 0003-5599, JCR-2020, Impact factor: 1.117**,** Q3 in the Category of Metallurgy & Metallurgical Engineering).

Garcia-Falcon, C.M.; Gil-Lopez, T.; Verdu-Vazquez, A.; Mirza-Rosca, J.C. Analysis and Comparison of the Corrosive Behavior of Nickel-Based and Cobalt-Based Dental Alloys. *Materials* **2021**, *14*, 4949.

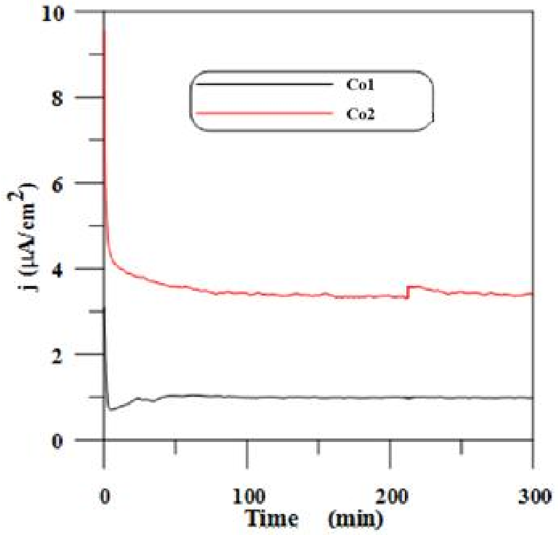
El tercer trabajo consiste en el análisis y comparación del proceso de corrosión en ambas aleaciones metálicas (a base de níquel y cobalto). Las aleaciones a base de níquel y cobalto son utilizadas con frecuencia en odontología. La introducción de varios elementos en la aleación modifica sus características, por lo que se debe realizar un estudio exhaustivo de cada aleación para determinar su adecuada resistencia a la corrosión y biocompatibilidad en contacto con fluidos fisiológicos. Existen escasas investigaciones sobre estas aleaciones dentales ampliamente utilizadas en disolución Ringer, y los hallazgos de esta investigación aportan nuevos datos experimentales e información. Este estudio evaluó y comparó el comportamiento frente a la corrosión de seis materiales dentales a base de NiCr y dos a base de CoCr en disolución Ringer, utilizando las siguientes técnicas: curvas de polarización potenciostática (cronoamperometría), análisis microestructural y EIS (espectroscopía de impedancia electroquímica).

Los resultados obtenidos en esta investigación mostraron que en los especímenes basados en NiCr Ni4, Ni5 y Ni6, la estabilidad de la capa pasiva se destruyó después de la polarización observándose un desarrollo y crecimiento de picadura en el análisis microestructural, después del tratamiento electroquímico. En términos de susceptibilidad a la corrosión, de esta investigación se derivaron dos grupos diferentes de especímenes. Un primer grupo que incluye las dos aleaciones de CoCr (Co1 y Co2) y tres de las seis aleaciones de NiCr estudiadas (Ni1, Ni2 y Ni3). Un segundo grupo con las otras aleaciones de NiCr investigadas Ni4, Ni5 y Ni6.

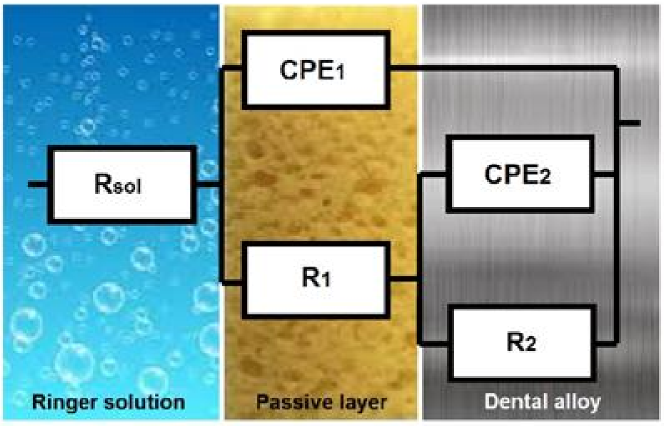
Al igual que en los anteriores, se incluyen algunas de las tablas y figuras publicadas en el artículo, a modo de muestra.



Potentiostatic polarization curves for specimens Ni1, Ni2, Ni3, Ni4, Ni5, and Ni6 in Ringer solution at a potential of 100 mV/ESC.



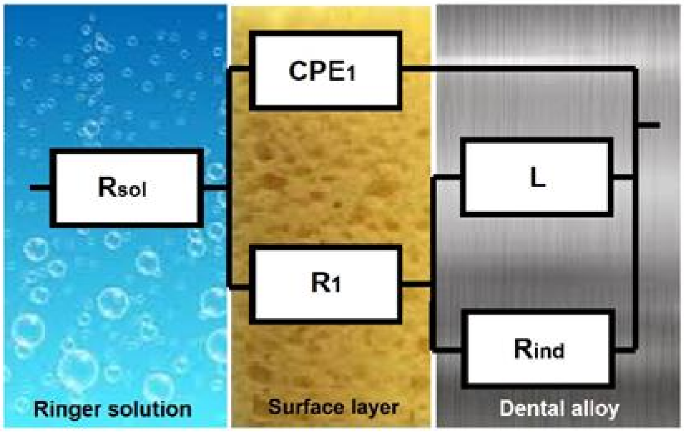
The potentiostatic polarization curves for specimens Co1 and Co2 in Ringer solution at a potential of 100 mV/ESC.



EC used to generate the simulated data for specimens Ni1, Ni2, Ni3, Co1, and Co2.

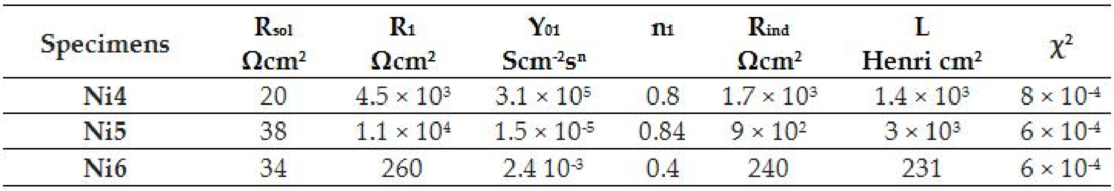
Main parameters of the EC used for specimens Ni1, Ni2, Ni3, Co1, and Co2.

Specimens	R_{sol} Ωcm^2	R_1 Ωcm^2	Y_{01} $Scm^{-2}s^n$	n_1	R_2 Ωcm^2	Y_{02} $Scm^{-2}s^n$	n_2	χ^2
Ni1	28	5×10^3	8.9×10^{-6}	0.83	5.5×10^5	9.7×10^{-6}	0.8	2×10^{-4}
Ni2	35	3×10^3	1.9×10^{-5}	0.9	6.2×10^5	1×10^{-5}	0.88	4×10^{-4}
Ni3	49	1.5×10^4	8.4×10^{-6}	0.89	5.9×10^5	7.1×10^{-6}	0.82	5×10^{-4}
Co1	37	1.5×10^4	7.8×10^{-6}	0.9	9.1×10^5	8.3×10^{-6}	0.83	2×10^{-4}
Co2	55	1.4×10^4	6.1×10^{-6}	0.9	1.2×10^6	8.6×10^{-6}	0.83	6×10^{-4}



EC used to generate the simulated data for specimens Ni4, Ni5, and Ni6.

Main parameters of the EC used for specimens Ni4, Ni5, and Ni6.



Specimens	R_{sol} Ωcm²	R_1 Ωcm²	Y_{01} $Scm^{-2}s^n$	n_1	R_{ind} Ωcm²	L Henri cm²	χ^2
Ni4	20	4.5×10^3	3.1×10^5	0.8	1.7×10^3	1.4×10^3	8×10^{-4}
Ni5	38	1.1×10^4	1.5×10^{-5}	0.84	9×10^2	3×10^3	6×10^{-4}
Ni6	34	260	$2.4\ 10^{-3}$	0.4	240	231	6×10^{-4}

Este trabajo fue publicado en el mes de agosto del año 2021 en la revista Materials (ISSN: 1996-1944, JCR-2020, Impact factor: 3.92, Q1 in Category of Metallurgy & Metallurgical Engineering).

1.3. JUSTIFICACIÓN

El objeto de la tesis se encuadra dentro de las siguientes líneas de investigación del programa de doctorado en Ingeniería Química, Mecánica y de Fabricación:

- ✓ Nanomateriales.

- ✓ Corrosión de los metales.
- ✓ Biomateriales para aplicaciones de ingeniería médica.

Los biomateriales se utilizan en aplicaciones médicas, en contacto con tejido vivo. Para ello, deben ser minuciosamente estudiados para asegurarse de que no causen ningún daño al cuerpo. La investigación en biomateriales es interdisciplinaria y requiere el esfuerzo y la colaboración de ingenieros, patólogos, ingenieros biomédicos, y clínicos.

Los biomateriales metálicos se clasifican en cuatro categorías: aleaciones a base de cobalto, aceros inoxidables, aleaciones a base de titanio y otros varios [1,2]. La aplicación médica específica determina la elección de un biomaterial. De las diferentes categorías de biomateriales metálicos presentados, las aleaciones a base de cobalto y de níquel son comunes y se encuentran entre las opciones escogidas, con aplicaciones diversas, en implantes ortopédicos así como en los campos cardíaco y dental. En el dental, composites, polímeros, cerámicas y metales/aleaciones son biomateriales posibles [3].

La investigación realizada se centra en las aleaciones metálicas a base de níquel y cobalto puesto que se utilizan con frecuencia y a nivel mundial en odontología para restauraciones protésicas, debido a sus características ventajosas [4,5,6,7,8,9,10,11].

El níquel en una aleación puede causar reacciones alérgicas y toxicidad, según algunos estudios [12,13,14,15,16], pero otros reportan resultados y conclusiones muy diferentes [17,18,19]. Además, la introducción de cromo en su composición favorece la estabilidad de la aleación para ser utilizada como biomaterial [20,21]. Según varias investigaciones, el porcentaje de cromo que se encuentra en la aleación es un factor decisivo en la formación de la capa pasiva y la resistencia a la corrosión [22,23,24].

Las aleaciones a base de cobalto son biomateriales de uso frecuente con aplicaciones en el campo dental y cardíaco, así como en implantes ortopédicos [25,26], debido a las considerables propiedades de resistencia al desgaste y a la corrosión que otorga este elemento metálico [27,28].

Como materiales dentales se utilizan para coronas con porcelana fundida al metal [29,30,31,32,33], en prótesis dentales fijas y removibles [34,35,36,37,38], cables de ortodoncia [39, 40], implantes orales [41,42,43], y son muy adecuados en pacientes cuya exposición al níquel podría provocar una reacción alérgica [44,45].

La introducción de otros elementos en la aleación varía sus características. Como ejemplo, se ha informado que el contenido de molibdeno aumenta la resistencia a la corrosión de las aleaciones [23,24] y su idoneidad para ser utilizado en el cuerpo humano [22] como biomaterial.

Por lo tanto, era necesario realizar un estudio exhaustivo de cada aleación para determinar su resistencia a la corrosión y su biocompatibilidad.

Las aleaciones estudiadas en esta investigación, ya sea a base de níquel o de cobalto, todas tenían cromo en su composición, lo que las hace supuestamente estables y seguras para ser utilizadas como aleaciones dentales y se encuentran en los mercados mundiales para restauraciones protésicas. Sin embargo, no todas las aleaciones tienen la misma biocompatibilidad en contacto con fluidos fisiológicos.

La resistencia a la corrosión es el factor más importante a tener en cuenta, ya que debido al proceso de corrosión se liberan elementos hacia la cavidad oral, ocasionando problemas que dificultan la seguridad biológica [46,47]. Ciertamente, los materiales en contacto con el tejido humano no deben ser tóxicos ni causar alergias o inflamaciones para ser biocompatibles [48].

En consecuencia, para poder utilizar con seguridad estas aleaciones de NiCr y CoCr, se debe realizar un análisis exhaustivo de su comportamiento frente a la corrosión.

Los resultados de estas investigaciones aportan nuevos datos experimentales e información sobre aleaciones dentales de NiCr y CoCr mundialmente utilizadas en contacto con los fluidos corporales simulados.

La primera publicación se centra en las aleaciones de cobalto, la segunda en las de níquel y la tercera en un análisis y comparación de ambas de forma conjunta, como se ha indicado con anterioridad. Por consiguiente, las tres publicaciones científicas realizadas no sólo justifican, sino que refuerzan claramente la unidad temática de la tesis, estando todas dentro de las líneas de investigación anteriormente mencionadas del programa de doctorado QUIMEFA.

Los hallazgos más relevantes de la investigación se incluyen más adelante en el capítulo 3.

