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Electrochemical behavior of a modified Ti-Ni alloy in artificial saliva solution

ABSTRACT

Modern humans increasingly encounter situations where bodily fluids such as sweat, saliva, lymph, or blood come into temporary or prolonged contact with metal objects. This occurs with dental materials, orthopedic implants, prostheses, and fashion jewellery, and can trigger various electrochemical processes. Such processes have dual consequences: they can alter the structure and properties of the metals while simultaneously causing harmful reactions in the adjacent human tissue. Titanium-nickel (Ti-Ni) alloys are among the most widely used materials for both fashion accessories and various implants (dental and orthopedic). Despite their many favorable properties, Ti-Ni alloys have a major drawback: nickel ions, released during the electrochemical reaction between the alloy and human electrolytes, are increasingly responsible for allergic reactions in a growing number of individuals. For this reason, there is significant interest in finding ways to prevent or minimize the release of nickel ions from the alloy. Accordingly, this study focused on monitoring the electrochemical characteristics of a thermally modified Ti-Ni alloy. The electrochemical behavior of the thermally modified Ni-Ti alloy was evaluated in an artificial saliva solution as a function of exposure time.

Keywords: Ti-Ni alloy; electrochemical properties; artificial saliva

1 INTRODUCTION

The widespread use of metal-based materials in direct and prolonged contact with the human body has become an integral part of modern life. From dental fillings, orthodontic wires, and orthopedic implants to temporary fashion jewelry, metallic objects regularly interact with physiological fluids such as saliva, sweat, lymph, and blood. These interactions are inherently electrochemical in nature, as the human body provides a conductive, corrosive environment (electrolyte) rich in ions, proteins, and varying levels of dissolved oxygen. Consequently, two parallel and often undesirable processes occur [1-3]: first, the metal surface undergoes degradation, corrosion, or structural alteration; second, the release of metal ions into the surrounding tissue can provoke local or systemic biological responses, including inflammation, allergic reactions and cytotoxicity.

Among the various alloys employed for this type of application, titanium-nickel (Ti-Ni) alloys (Nitinol), have gained exceptional popularity [4,5]. Their unique combination of properties shape memory effect, superelasticity, high corrosion resistance, and good biocompatibility makes them suitable for both functional implants (e.g., vascular stents, orthodontic arch wires) and decorative items (e.g., body jewelry, watch bands) [6-8].

The application of Nitinol is an established practice in dentistry, i.e., as a standard material in the field of orthodontics. Nitinol was initially used as a material for manufacturing wires in dental braces. These wires exerted less force compared to stainless steel wires. The number of wire changes during treatment has been reduced due to the strength and elasticity of Nitinol, and faster tooth rotation has also been enabled, which implies a shorter duration of orthodontic therapy [9]. Nitinol is also used in oral bone surgery following mandibular fractures [10].

Nitinols possess good corrosion properties, i.e., they exhibit corrosion resistance in many corrosive environments. The corrosion behavior of Nitinol with a composition of 50.7% Ni, 49.3% Ti was first studied by Khalil-Allafi and collaborators [11] in two

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physiological solutions: Ringer's solution and 0.9% NaCl. In this study, they concluded that the breakdown potential is higher in sodium chloride solution compared to Ringer's solution, while the corrosion products were almost the same in all solutions. The most important finding was that the alloy showed no toxicity in physiological environments simulating body fluids [11].

Nitinol represents a self-passivating alloy, as does titanium, which is its constituent part. This means that it protects itself from corrosion by forming a stable oxide layer [12]. However, corrosion resistance and nickel ion release as is a well-known allergen and potential cytotoxin [13,14] vary greatly depending on the thickness, composition, and morphology of the formed oxide layer [15].

Upon prolonged exposure to human electrolytes, the passive oxide layer (primarily TiO_2) that forms on the alloy surface can be locally disrupted, allowing nickel to leach out as Ni^{2+} ions. The increasing prevalence of nickel allergy in the general population affecting 10–20% of women and a growing number of men [14] has raised serious concerns regarding the long-term safety of Ti-Ni alloys, especially in oral and orthopedic applications.

Given that the rate and extent of nickel ion release depend critically on the stability and composition of the surface oxide layer, various surface modification strategies have been explored to improve the corrosion performance of Ti-Ni alloys [16].

Heat treatment offers a relatively simple and cost-effective approach to alter the thickness, crystallinity, and stoichiometry of the oxide layer, potentially reducing nickel leaching. Studies by Khmelova [17] and Dmitrievskiy [18] have shown that heat treatment of NiTi alloys induces structural modifications, including changes in the proportion of austenitic and martensitic phases within the alloy, as well as the formation of NiTi nanocomposites. Heat treatment has also pronounced effect on the composition and structure of the passive oxide layer formed on NiTi alloys. Previous studies have shown that annealing at approximately 500 °C promotes the formation of a dense and protective TiO_2 surface film while significantly reducing the nickel content in the oxide due to the preferential oxidation of titanium [19, 20, 21]. At this temperature, the oxide undergoes a structural transformation from an amorphous phase to crystalline anatase TiO_2 , whereas higher annealing temperatures promote the formation of rutile. Simultaneously, the outward diffusion of

titanium and inward enrichment of nickel result in the development of a nickel-depleted oxide layer and a Ni-rich region beneath the oxide film. Such changes in oxide composition and morphology are considered beneficial for improving corrosion resistance and biocompatibility by limiting the direct exposure and release of nickel from the alloy surface.

These changes are associated with improved functional properties of the material. However, the electrochemical behavior of thermally modified Ti-Ni alloys under physiologically relevant conditions, especially in artificial saliva over extended exposure times, remains insufficiently characterized.

Therefore, the focus of this work was monitoring the electrochemical characteristics of the thermally modified Ti-Ni alloy. The electrochemical behavior of the thermally modified Ti-Ni alloy was monitored in an artificial saliva solution as a function of the exposure time.

2. EXPERIMENTAL PART

2.1. Materials and sample preparation

The electrochemical behavior of a selected Nitinol alloy (55% Ni, 45% Ti) was monitored in an artificial saliva solution. The composition of artificial saliva (modified Fusayama's solution) is given in Table 1. All chemicals used were of analytical reagent (p.a.) grade. The substances were dissolved in distilled water, and the solution was made up to a final volume of 1 dm³ in a volumetric flask. The pH of the prepared artificial saliva solution was 4.45.

Table 1. Composition of artificial saliva

Compounds	Concentration (g/L)
NaCl	0.4000
KCl	0.4000
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.7950
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.6900
$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	0.0050
Urea	1.0000

All measurements were carried out at room temperature (298 K) under constant stirring.

Measurements were performed on three different Nitinol plates. One plate was kept at room temperature without any thermal treatment and designated as Alloy 1. The other two plates were thermally treated at 500°C for different durations prior to exposure to artificial saliva: Alloy 2 was treated for 30 minutes, and Alloy 3 was treated for 60 minutes.

2.2. Electrochemical measurements

Electrochemical measurements were performed using a computer controlled potentiostat, Volta Lab PGZ 301. A standard three-electrode electrochemical cell was used. The working electrode was a Nitinol plate with a surface area of 4 cm², the counter electrode was a platinum mesh, and the reference electrode was a saturated calomel electrode (SCE). All measurements