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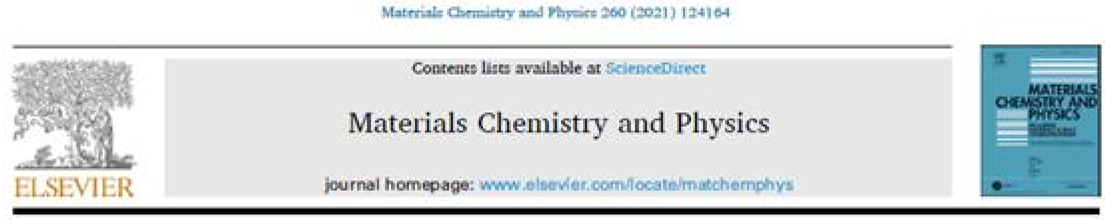

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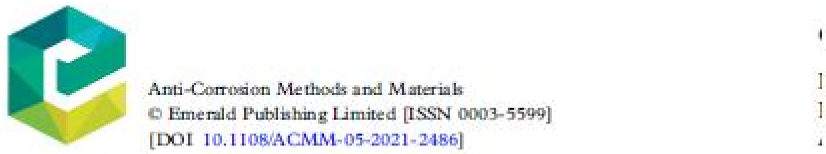
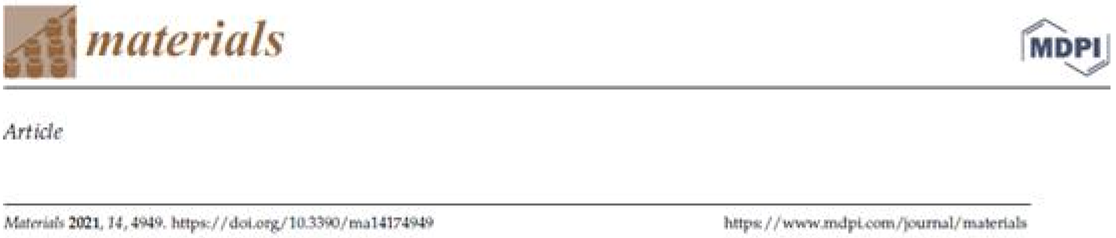


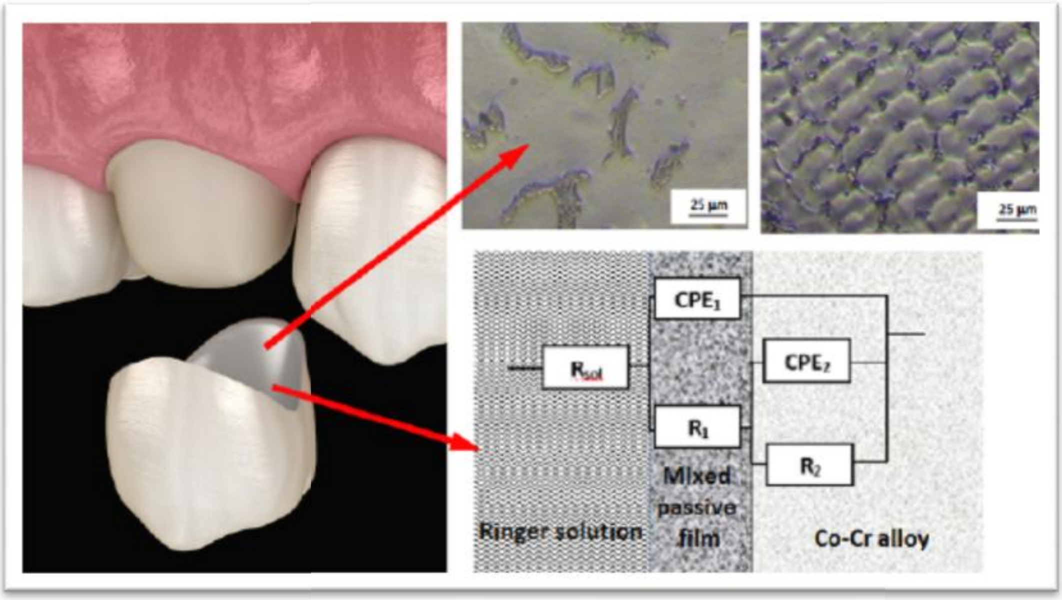
Anti-Corrosion Methods and Materials
© Emerald Publishing Limited [ISSN 0003-5599]
[DOI 10.1108/ACMM-05-2021-2486]



Article

Materials **2021**, *14*, 4949. https://doi.org/10.3390/ma14174949 https://www.mdpi.com/journal/materials

Electrochemical characterization of some cobalt base alloys in Ringer solution


25 µm
25 µm
CPE₁
R_sol
R₁
CPE₂
R₂
Ringer solution
Mixed passive film
Co-Cr alloy

Materials Chemistry and Physics 260 (2021) 124164

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Electrochemical characterization of some cobalt base alloys in Ringer solution

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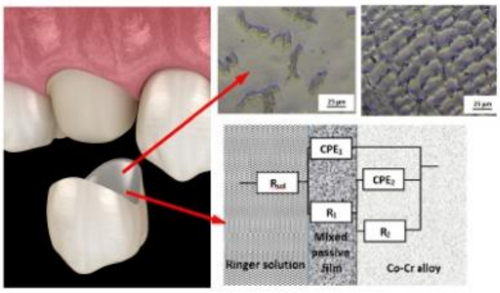
HIGHLIGHTS

- 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 $Cr_2O_3 \cdot CoO$.
- The high stability of passive film substantially improves their biocompatibility.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Metal alloys
Co–Cr
Dental materials
Corrosion
Ringer solution

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 $Cr_2O_3 \cdot CoO$ 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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https://doi.org/10.1016/j.matchemphys.2020.124164
Received 7 September 2020; Received in revised form 7 December 2020; Accepted 10 December 2020

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.

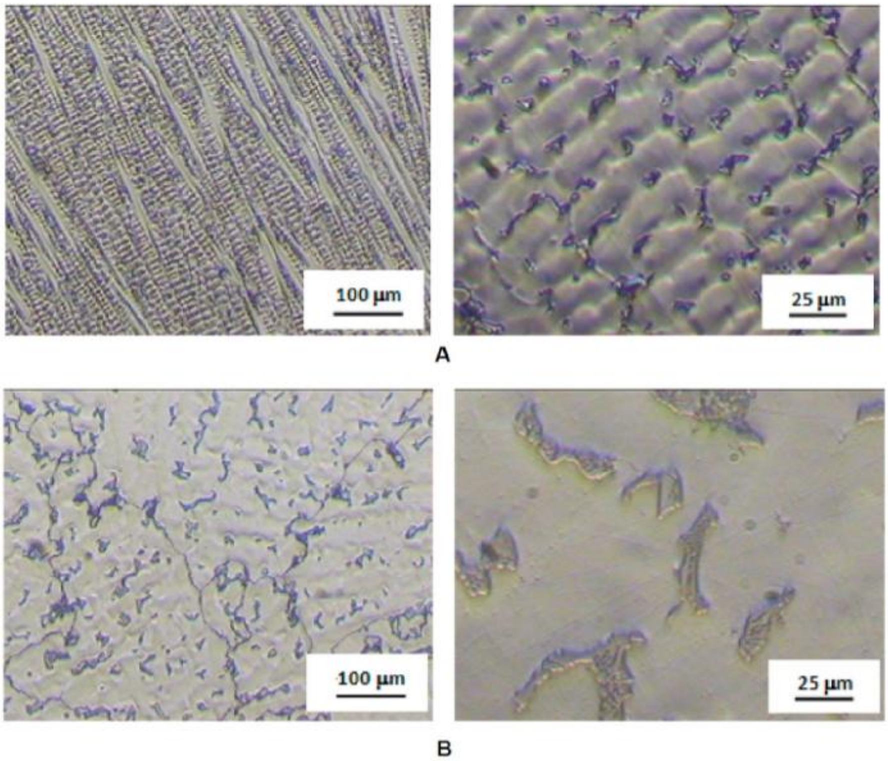


Fig. 1. Metallography analysis: (A)- Vitallium 2000 Plus alloy, (B)- Vera PDI alloy.

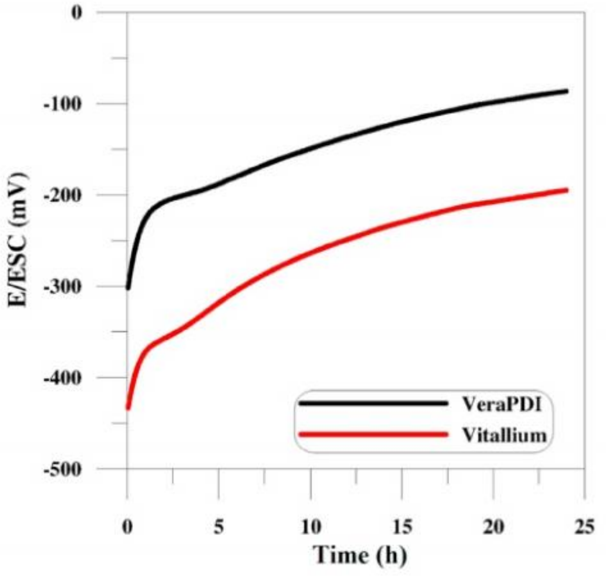


Fig. 2. Open-circuit potential variation versus time immersion in Ringer Solution for Vera PDI and Vitallium 2000 Plus.

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]:

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

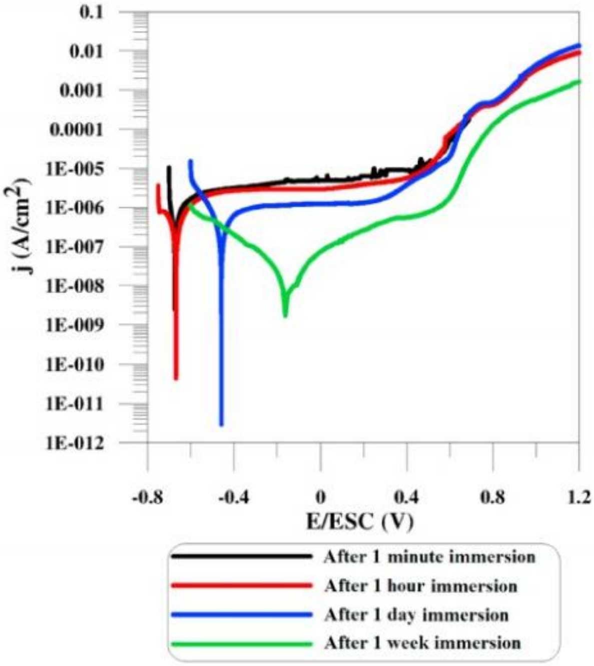


Fig. 3. Polarization curves for Vitallium 2000 Plus dental alloy at different immersion times in Ringer solution.

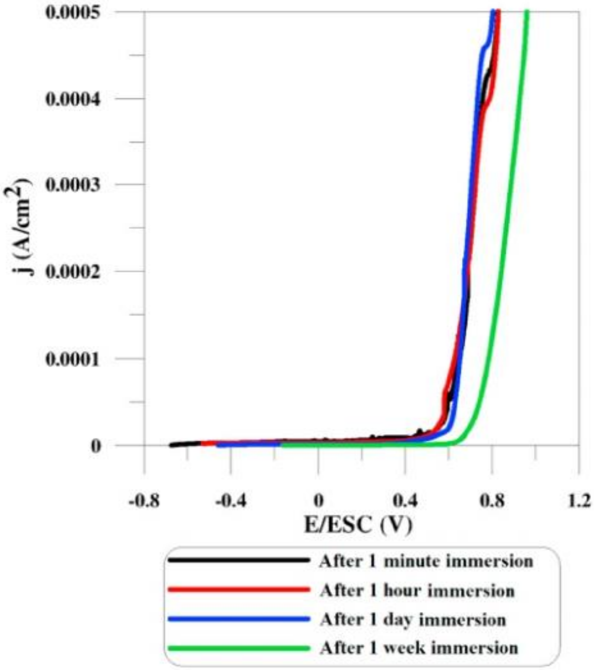


Fig. 4. Potentiodynamic anodic polarization curves for Vitallium 2000 Plus at different immersion times in Ringer solution.

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.

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

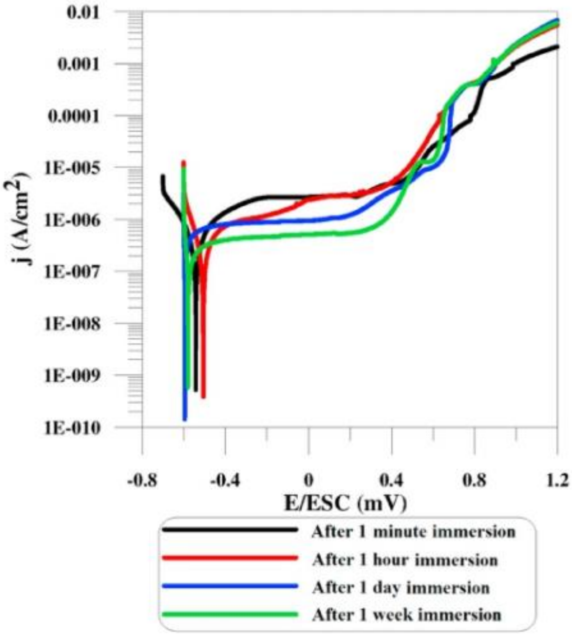


Fig. 5. Polarization curves for Vera PDI dental alloy at different immersion times in Ringer solution.

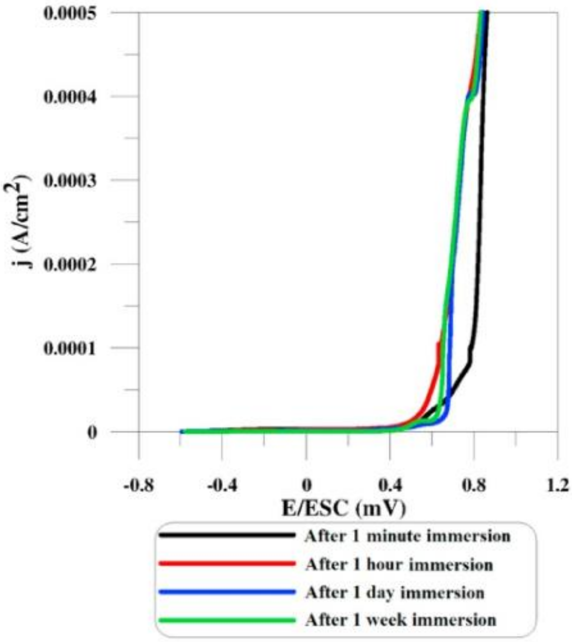


Fig. 6. Potentiodynamic anodic polarization curves at different immersion times in Ringer solution for Vera PDI dental alloy.

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]:

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

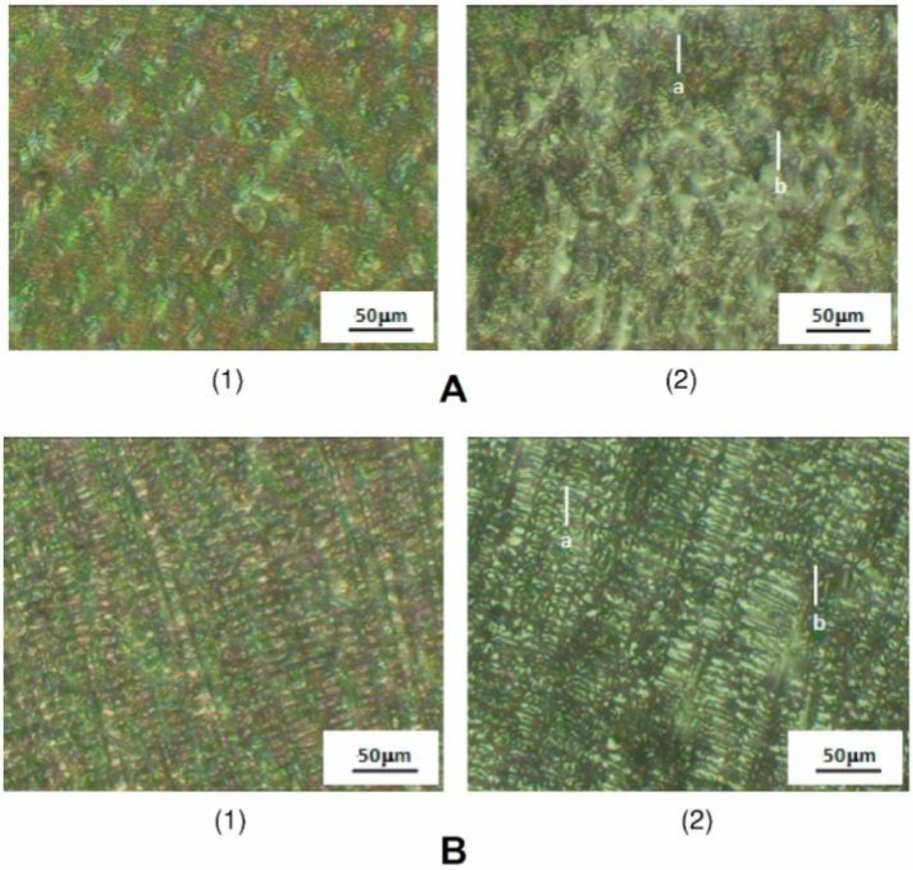
The large amount of cobalt promoted the formation of a passive film, following the reaction:

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

This meant that on the surface of the alloys there was a mixed passive film formed, $Cr_2O_3{\cdot}CoO$. 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



(1) **A** (2)

(1) **B** (2)

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

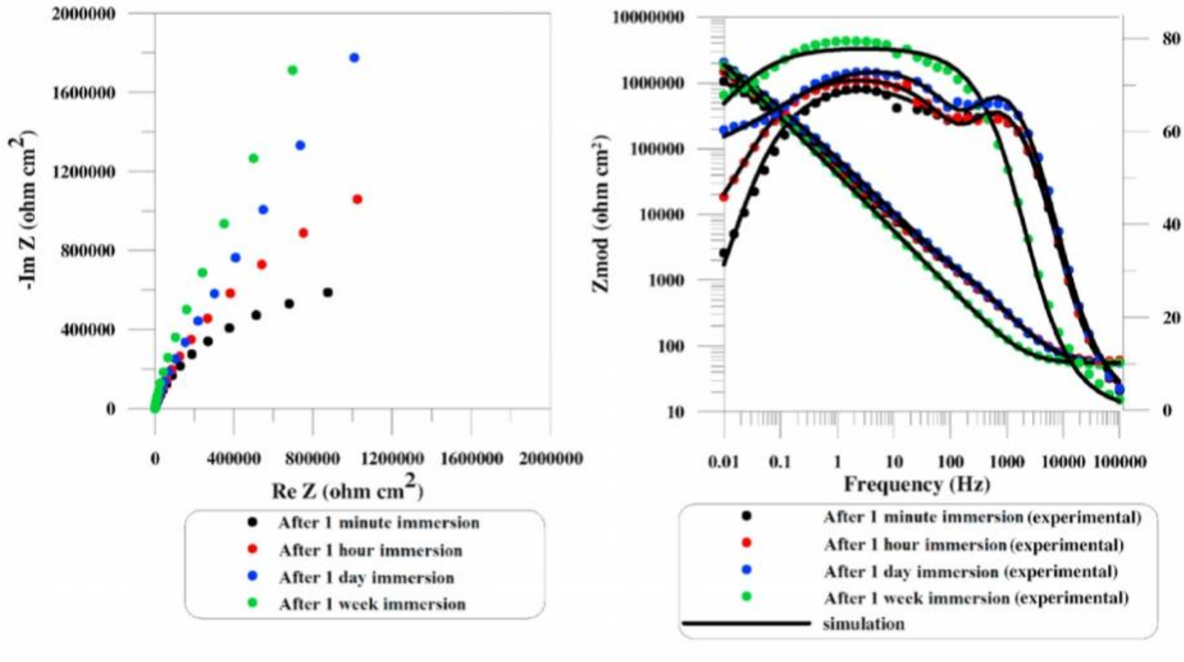


Fig. 8. Representative Nyquist and Bode spectra for Vitallium 2000 Plus alloy after 1 min, 1 h, 24 h, and 1 week of immersion in Ringer solution.

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

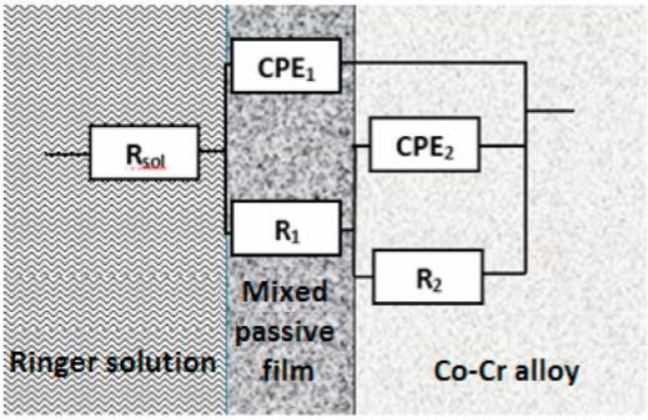


Fig. 9. The equivalent circuit used to fit the experimental impedance data.

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 $Cr_2O_3 \cdot CoO$ 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	$10^6 CPE_2$ $Scm^{-2}s^n$	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	$6\ 10^{-4}$

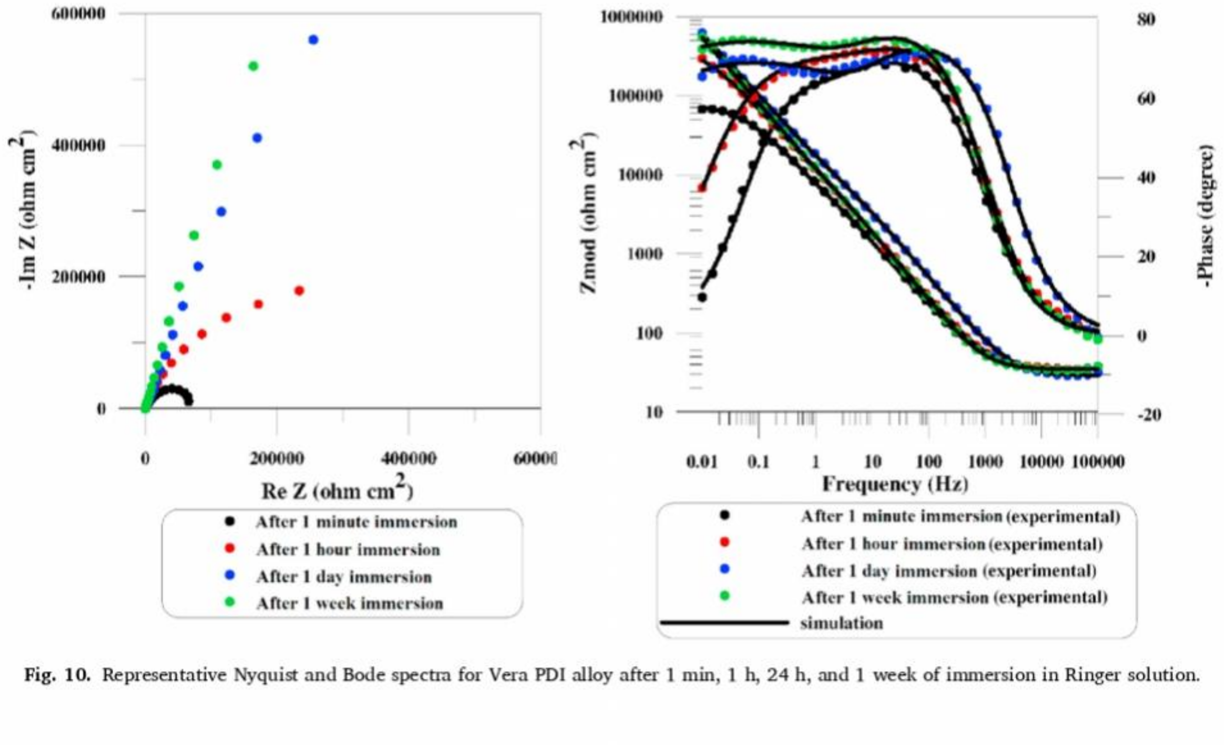


Fig. 10. Representative Nyquist and Bode spectra for Vera PDI alloy after 1 min, 1 h, 24 h, and 1 week of immersion in Ringer solution.

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	$10^6 CPE_2$ $Scm^{-2}s^n$	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.

Acknowledgments

The authors acknowledge Dr. Daniel Mareci from the "Gheorghe Asachi" Technical University of Iasi, Romania, for providing the materials and his valuable advice.

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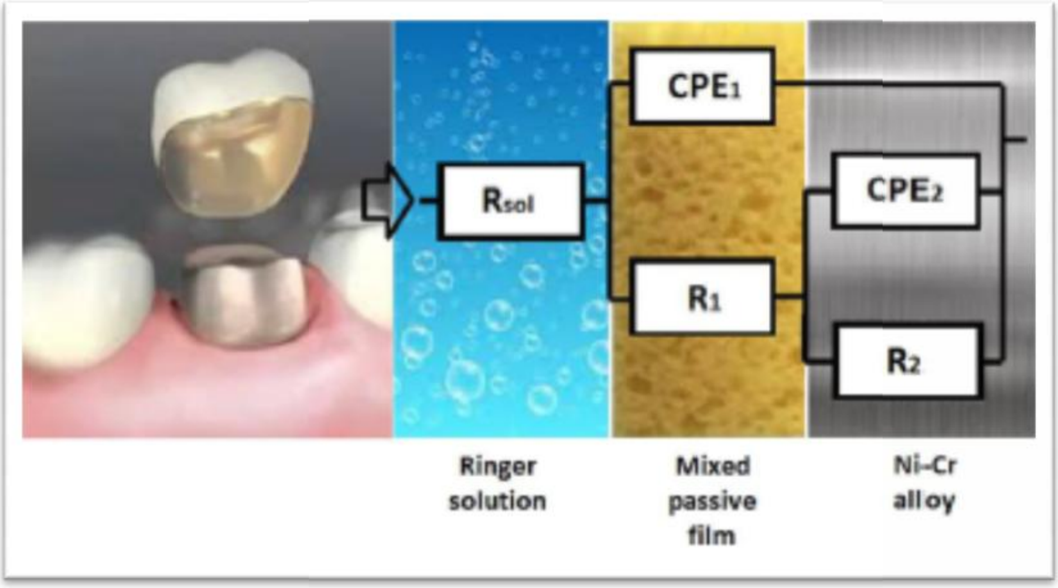
Corrosion behavior in Ringer solution of several commercially used metal alloys



Rsol
CPE1
R1
CPE2
R2
Ringer solution
Mixed passive film
Ni-Cr alloy

Corrosion behavior in Ringer solution of several commercially used metal alloys

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Abstract

Purpose – This paper aims to analyze the corrosion behavior in Ringer solution of six commercially used Ni-based alloys that are present and commonly used as metallic biomaterials.

Design/methodology/approach – The specimens were received in the form of cylindrical ingots and were cut to get five samples of each brand with a cylindrical shape of 2 mm height to conduct the study. In this scientific research, the following techniques were used: open circuit potential, potentiodynamic polarization studies, and electrochemical impedance spectroscopy.

Findings – The study findings revealed the passivation tendency of the different specimens. Additionally, when the materials were compared, it was discovered that the decisive factor for high corrosion resistance was the chromium concentration. However, with similar chromium content, the stronger concentration in molybdenum increased the resistance. According to the results obtained in this investigation, the biological safety of the dental materials studied in Ringer solution was considered very high for specimens 1 and 2, and adequate for the other samples.

Originality/value – Metal alloys used as biomaterials in contact with the human body should be deeply investigated to make sure they are biocompatible and do not cause any harm. The corrosion resistance of an alloy is the most important characteristic for its biological safety, as all problems arise because of the corrosion process. There is scarce investigation in these Ni-based dental biomaterials, and none found in these commercially used dental materials in Ringer solution.

Keywords Nickel-based alloys, Metallic biomaterials, Corrosion, Passivity, Dental materials, Ringer solution

Paper type Research paper

1. Introduction

There are many possible alloys for prosthetic restorations (Lee *et al.*, 2006; Mareci *et al.*, 2008; Mareci *et al.*, 2010; Souza *et al.*, 2019), and among them Ni-based alloys are typically used in porcelain fused to metal (PFM) and casting crowns and bridges. This is due to the easy manufacturing procedure, availability, low price and last but certainly not least, corrosion resistance of these metallic biomaterials. Nickel-based alloys containing chromium develop a thin protective oxide layer on their surfaces, although they show unstable galvanic corrosion (Gushcha *et al.*, 2019; Taher and Al Jabab, 2003). Certainly, the body environment is complex and presents difficult challenges regarding corrosion control that may be experienced by metallic biomaterials (Eliaz, 2019). The resistance to corrosion of an alloy is the most important characteristic for its biological safety, as all problems (local toxicity, allergies, etc.) arise from the elements released into the mouth because of the corrosion process (Rupp *et al.*, 2018). Electrochemical studies for a limited number of Ni-Cr dental materials in artificial saliva medium were conducted by our group (Mareci *et al.*, 2007; Mareci *et al.*, 2008; Mareci *et al.*, 2010), and we are now investigating in simulated body fluid (Ringer solution). We have recently presented the study of Co-Cr dental materials in Ringer solution (Garcia-Falcon *et al.*, 2021).

Nickel was found to be highly toxic with epithelial cells and fibroblasts (Hornez *et al.*, 2002). However, contradictory results were reported (Alp *et al.*, 2018; Craig and Hanks, 1988; Craig and Hanks, 1990; McGinley *et al.*, 2013; López-Alías *et al.*, 2006). Additionally, to improve clinical characteristics,

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Author contributions: conceptualization, C.M. Garcia-Falcon; writing – original draft, C.M. Garcia-Falcon; methodology, C.M. Garcia-Falcon and T. Gil-Lopez; investigation, C.M. Garcia-Falcon and T. Gil-Lopez; validation, T. Gil-Lopez; formal analysis, C.M. Garcia-Falcon and T. Gil-Lopez; data curation, T. Gil-Lopez and A. Verdu-Vazquez; writing – review and editing, A. Verdu-Vazquez; software, J.C. Mirza-Rosca; and supervision, J.C. Mirza-Rosca. All authors have read and agreed to the published version of the manuscript. Please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

Funding: This research received no external funding.

Conflicts of interest: The authors declare no conflict of interest.

Received 1 June 2021
Revised 25 June 2021
Accepted 25 June 2021

The current issue and full text archive of this journal is available on Emerald Insight at: **https://www.emerald.com/insight/0003-5599.htm**

Anti-Corrosion Methods and Materials
© Emerald Publishing Limited [ISSN 0003-5599]
[DOI 10.1108/ACMM-05-2021-2486]

manufacturers produced by casting or SLM (Selective Laser Melting) Ni-Cr alloys with an increased percentage of nickel (Honga *et al.*, 2019).

Although nickel allergies are common, it is clear that the use of Ni-Cr alloys in the oral cavity does not always cause an allergic reaction. Nickel is an essential element, with approximately 10 mg contained in the human body, and adults consume between 79 and 105 micrograms of nickel per day from dietary sources and supplements (Insel *et al.*, 2018). The methods used in measuring and predicting how the body responds to dental alloys remain to some extent unsuccessful, as well as confusing and controversial. However, what is clear is that allergies to alloys cannot occur if there is no corrosion and the corresponding release of metal ions.

Ni-Cr dental alloys are available and commonly used. This investigation evaluated and compared six commercially used nickel–chromium dental materials manufactured in Germany, Romania and the USA. Their corrosion behavior in Ringer solution was analyzed using various techniques: open circuit potential (OCP), potentiodynamic polarization studies and electrochemical impedance spectroscopy (EIS). In service conditions, these metal alloys are in contact with the physiological fluids. Corrosion products may cause not only local reactions but also systemic reactions that could affect the body's immune system. For this reason, it is imperative to know the corrosion behavior of these metal alloys in Ringer solution.

Table 1 Composition of the used nickel-based alloys

	Composition (Wt%)								
SPECIMENS	**Ni**	**Cr**	**Mo**	**Fe**	**Nb**	**Si**	**Cu**	**Mn**	**Al**
1	60.1	24.3	10.1	2.1	1	–	–	2	–
2	60.8	23.9	8.8	2.4	3.8	–	–	–	–
3	63.4	23.2	3	9	–	1	–	–	–
4	72.1	20	–	7.5	–	–	–	–	–
5	64.9	17.9	–	–	–	1.8	9.9	3.6	1.5
6	53.4	14.4	–	–	–	1.5	9.5	19.4	1.6

2. Materials and methods

Six commercial Ni-Cr alloys used in dental medicine were studied: three manufactured in Germany, two in Romania and one in the USA. The dental materials will be hereinafter referred to as specimens 1–6. Their composition can be found in the Table 1.

The specimens were received in the form of cylindrical ingots, with a diameter of 11.2 mm and a height between 1.2 and 2.5 cm, depending on the brand. Specimens were cut along a plane at right angles to the axis of the cylinders, to get five samples of each brand with a cylindrical shape of 2 mm height and were then embedded into epoxy resin disks. Deionized water was used to ultrasonically clean, after grinding with 320 to 2,500 grit silicon carbide (SiC) abrasive papers and polishing with 1 μm suspension of alumina for a smooth reflective finish, techniques used to prepare the test specimens.

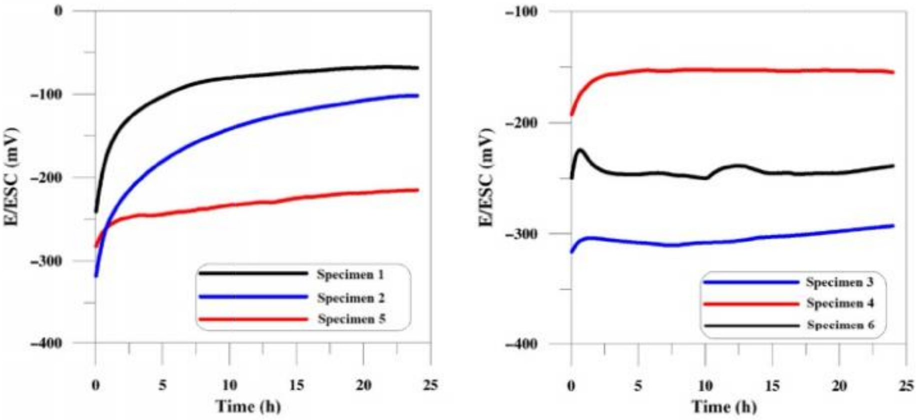
The Ringer solution had the following composition: NaCl (6.8 g/L), KCl (0.4 g/L), $CaCl_2$ (0.2 g/L), $NaCO_3H$ (1 g/L), glucose (1 g/L), $MgSO_4 \cdot 7H_2O$ (0.2 g/L) and $NaH_2PO_4 \cdot H_2O$ (0.14 g/L).

Using a Pt-grid as auxiliary or counter electrode in a conventional electrochemical cell of three electrodes, electrochemical measurements were performed. As reference electrode, the saturated calomel electrode (SCE) was used. Connected to a computer with a lock-in amplifier PAR 5210 (Princeton Applied Research, USA), a PAR model 263 A potentiostat was used, using PAR software Electrochemistry Power Suite. The measurements complied with the test procedures and methods provided by the ISO standard for Dentistry, to analyze the corrosion behavior in the oral environment of metallic materials (ISO 10271:2020, Dentistry–Corrosion test methods for metallic materials).

OCP measurements during 24 h were performed, followed by linear potentiodynamic polarization measurements, using a 0.5 mV/s scanning rate, stepping the potential from −600 mV to +1200 mV (SCE). The PowerCorr software was used to collect and process the experimental data.

Linear potentiodynamic polarization studies were conducted to identify the Tafel slopes (b_A and b_C) for the partial anodic

Figure 1 OCP variation with time



(a) (b)

Notes: (a) specimens 1, 2 and 5; (b) specimens 3, 4 and 6 and cathodic processes, using a 0.25 mV/s scanning rate, from E_{OCP} −150 mV to E_{OCP} +150 mV. The passivation process was evaluated from −600 mV to +1200 mV (SCE), at a scan rate of 0.5 mV/s. The potentiostat used for the tests was from Princeton Applied Research, as well as the PowerCorr software used to process the data. The potentiodynamic polarization curves and breakdown potential were also obtained from the experimental information.

Table 2 OCP measurements: initial, after 1 h and 24 h for Ni-Cr alloys immersed in ringer solution

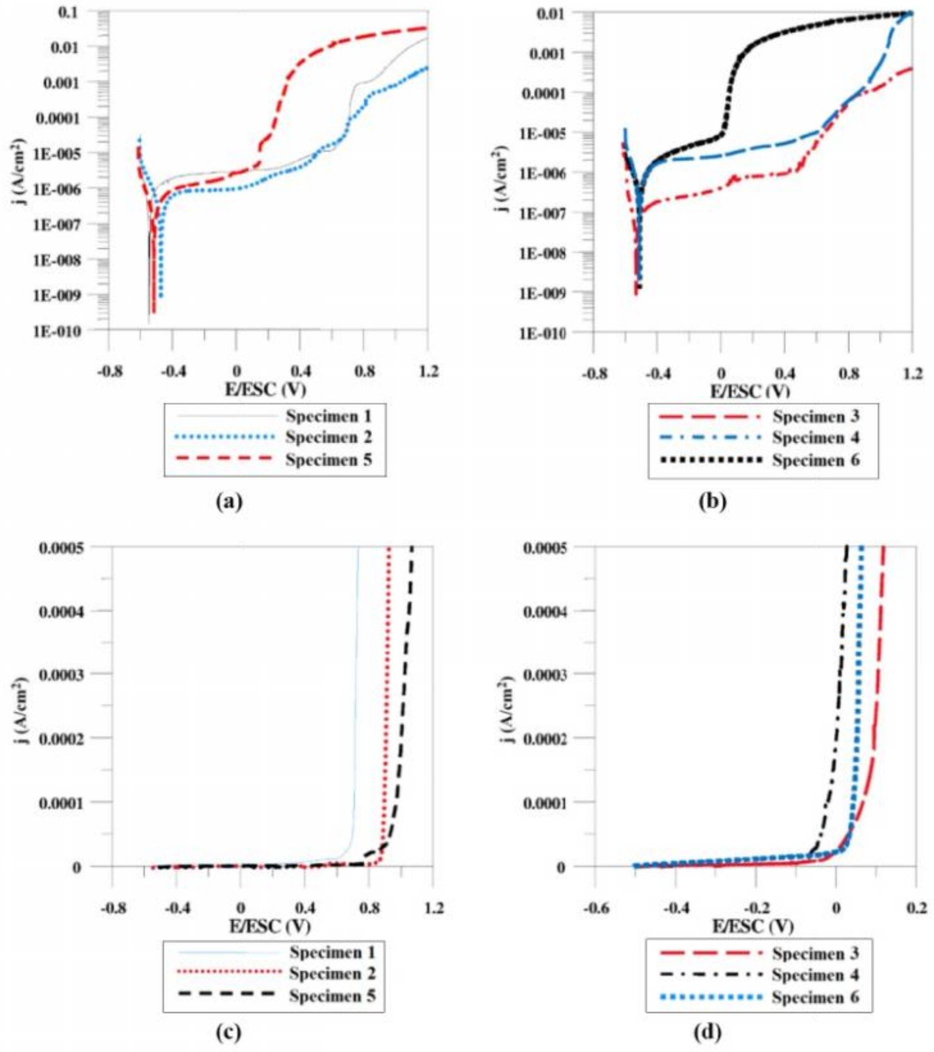
	OCP, mV/ESC		
Alloys	**Initial**	**After 1 h**	**After 1 day (24 h)**
1	−237	−170	−73
2	−314	−241	−106
3	−322	−311	−288
4	−190	−173	−152
5	−279	−263	−209
6	−247	−232	−244

The alternating current impedance spectra for the six alloys were carried out at the OCP in the aerated solution. The spectra were recorded in the 10^{-2} Hz to 10^{5} Hz frequency range, with an amplitude of 10 mV.

The EIS tests were performed after 24 h of immersion at the OCP to examine the corrosion resistance of the alloys studied.

The results were analyzed using ZSimp Win (PAR software), and the relevant equivalent circuit was obtained, having the simulated responses and measured data well-fitted. Impedance data was displayed as Nyquist plot, Bode |Z| and Bode phase diagrams, following each experiment. The tests were performed three times.

Figure 2 Polarization curves



Notes: (a) specimens 1, 2 and 5; (b) specimens 3, 4 and 6; potentiodynamic anodic polarization curves: (c) specimens 1, 2 and 5; (d) specimens 3, 4 and 6. After one-day immersion in Ringer solution

Table 3 Electrochemical parameters of the dental alloys at different immersion times in ringer solution

Specimens		i_{corr} µA/cm^2	R_p Ωcm^2	b_A mV/DIV	b_C mV/DIV	i_{pass} µA/cm^2	E_{bd} mV
1	After 1 min	0.23	$9.2\ 10^4$	188	68	4.21	500
	After 1 h	0.21	$1.1\ 10^5$	174	72	3.18	500
	After 1 day	0.20	$1.2\ 10^5$	157	88	4.14	620
2	After 1 min	0.21	$9.2\ 10^4$	128	66	2.4	720
	After 1 h	0.17	$1.1\ 10^5$	116	68	1.3	680
	After 1 day	0.13	$1.5\ 10^5$	118	70	3.5	820
3	After 1 min	0.78	$2.8\ 10^4$	140	79	10.23	620
	After 1 h	0.66	$3.9\ 10^4$	150	97	12.1	480
	After 1 day	0.58	$4.2\ 10^4$	163	85	4.66	680
4	After 1 min	0.65	$2.9\ 10^4$	129	66	5.62	650
	After 1 h	0.39	$3.9\ 10^4$	124	131	3.98	410
	After 1 day	0.30	$8.2\ 10^5$	136	95	2.58	570
5	After 1 min	0.76	$3.3\ 10^4$	178	85	4.60	160
	After 1 h	0.43	$7.1\ 10^4$	175	117	3.48	160
	After 1 day	0.25	$9.1\ 10^4$	170	74	4.79	160
6	After 1 min	0.92	$1.5\ 10^4$	174	39	8.3	70
	After 1 h	0.90	$1.9\ 10^4$	156	54	8.6	130
	After 1 day	0.63	$2.5\ 10^4$	162	47	10.1	40

Table 4 Corrosion indicators. Comparison of Ni-Cr dental materials after one week of immersion in simulated body fluid (SBF)

Alloys	i_{corr} µA/cm^2	R_p Ω cm^2	E_{bd} mV
1	0.15	$1.8\ 10^5$	780
2	0.11	$1.6\ 10^5$	820
3	0.22	$6.6\ 10^4$	680
4	0.20	$1.3\ 10^5$	570
5	0.21	$1.4\ 10^5$	180
6	0.31	$5.4\ 10^4$	180

3. Results

The different specimens in this investigation were divided into two groups according to the greater similarity of the analyzed properties. This categorization was useful for the comprehensive interpretation of the graphs and the full analysis of the results.

3.1 Open circuit potential

Figure 1 shows OCP measurements after one day of immersion. The curves represent the potentials vs time of the six specimens.

The OCP values for the different alloys studied are summarized in Table 2.

After 1-h immersion, all test specimens had approximately a corrosion potential between −150 mV and −350 mV. Therefore, in all the dental materials studied, after 1 h of immersion, there was no passive layer deterioration.

The corrosion potential for Specimens 1, 2, 4 and 5 steadily increased over time to −73 mV, −106 mV, −152 mV and −209 mV, respectively. In the case of specimen 3, it was found that after 4 h of immersion, the corrosion potential began to decrease. However, this decline was followed by a new growth, a repassivation, so the passive layer recovered over time, and after 24 h, the corrosion potential stabilized in a fairly negative value of −288 mV. Specimen 6 had continuous patches and repairs of the passive layer. The variation curve of the corrosion potential showed two downward slopes followed by increases. Overall, results showed that after 24-h immersion in Ringer solution, the corrosion potential of specimen 6 changed within a fairly narrow range.

3.2 Potentiodynamic polarization results

The curves obtained for the six alloys studied are displayed in Figure 2.

The values of the electrochemical parameters at different immersion times in Ringer solution were determined with the PowerCorr program (see Table 3): R_p (polarization resistance), b_A and b_C (Tafel slope for anodic and cathodic process), i_{corr} (corrosion current density), i_{pass} (passive current density) and E_{bd} (breakdown potential).

However, for the purpose of this investigation, the most important indicators of the corrosion process obtained after one week of immersion are presented in a separate table (Table 4).

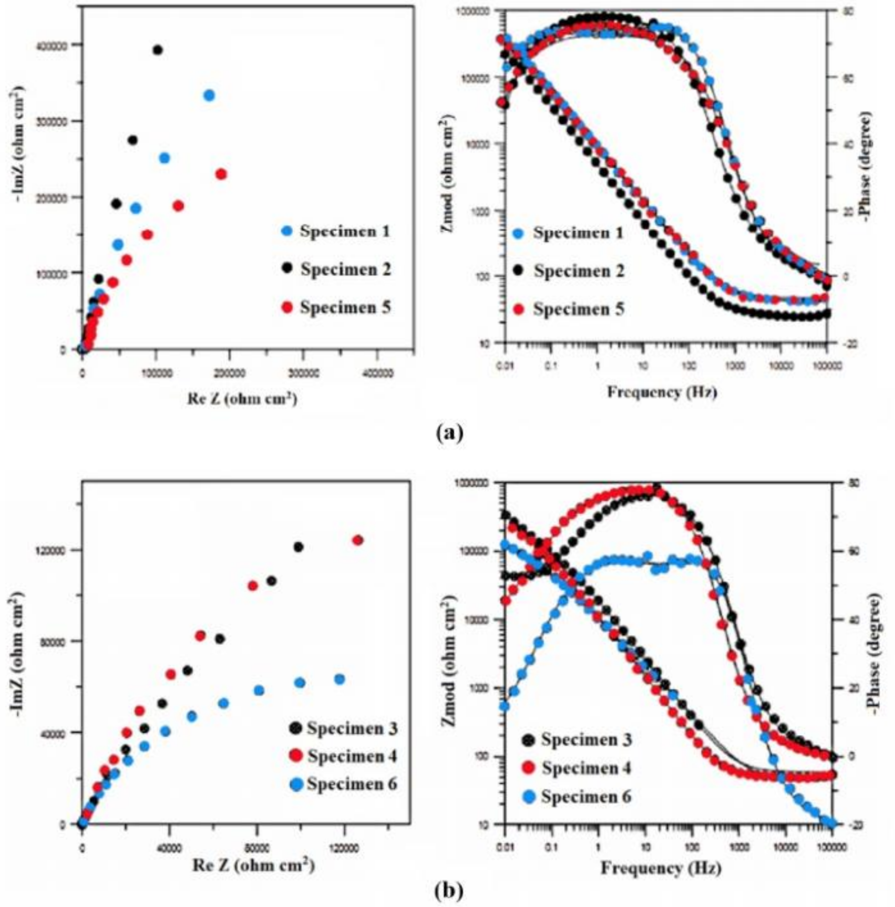
Results in Table 4 showed that specimens 1 and 2 (both with a high concentration of Mo) exhibited lower values of i_{corr} and higher R_p and E_{bd} in comparison to the other test specimens, with a lower Mo bulk content.

3.3 Electrochemical impedance spectroscopy

Representative EIS data of the six alloys in Ringer solution, after one day of immersion, are displayed in Figure 3. Experimental measurements are represented by individual points and the theoretical spectra obtained from the fits to the equivalent circuit (EC) model by lines.

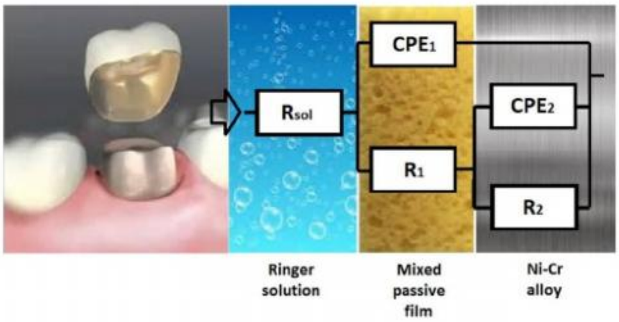
In all the specimens studied, the Nyquist diagram showed a capacitive arc. The Bode |Z| spectra obtained indicated that in the higher frequency region, with increasing frequency, phase angle values approached 0 degrees and log |Z| exhibited a tendency to be constant. In the examination of the impedance

Figure 3 Representative Nyquist and Bode spectra after one day of immersion in Ringer solution



Notes: (a) specimens 1, 2 and 5; (b) specimens 3, 4 and 6

Figure 4 EC used in the experimental data fitting



spectra obtained, and after various models were tested starting with the simplest one (Turdean *et al.*, 2019; Qian *et al.*, 2016), it was found that all determinations could be adequately fitted with the equivalent circuit (EC) given in Figure 4. The resulting parameters are provided in Table 5.

In the model, the ohmic resistance of the electrolyte was represented R_{sol}, the charge transfer resistance (R_{ct}) was represented as R_2, the resistance of the passive film was designated R_1, the passive film capacitance was designated CPE_1 and the double layer capacitance CPE_2. The EC model shows similarity to that proposed by other authors for cobalt–chromium alloys immersed in simulated physiological solution (Metikoš-Huković *et al.*, 2006) and for nickel–chromium–molybdenum alloys in artificial saliva (Moslehifard *et al.*, 2019).

4. Discussion

All the Ni-Cr dental alloys, after 1-h of immersion, presented an increase in the corrosion potential because of the formation of passive layers on the surface. An anodic control of the process of corrosion, which suggested the existence of a passive film on the surface of the materials, was indicated by the higher value of b_A vs b_C in the six specimens (Table 3).

The comparison of the corrosion data obtained revealed that the six specimens changed, from the Tafel region, into a passive stable behavior, not showing an active–passive traditional transition (Table 4). This was due to the chromium content, which was reported to be passive at the anode polarization (Qiu *et al.*, 2011). Additionally, specimens 1, 2 and 3 containing molybdenum had smaller corrosion current densities that decreased with the increase of Mo content.

Table 5 Fitted EIS parameters of the Ni-Cr dental materials after one day of immersion in Ringer solution

Specimens	R_{sol} Ω cm^2	R_1 Ω cm^2	CPE_1 S cm^{-2}s^n	n_1	R_2 kΩ cm^2	CPE_2 S cm^{-2}s^n	n_2	χ^2
1	28	$1.8\ 10^4$	$2.0\ 10^{-5}$	0.87	350	$6.7\ 10^{-6}$	0.82	$3\ 10^{-4}$
2	39	$1.3\ 10^3$	$1.9\ 10^{-5}$	0.9	460	$2\ 10^{-5}$	0.85	$3\ 10^{-4}$
3	56	$8.8\ 10^4$	$1.2\ 10^{-5}$	0.87	500	$1.0\ 10^{-5}$	0.8	$3\ 10^{-4}$
4	39	10^4	$1.8\ 10^{-5}$	0.87	430	$1.3\ 10^{-5}$	0.78	$9\ 10^{-4}$
5	42	$6\ 10^4$	$1.4\ 10^{-5}$	0.9	400	$2.4\ 10^{-5}$	0.81	$3\ 10^{-4}$
6	57	$1.2\ 10^3$	$0.7\ 10^{-5}$	0.87	200	$1.8\ 10^{-5}$	0.63	$6\ 10^{-4}$

Based on the chemical composition, the pitting resistance equivalent number (PREN) index is a measurement that predicts a material's resistance to pitting corrosion. This investigation analyzed the PREN-value and the results obtained in the investigation to draw conclusions. The greater PREN value meant the material was more resistant to localized pitting corrosion (Tian *et al.*, 2019). The index was calculated with the mathematical expression:

$$\text{PREN index} = \text{wt\%Cr} + 3.3(\text{wt\%Mo}) \qquad (1)$$

For the dental alloys studied, the PREN values are presented in Table 6.

A PREN value higher than 38 provides an increased resistance to pitting corrosion. Therefore, only specimens 1 and 2 were pitting corrosion resistant.

According to the polarization curves in the 300 to 600 mV anodic area, specimens 1, 2, 3 and 4 displayed the best behavior with anodic currents in the order of μA. Specimens 5 and 6 exhibited the worst behavior in the mentioned area, with anodic currents in the order of mA, because of Al content.

From the analysis of the impedance spectra obtained, different results were found for the two groups of alloys: specimens 1, 2 and 5; specimens 3, 4 and 6. The Bode phase spectra for the first group exhibited, at low and medium frequencies, phase angles close to 90°, indicating the development of a compact passive layer on their surface. The second group did not exhibit high phase angles in the low and medium frequency range, indicating that the passive film formed on these alloys was defective in nature.

In Table 5, specimen 1 with an important concentration in Cr and the highest concentration on Mo showed the best corrosion behavior. Chromium formed a passive and resistant Cr_2O_3 pellicle and molybdenum a $(Mo_7O_{24})^{6-}$polymolybdate compound that had low solubility and slowed down the pitting corrosion. It was found that the addition of Nb was also beneficial for the corrosion behavior, because it formed oxides (NbO and Nb_2O_5) in the passive film.

Table 6 PREN values of the six Ni-Cr alloys

Specimens	PREN
1	57.6
2	52.9
3	33.1
4	20.0
5	17.9
6	14.4

The sum of R_1 and R_2 is the polarization resistance (R_p) of the dental materials in Ringer solution. This value represents the level of resistance of the passive films formed on their surfaces. According to *ASM International Handbook* (Vander, 2004), Rp can reach values of 1MΩ·cm2 in those materials with high resistance to corrosion. For all the determinations, R_p is high (more than 10^5 $\Omega \cdot cm^2$), indicating the great stability of the specimens in Ringer solution. Therefore, findings in this investigation revealed that the passive films formed on the surfaces of the six Ni-Cr alloys examined in Ringer solution had a satisfactory resistance to corrosion.

5. Conclusions

The following items were concluded in this investigation:

- The dental materials examined were under the influence of an anodic control, due to the formation of protective layers, most likely of oxide, on their surfaces.
- When the materials were compared, it was discovered that the decisive factor for high corrosion resistance was the chromium content. Findings showed that specimens 1 and 2 exhibited a similar behavior at the same concentration, approximately 24%Cr.
- In terms of predisposition to corrosion, although the chromium concentration was similar for specimens 2 and 3, specimen 2 presented a higher corrosion resistance attributable to the stronger concentration in molybdenum, because of the low solubility of its products in Ringer solution, which inhibited pitting corrosion.
- Findings in this investigation showed that the alloys studied had an adequate corrosion resistance in Ringer solution. However, this study revealed specimens 1 and 2 presented an increased corrosion resistance in Ringer solution and displayed higher polarization resistance values (R_p).
- According to the results obtained, the biological safety of the six Ni-Cr dental materials examined in Ringer solution was considered very high for specimens 1 and 2 and adequate for the other samples.

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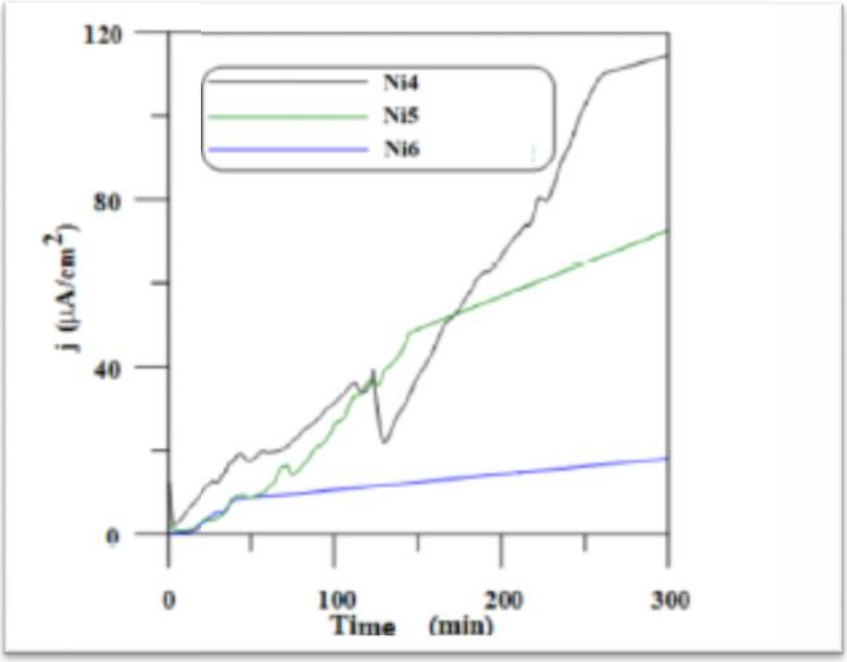
120
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40
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Ni4
Ni5
Ni6
0
100
200
300
Time (min)

materials

MDPI

Article

Analysis and Comparison of the Corrosive Behavior of Nickel-Based and Cobalt-Based Dental Alloys

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Abstract: Nickel-based and cobalt-based metal alloys are frequently used in dentistry. The introduction of various elements in the alloy changes its characteristics, and a thorough study of each alloy should be completed to determine its appropriate corrosion resistance and biocompatibility in contact with physiological fluids. There are scarce investigations on these widely used dental alloys in Ringer solution, and findings in this research bring new experimental data and information. The present study evaluated and compared the corrosion behavior of six NiCr- and two CoCr-based dental materials in Ringer solution, using the following techniques: potentiostatic polarization curves (chronoamperometry), microstructural analysis, and EIS (electrochemical impedance spectroscopy). The results obtained in this investigation showed that in the NiCr-based specimens Ni4, Ni5, and Ni6 the stability of the passive layer was destroyed after polarization and a development and growth of stable pits was found in the microstructural analysis after electrochemical treatment. In terms of susceptibility to corrosion, two different groups of specimens were derived from this investigation. A first group which included the two CoCr (Co1 and Co2) and three of the six NiCr alloys studied (Ni1, Ni2, and Ni3). A second group with the other NiCr alloys investigated Ni4, Ni5, and Ni6.

Keywords: metal alloys; NiCr; CoCr; electrochemical characterization; corrosion; Ringer solution

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Citation: Garcia-Falcon, C.M.; Gil-Lopez, T.; Verdu-Vazquez, A.; Mirza-Rosca, J.C. Analysis and Comparison of the Corrosive Behavior of Nickel-Based and Cobalt-Based Dental Alloys. *Materials* **2021**, *14*, 4949. https://doi.org/10.3390/ma14174949

Academic Editor: Nikolaos Silikas

Received: 23 July 2021
Accepted: 23 August 2021
Published: 30 August 2021

1. Introduction

Nickel-based and cobalt-based metal alloys are frequently used in dentistry for prosthodontic restorations due to their advantageous characteristics [1–8]. Nickel in an alloy can cause allergic reactions and toxicity, according to some studies [9–13], but others report very different results and conclusions [14–16]. Furthermore, the introduction of chromium in their composition favors the stability of the alloy in order to be used as biomaterial [17,18]. According to several investigations, the chromium's percentage found in the alloy is a decisive factor in the formation of the passive layer and the resistance to corrosion [19–21]. Cobalt-based alloys are frequently used biomaterials with applications in the dental and cardiac fields, as well as in orthopedic implants [22,23], due to the considerable wear and corrosion resistance properties given by this metallic element [24,25]. As dental materials, they are used for crowns with porcelain fused to metal [26–30], in fixed and removable dental prostheses [31–35], orthodontic wire leads [36,37], oral implants [38–40], and are very suitable in patients whose exposure to nickel might cause an allergic reaction [41,42].

The introduction of other elements in the alloy varies its characteristics. Aluminum, iron, copper, manganese, molybdenum, niobium, silicon, and tungsten can be found on different Ni- and Co-based alloys. As an example, it has been reported that the molybdenum content increases the corrosion resistance of the alloys [20,21] and their appropriateness to be used in the human body [19] as a biomaterial. Therefore, a thorough study of each alloy should be completed in order to determine its corrosion resistance and biocompatibility. Current research is focused on the investigation of materials to be used in the human body [43].

The alloys studied in this investigation, whether nickel- or cobalt-based, all had chromium in their composition, which makes them supposedly stable and safe to be used as dental alloys and are found in world markets for prosthodontic restorations. However, not all alloys have the same biocompatibility in contact with physiological fluids. The resistance to corrosion is the most important factor to be taken into account, because due to the corrosion process, elements are released into the oral cavity, causing problems that make biological safety difficult [44,45]. Certainly, materials in contact with human tissue must be non-toxic and not cause allergies or inflammations to be biocompatible [46].

Accordingly, in order to safely use these NiCr and CoCr alloys, a thorough analysis must be performed regarding their corrosion behavior. Electrochemical studies for a limited number of NiCr and CoCr alloys in artificial saliva medium were conducted by our group [47–49], and we are now investigating in simulated body fluid (Ringer solution). We have recently presented our study of CoCr alloys [50], but there are scarce investigations on these widely used materials in Ringer solution, and further studies are imperative to analyze and compare these alloys. Findings in this research bring new experimental data and information on these worldwide used NiCr and CoCr dental alloys in simulated body fluid. The present study evaluated and compared the corrosion behavior of six NiCr and two CoCr dental materials in Ringer solution, using microstructural analysis, potentiostatic polarization curves (chronoamperometry), and EIS techniques.

2. Materials and Methods

2.1. Materials, Specimens Preparation

Six NiCr and two CoCr dental alloys commercially used for prosthodontic restorations were studied: three manufactured in Germany, two in Romania, and three in the United States. The dental materials will hereinafter be referred to as specimens Ni1–6 and Co1,2.

The compositions of the eight investigated dental materials are shown in Tables 1 and 2.

The specimens were cut to 1 cm^2 size and each was inserted into an epoxy resin disk. Then, the samples were mechanically abraded using emery paper up to 2500 grit and polished with a 1 μm suspension of alumina. Before testing, the specimens used were cleaned completely in ethyl alcohol and deionized water.

The Ringer solution used as corrosion medium in this investigation had the following composition: NaCl—6.8 g/L, KCl—0.4 g/L, CaCl2—0.2 g/L, $NaCO_3H$—1 g/L, glucose—1 g/L, $MgSO_4 \cdot 7H_2O$—0.2 g/L and $NaH_2PO_4 \cdot H_2O$—0.14 g/L.

Table 1. NiCr dental material composition.

Composition (in wt.%)	**Specimens**					
	Ni1	**Ni2**	**Ni3**	**Ni4**	**Ni5**	**Ni6**
Ni	60.1	60.8	63.4	72.1	64.9	53.4
Cr	24.3	23.9	23.2	20	17.9	14.4
Mo	10.1	8.8	3			
Fe	2.1	2.4	9	7.5		
Nb	1	3.8				
Si			1		1.8	1.5
Cu					9.9	9.5
Mn	2				3.6	19.4
Al					1.5	1.6

Table 2. CoCr dental material composition.

Composition (in wt.%)	Specimens	
	Co1	**Co2**
Co	63.5	63.4
Cr	27	29.0
Mo	5.5	5.2
Fe	2	
Ni	1	

2.2. Microstructural Characterization

To study the microstructure of the six NiCr- and two CoCr-based dental materials, a chemical reactant containing 10 mL HNO_3, 30 mL HCl and 20 mL glycerine [51] and an PME 3-ADL microscope (Olympus, Tokyo, Japan), were utilized in the investigation. After electrochemical treatment, an analysis of the surface modifications of the NiCr and CoCr alloys using the microscope was conducted.

2.3. Electrochemical Measurements

The analysis was conducted in a three-electrode electrochemical cell, using as a reference electrode a saturated calomel electrode (or SCE), a platinum auxiliary electrode, and the sample as working electrode. A Princeton Applied Research (PAR, Oak Ridge, TN, USA) model 263A potentiostat, a lock-in amplifier 5210 (PAR, Oak Ridge, TN, USA), and a computer with Electrochemistry Power Suite software (PAR, Oak Ridge, TN, USA) were used.

2.3.1. Potentiostatic Polarization Studies—Chronoamperometry

Chronoamperometry measurements were performed at a potential of 0.1 V/ESC on the working electrode. Using the electrochemical chronoamperometry technique, the induction time could be determined prior to the increase in the current density due to the breakdown of the passive layer. The current density variations of each of the different NiCr and CoCr dental alloys polarized at +100 mV/ESC in Ringer solution for 5 h were analyzed in this research. All tests were performed three times, and data acquisition and processing was performed with PowerCorr Princeton Applied Research software (PAR, Oak Ridge, TN, USA). After the potentiostatic polarization tests, the microstructures of the alloys' surfaces were examined with the ADL microscope OLYMPUS PME3 (Olympus, Tokyo, Japan).

2.3.2. EIS—Electrochemical Impedance Spectroscopy

EIS tests of the eight NiCr- and CoCr-based alloys were conducted for analysis and comparison of the corrosion resistance in Ringer solution following the potentiostatic polarization studies. The EIS spectra were recorded at the 100 mV/ESC potential after plotting the potentiostatic curves for 5 h.

Experimental EIS results were analyzed with ZSimpWin Princeton Applied Research software (PAR, Oak Ridge, TN, USA) to obtain the equivalent circuit (EC) where experimental data and simulated responses fitted well. Following each experiment, impedance data were displayed as Nyquist plots, Bode |Z|, and Bode phase diagrams. All tests were performed three times.

3. Results and Discussions

The potentiostatic polarization curves (chronoamperometry) for NiCr alloys in Ringer solution at a potential of 100 mV/ESC are shown in Figure 1.

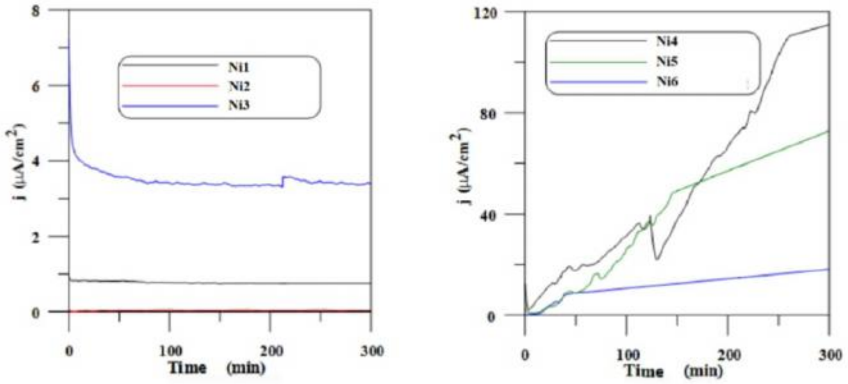


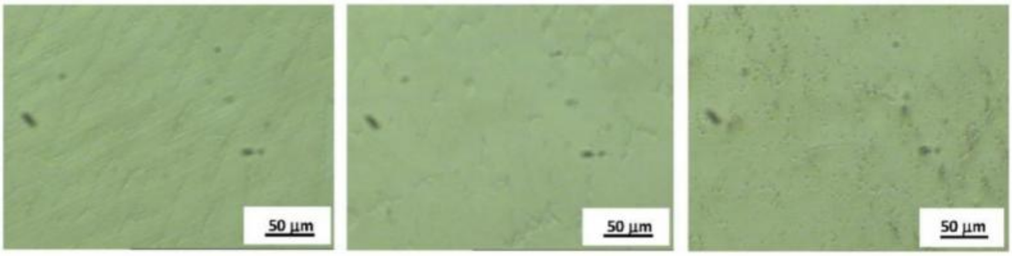
Figure 1. Potentiostatic polarization curves for specimens Ni1, Ni2, Ni3, Ni4, Ni5, and Ni6 in Ringer solution at a potential of 100 mV/ESC.

In human organisms, pure titanium may be exposed to a maximum potential of about 450 or 550 mV/ESC [52]. For Co–Cr–Mo biomaterials, this information could not be found. Nevertheless, for physiological conditions in the human body, a metallic biomaterial's potential value may fluctuate between −1.0 and 1.2 V, according to Black's diagram of the potential pH [53].

In these conditions, it was found for some tested materials with very low potentials, that the stability of the passive layer in human organisms may be achieved at +100 mV/ESC. For this purpose, the potentiostatic polarization curves were plotted at a potential of +100 mV/ESC for 5 h, to prove the stability of the passive layer at this potential of +100 mV/ESC potentially achievable in the human body.

In the case of NiCr-based dental alloys, the polarization current of specimens Ni1, Ni2, and Ni3 at 100 mV/ESC in Ringer solution oscillated around 0.8 μA/cm², 0.2 μA/cm², and 3.8 μA/cm², respectively. Specimens Ni4, Ni5, and Ni6 showed an increase in current density, higher in the cases of specimens Ni4 and Ni5.

Microstructures of specimens Ni1, Ni2, and Ni3 after the 5 h potentiostatic treatment are shown in Figure 2. No degradation was observed in these specimens after the 5 h potentiostatic treatment.



(a) (b) (c)

Figure 2. Microstructures after electrochemical treatment for (**a**) specimen Ni3, (**b**) specimen Ni1, and (**c**) specimen Ni2.

For specimens Ni4, Ni5, and Ni6 the increase in current density is probably caused by the active anodic dissolution of the surface due to the film breakdown, with the formation and growth of stable pits. In Figure 3, microstructures of specimens Ni4, Ni5, and Ni6 before and after electrochemical treatments are presented.

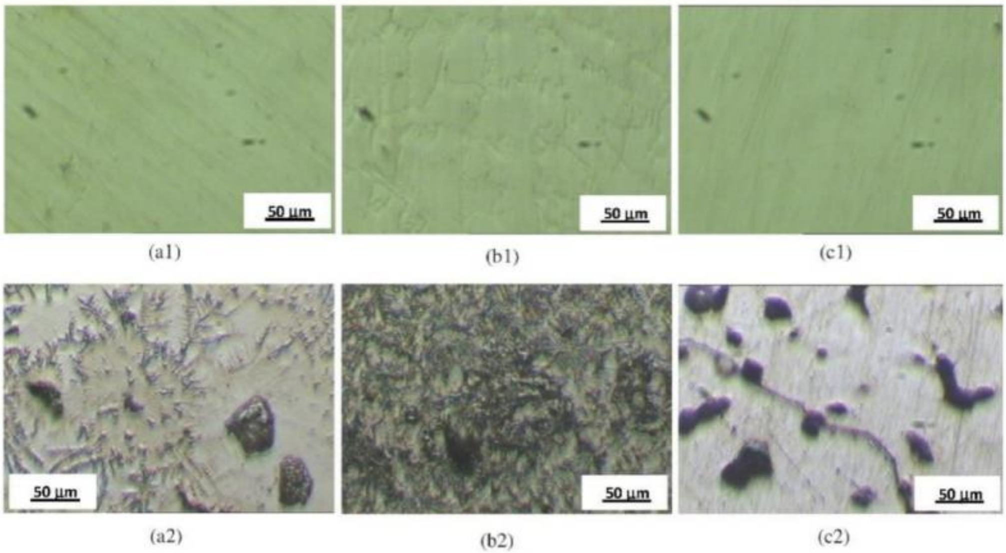


Figure 3. Microstructures before electrochemical treatments for (**a1**) specimen Ni5, (**b1**) specimen Ni4, (**c1**) specimen Ni6; after electrochemical treatments for (**a2**) specimen Ni5, (**b2**) specimen Ni4, and (**c2**) specimen Ni6.

The potentiostatic polarization curves for CoCr alloys in Ringer solution at a potential of 100 mV/ESC are displayed in Figure 4.

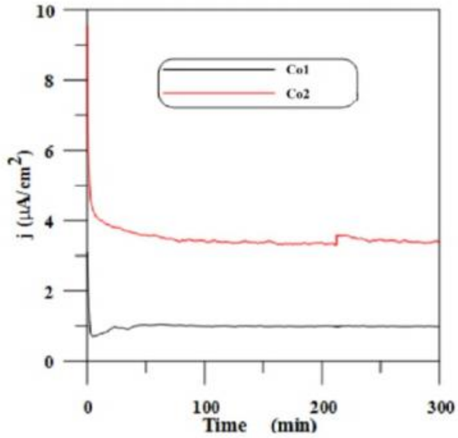
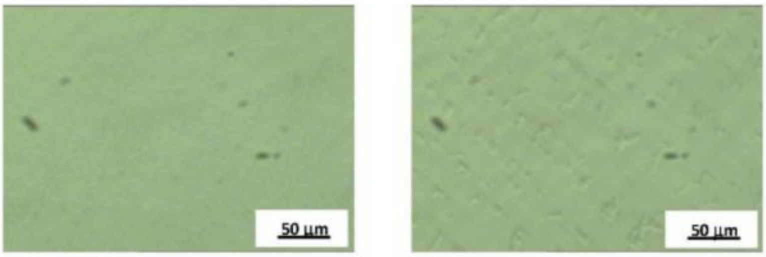


Figure 4. The potentiostatic polarization curves for specimens Co1 and Co2 in Ringer solution at a potential of 100 mV/ESC.

The polarization current of specimens Co1 and Co2 at 100 mV/SCE in Ringer solution fluctuated around 1 µA/cm^2 and 4 µA/cm^2, respectively.

Microstructures of specimens Co1 and Co2 after 5 h of potentiostatic treatment are shown in Figure 5. No degradation was observed in the CoCr-based dental alloys studied after the 5 h potentiostatic treatment.

After plotting the potentiostatic curves for 5 h, EIS spectra were recorded at the same potential of 100 mV/ESC. Representative results of Bode spectra and Nyquist plot diagrams for the NiCr-based dental alloys, polarized at 100 mV/ESC in Ringer solution, are shown in Figure 6.



(a) (b)

Figure 5. Microstructures after electrochemical treatments for (**a**) specimen Co2 and (**b**) specimen Co1.

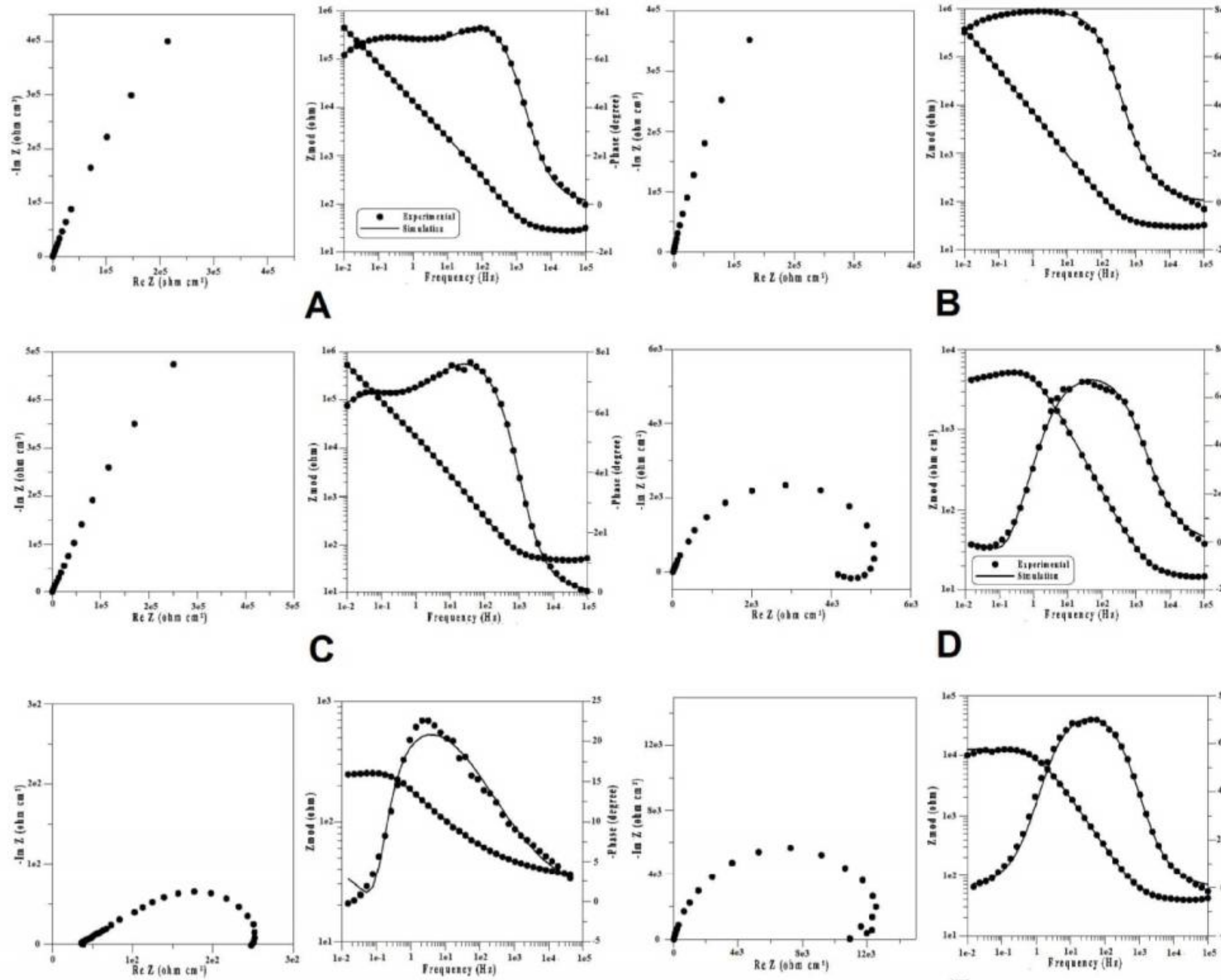


Figure 6. Bode spectra and Nyquist plot diagrams for NiCr-based dental alloys in Ringer solution at a potential of 100 mV/ESC. (**A**) Specimen Ni1. (**B**) Specimen Ni2. (**C**) Specimen Ni3. (**D**) Specimen Ni4. (**E**) Specimen Ni6. (**F**) Specimen Ni5.

Representative results of Bode spectra and Nyquist plot diagrams for the studied CoCr-based dental alloys, polarized at 100 mV/ESC in Ringer solution, are shown in Figure 7.

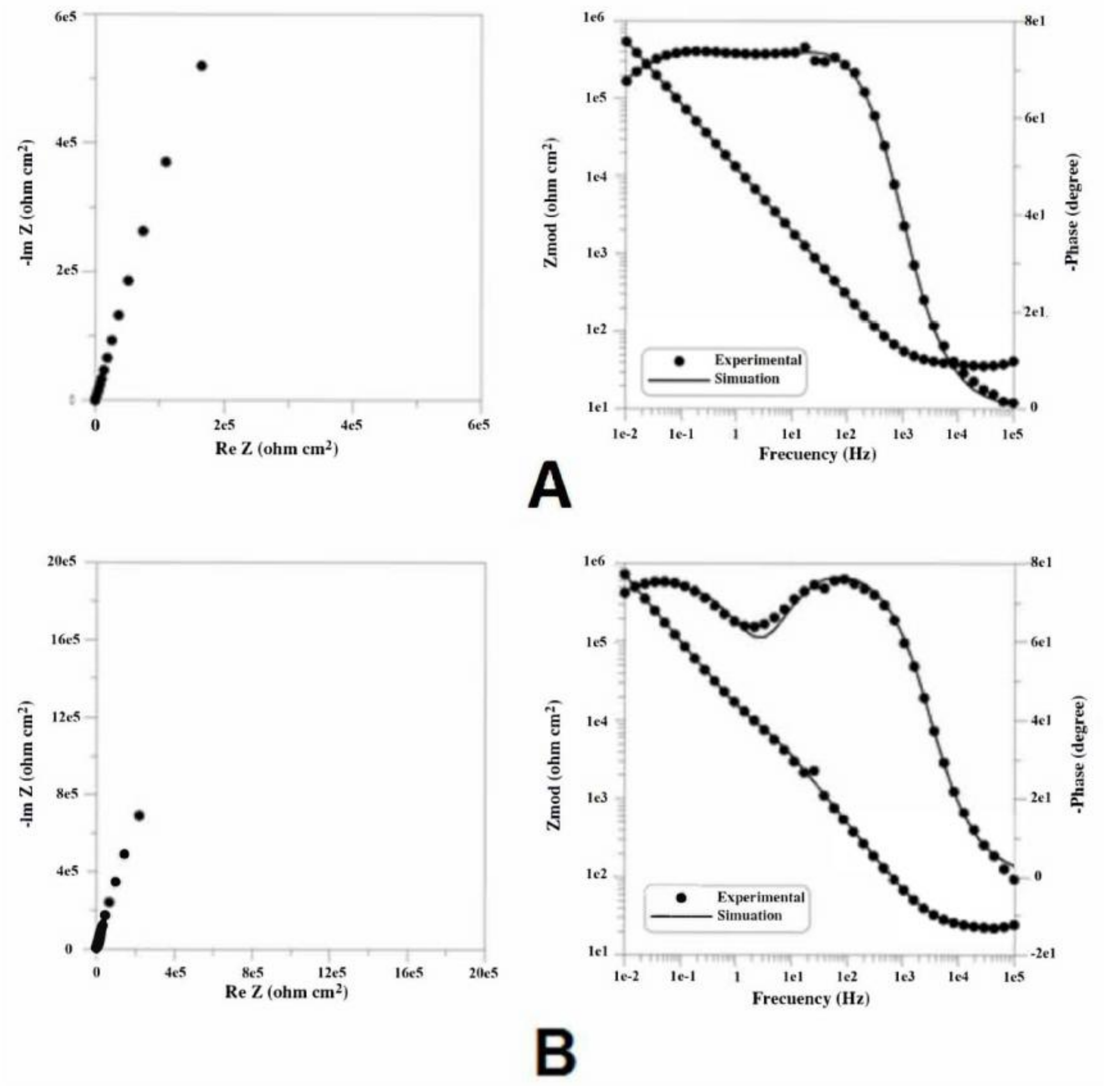


Figure 7. Bode spectra and Nyquist plot diagrams for CoCr-based dental alloys in Ringer solution at a potential of 100 mV/ESC. (**A**) Specimen Co1. (**B**) Specimen Co2.

The experimental measurements are presented in the diagrams as distinct points, and the theoretical spectra that resulted from the equivalent circuit model used are displayed as lines.

The Nyquist spectrum showed that all alloys had a capacitive behavior with the immersion time in Ringer solution, except specimens Ni4, Ni5, and Ni6, which showed an inductive arc. In the electrochemical system, this arc can be associated with the process of metallic dissolution, showing values that are negative for the imaginary impedance [54].

An equivalent circuit, EC, gives the most notable corrosion indicators that can be applied to the substrate–electrolyte system and is formed by a group of different capacitors, resistances, and other circuit components. It is essential to have a proper model of the electrochemical reactions taking place at the electrodes to be able to interpret the system's electrochemical behavior from EIS spectra. An EC representing an electrochemical cell displays impedance to a small sinusoidal excitation.

Starting with the easiest one, several models of electrical circuits were examined when analyzing the impedance data [28,55] for specimens Ni1, Ni2, Ni3, Co1, and Co2, with the best fit obtained for all the determinations using the EC presented in Figure 8.

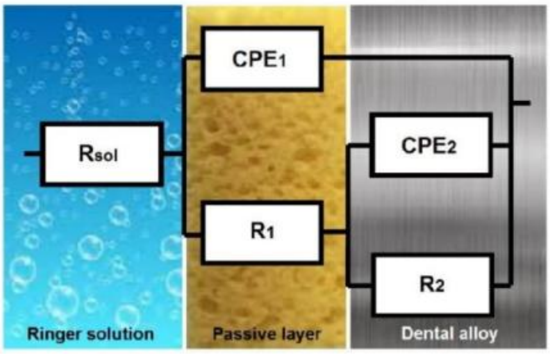


Figure 8. EC used to generate the simulated data for specimens Ni1, Ni2, Ni3, Co1, and Co2.

In the model presented in Figure 8, the ohmic resistance of the electrolyte was designated R_{sol}, the resistance of the passive film was designated R1, the passive film capacitance was represented as CPE_1, the charge transfer resistance (R_{ct}) was designated R_2, and the double-layer capacitance was represented as CPE_2. The EC model was very similar to that from M. Meticos-Hukovic et al. [56] for CoCr alloys dipped in Hank's solution. As a result of the heterogeneous and thin oxide layer formed on the surface of the metallic alloys and the noticeable Bode plots' deviations, it was necessary to substitute the "ideal" capacitance with a constant phase element (CPE), for which impedance is given by $Z = (j\omega){-}nY_0$, where j is an imaginary number ($j^2 = -1$), ω is the angular frequency ($rad{\cdot}s^{-1}$), Y_0 is the constant of CPE ($Scm^{-2}s^n$), n is the power number indicating the deviation from ideal behavior, $n = \alpha(\pi/2)$, and α is the constant phase angle of the CPE (rad).

The main parameters of the EC model for specimens Ni1, Ni2, Ni3, Co1, and Co2 are shown in Table 3. These parameters had the same meaning for all the alloys studied. The value around 10^{-4} from the χ^2 or chi-squared distribution test proves that it was correct to use the constant phase element in the EC model, and also indicated a very good correspondence of fitted values and experimental data.

Table 3. Main parameters of the EC used for specimens Ni1, Ni2, Ni3, Co1, and Co2.

Specimens	R_{sol} Ω cm^2	R_1 Ω cm^2	Y_{01} $Scm^{-2}s^n$	n_1	R_2 Ω cm^2	Y_{02} $Scm^{-2}s^n$	n_2	χ^2
Ni1	28	5×10^3	8.9×10^{-6}	0.83	5.5×10^5	9.7×10^{-6}	0.8	2×10^{-4}
Ni2	35	3×10^3	1.9×10^{-5}	0.9	6.2×10^5	1×10^{-5}	0.88	4×10^{-4}
Ni3	49	1.5×10^4	8.4×10^{-6}	0.89	5.9×10^5	7.1×10^{-6}	0.82	5×10^{-4}
Co1	37	1.5×10^4	7.8×10^{-6}	0.9	9.1×10^5	8.3×10^{-6}	0.83	2×10^{-4}
Co2	55	1.4×10^4	6.1×10^{-6}	0.9	1.2×10^6	8.6×10^{-6}	0.83	6×10^{-4}

In the case of specimens Ni4, Ni5, and Ni6 polarized for 5 h in Ringer solution at a potential of 100 mV/ESC, the best simulations were performed using the equivalent circuit exhibited in Figure 9; the main parameters are shown in Table 4.

As previously stated, the value of around 10^{-4} from the χ^2, or chi-squared distribution test, proved that it was correct to use the constant phase element in the EC model, and indicated an outstanding correspondence of fitted values and experimental data.

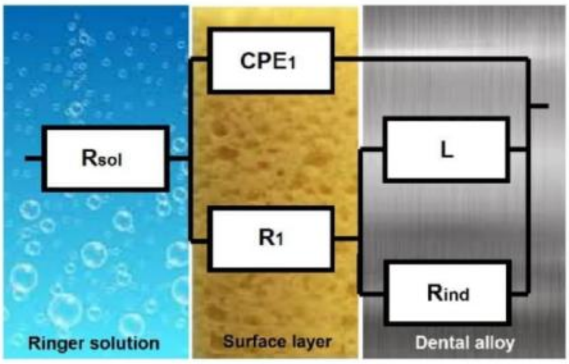


Figure 9. EC used to generate the simulated data for specimens Ni4, Ni5, and Ni6.

Table 4. Main parameters of the EC used for specimens Ni4, Ni5, and Ni6.

Specimens	R_{sol} Ω cm^2	R_1 Ω cm^2	Y_{01} Scm^{-2}s^n	n_1	R_{ind} Ω cm^2	L Henri cm^2	χ^2
Ni4	20	4.5×10^3	3.1×10^5	0.8	1.7×10^3	1.4×10^3	8×10^{-4}
Ni5	38	1.1×10^4	1.5×10^{-5}	0.84	9×10^2	3×10^3	6×10^{-4}
Ni6	34	260	$2.4\ 10^{-3}$	0.4	240	231	6×10^{-4}

In the model exhibited in Figure 9, the ohmic resistance of the electrolyte was designated R_{sol}, and the surface film resistance and capacitance were designated R_1 and CPE_1, respectively. It was found that the presence of an inductive process was characterized by a resistance R_{ind} and an inductance L, associated with an adsorption–desorption process that occurred in the formation of the surface film.

For this circuit, the total impedance was:

$$\mathbf{Z_{eq}} = \mathbf{R_{sol}} + \frac{1}{\mathbf{jwC}_1 + \frac{1}{\mathbf{R}_1 + \frac{1}{\frac{1}{\mathbf{R_{ind}}} + \frac{1}{\mathbf{jwL}}}}} \tag{1}$$

After standard calculations, the following equation was obtained:

$$\mathbf{Z_{eq}} = \mathbf{R_{sol}} + \frac{\mathbf{R - w^2RT + w^2AB}}{(1 - \mathbf{w^2T})^2 + \mathbf{w^2R^2}} + \mathbf{jw}\frac{\mathbf{B - RA - w^2TB}}{(1 - \mathbf{w^2T})^2 + \mathbf{w^2A^2}} \tag{2}$$

where R = R_1 + R_{ind}, T = $\tau_1\ \tau_2$, A = $\tau_1 + \tau_2 + C_1\ R_{ind}$, B = $\tau_2\ R_1$, $\tau_1 \equiv$ time constant of process at passive layer [s], and $\tau_2 \equiv$ time constant of inductive process [s].

The equivalent circuit has a physical meaning associated with the passive layer itself, R_2CPE_2, and the passive layer/electrolyte interface, R_1CPE_1. The passive film was not destroyed by polarization at 100 mV/ESC for the two CoCr-based alloys (Co1 and Co2) or the NiCr-based alloys Ni1, Ni2, and Ni3. This fact was confirmed by potentiostatic polarization curves and surface microscopy after polarization.

From the data presented in Table 3, it was found that the stability of the materials was high at this potential due to the polarization resistance, which had high values compared to those obtained after one week of immersion in Ringer solution (greater than 10^5 Ω cm^2). The most stable alloy at the 100 mV/ESC potential was one based on CoCr, specimen Co2. Its polarization resistance of 10^6 Ω cm^2, according to different studies and the ASM Handbook [57–60], is characteristic of alloys with very high corrosion resistance.

The resultant parameters of the equivalent circuit, for the other three NiCr alloys, are presented in Table 4. Results showed that after polarization at 100 mV/ESC, the passive layer was destroyed (the inductance L is associated with the film dissolution).

When specimens Ni4, Ni5, and Ni6 were polarized at 100 mV/ESC, the passive layer developed on these alloys was considerably destroyed, and the impedance of the alloys was related to the R_{ct} or charge transfer resistance. As a result, there was no protective passive layer.

Additionally, it was observed that out of the three alloys, depending on the value of the polarization resistance ($R_p = R_1 + R_{ind}$), the highest stability was presented by specimen Ni5 and the lowest by specimen Ni6. A comparison with the polarization resistance values obtained after 7 days of immersion in Ringer solution revealed decreases of approximately 70-fold in the case of specimen Ni5, nearly 100-fold in the case of specimen Ni4, and about 500-fold for Specimen Ni6.

4. Conclusions

This investigation evaluated and compared the corrosive behavior of six NiCr- and two CoCr-based dental alloys in Ringer's solution. Using potentiostatic polarization curves (chronoamperometry), microstructural analysis, and EIS, the following conclusions were derived:

1. The stability of the passive layer was not destroyed for the CoCr-based specimens Co1 and Co2, or the NiCr-based specimens Ni1, Ni2, and Ni3. This fact was confirmed by potentiostatic polarization curves and surface microscopy after polarization;
2. In the cases of specimens Ni4, Ni5, and Ni6, it was found that the passive layer was destroyed after polarization. Therefore, there was no longer a protective passive layer on these alloys;
3. Findings from the micrographs of the different NiCr and CoCr dental alloys studied after electrochemical treatments showed that there was no degradation for specimens Ni1, Ni2, Ni3, Co1, and Co2, but the development and growth of stable pits was discovered on the surfaces of specimens Ni4, Ni5, and Ni6;
4. According to the results obtained, in terms of susceptibility to corrosion from the spectral data, the NiCr and CoCr dental alloys were divided in two different groups. A first group which included the two CoCr (Co1 and Co2) and three of the six NiCr alloys studied (Ni1, Ni2, and Ni3), where the polarization resistance showed high values. In this group, the most stable alloy was specimen Co2, with a polarization resistance in the order of 10^6 Ω cm^2, characteristic of alloys highly resistant to corrosion. A second group with the other NiCr alloys investigated, Ni4, Ni5, and Ni6, where the passive layers were destroyed after polarization and the polarization resistance determinations were significantly lower than those exhibited by the first group. In this second group, specimen Ni5 had the highest stability and specimen Ni6 the lowest, based on polarization resistance values.

Author Contributions: Conceptualization, C.M.G.-F.; Writing—original draft, C.M.G.-F.; Methodology, C.M.G.-F. and T.G.-L.; Investigation, C.M.G.-F. and T.G.-L.; Validation, T.G.-L.; Formal analysis, C.M.G.-F. and T.G.-L.; Data curation, T.G.-L. and A.V.-V.; Writing—review and editing, A.V.-V.; Software, J.C.M.-R.; Supervision, J.C.M.-R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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2.4. DOCUMENTOS DE AUTORÍA PRINCIPAL PARA LA TESIS

Se incluyen a continuación los documentos de autoría principal de las publicaciones científicas derivadas de esta investigación, cumpliendo con lo exigido por el Reglamento de Doctorado de la ULPGC, que establece en su artículo 12:

“Para acreditar la condición de autor principal, esta deberá ser reconocida por el resto de los autores de las publicaciones presentadas como núcleo de la tesis doctoral, al mismo tiempo que estos deberán renunciar a utilizar estas publicaciones como núcleo principal de otras tesis doctorales, sin perjuicio de que dichas publicaciones puedan ser presentadas como méritos complementarios en las tesis doctorales que pudieran presentar los otros autores de dichas publicaciones.”

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DOCUMENTO DE AUTORÍA PARA TESIS POR COMPENDIO

Los abajo firmantes, coautores del artículo titulado “Electrochemical characterization of some cobalt base alloys in Ringer solution“, publicado en Materials Chemistry and Physics a 15/02/2021:

- Reconocemos como autor principal del artículo a Dña. Carmen Marina García Falcón, con DNI 44311358-H.
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3. CONCLUSIONES

En este capítulo se resumen las principales conclusiones derivadas de la investigación, y que se encuentran recogidas en las publicaciones científicas. También se presentan futuras líneas de investigación derivadas del trabajo realizado en esta tesis doctoral.

3.1. CONCLUSIONES PRINCIPALES

- Las dos aleaciones de Co-Cr estudiadas tienden a pasivarse espontáneamente y presentan una tendencia a la pasivación muy alta. Las aleaciones presentaron la formación de capas protectoras mixtas $Cr_2O_3 \cdot CoO$ con una alta estabilidad en sus superficies, lo que mejora sustancialmente su biocompatibilidad en disolución Ringer.

- Las aleaciones estudiadas con cobalto en su composición (cobalt base alloys) exhibieron un comportamiento de corrosión uniforme o general, homogéneo en la superficie. No obstante, en una de las aleaciones estudiadas se encontró un mayor grado de corrosión debido al contenido de Fe y Ni en su composición. Además, los parámetros cinéticos del proceso de corrosión en el estudio indicaron un proceso con un control anódico, atribuible a la formación de películas pasivas en sus superficies.

- En términos de susceptibilidad a la corrosión, las dos aleaciones de Co-Cr presentaron una resistencia a la corrosión más que adecuada en disolución Ringer, si bien la aleación dental Vitallium 2000 Plus presentó una mayor resistencia a la corrosión precisamente por tener Fe y Ni en su composición.

- La resistencia a la polarización de las dos aleaciones de Co-Cr examinadas en disolución Ringer alcanzó valores de biomateriales con alta resistencia a la corrosión; las capas pasivas formadas en sus superficies tuvieron una resistencia a la corrosión más que adecuada.

- Respecto a las aleaciones de Ni-Cr examinadas, se encontró que estaban bajo la influencia de un control anódico, debido a la formación de capas protectoras, muy probablemente de óxido, en sus superficies.

- En su comparación se descubrió que el factor decisivo para la alta resistencia a la corrosión fue el contenido de cromo. Los hallazgos mostraron que los especímenes Ni1 y Ni2 de las aleaciones a base de Ni exhibieron un comportamiento similar a la misma concentración, aproximadamente de 24%Cr.

- En cuanto a la predisposición a la corrosión, aunque la concentración de cromo era similar para los especímenes Ni2 y Ni3, el espécimen Ni2 presentó una mayor resistencia a la corrosión, atribuible a la concentración más fuerte en molibdeno, con una baja solubilidad de sus productos en disolución de Ringer que inhibió la corrosión por picadura.

- Los resultados de la investigación en aleaciones Ni-Cr mostraron que las aleaciones tuvieron una adecuada resistencia a la corrosión en disolución Ringer, si bien revelaron que los especímenes Ni1 y Ni2 presentaron una mayor resistencia a la corrosión en disolución Ringer y mostraron valores más altos de resistencia a la polarización (R_P).

- Según los resultados obtenidos, la seguridad biológica de los seis materiales dentales de Ni-Cr examinados en disolución de Ringer se consideró muy alta para los especímenes Ni1 y Ni2, y adecuada para el resto.

- En el estudio conjunto de aleaciones de níquel y cobalto se encontró que la estabilidad de la capa pasiva no fue destruida en las muestras basadas en CoCr, la Co1 y Co2, ni en las muestras basadas en NiCr, Ni1, Ni2 y Ni3, lo que fue confirmado por curvas de polarización potenciostática y microscopía de superficie tras la polarización.

- En las muestras Ni4, Ni5 y Ni6, se encontró que la capa pasiva sí fue destruida tras la polarización, no encontrándose ya por tanto una capa protectora en estas aleaciones.

- El análisis micrográfico después de los tratamientos electroquímicos de las diferentes aleaciones dentales de NiCr y CoCr estudiadas demostró que no había degradación para los especímenes Ni1, Ni2, Ni3, Co1 y Co2, pero se descubrió el desarrollo y crecimiento de picadura en las superficies de los especímenes Ni4, Ni5 y Ni6.

- De acuerdo con los resultados obtenidos, en cuanto a susceptibilidad a la corrosión, las aleaciones dentales de NiCr y CoCr se dividieron en dos grupos diferenciados. Un primer grupo incluyendo aleaciones CoCr, Co1-Co2, y aleaciones NiCr Ni1-Ni2-Ni3, donde la resistencia a la polarización mostró valores altos. En este grupo la aleación más estable fue la Co2, con una resistencia a la polarización del orden de 10^6 Ω cm^2, característica de aleaciones altamente resistentes a la corrosión. El segundo grupo incluye las otras aleaciones de NiCr investigadas, Ni4, Ni5 y Ni6, donde las capas pasivas fueron destruidas después de la polarización y las determinaciones R_p fueron significativamente inferiores a las exhibidas por el primer grupo. En este segundo grupo, el espécimen Ni5 tuvo la mayor estabilidad y el espécimen Ni6 la más baja, según los valores de resistencia a la polarización obtenidos.

3.2. LÍNEAS FUTURAS DE INVESTIGACIÓN

Las pruebas realizadas en la investigación son necesarias para evaluar y comparar las diferentes aleaciones objeto de estudio, con cobalto y níquel en su composición. Numerosas técnicas se han utilizado en esta investigación, como se han recogido en las tres publicaciones realizadas. Las técnicas de potencial en circuito abierto, estudios de polarización potenciodinámica, cronoamperometría, espectroscopía de impedancia electroquímica y análisis microestructural, han sido las utilizadas para el objeto de esta investigación, considerándose primordiales para el estudio.

Claramente, la resistencia a la corrosión de una aleación es la característica más importante para su seguridad biológica, como se ha comentado con anterioridad, por lo que investigaciones similares en esta línea con otros biomateriales son imperativas, así como con otras aleaciones usadas para aplicaciones biomédicas o instrumentos médicos, siguiendo los procesos enumerados en esta tesis.

El estudio pormenorizado de aleaciones de titanio y tantalio o de aleaciones de alta entropía como puede ser la de AlCoCrFeNi con varias concentraciones de contenido de Al, por ejemplo, son líneas de investigación prometedoras. Dado el gran número de aleaciones posibles atendiendo a sus características físicas y químicas, las futuras investigaciones deben focalizarse en aquellas cuyo contacto con el cuerpo humano es continuo, haciéndose necesarios estudios en profundidad sobre su comportamiento frente a la corrosión. Un mayor conocimiento del comportamiento a lo largo del tiempo de los biomateriales sin duda redundará en beneficio de las personas.

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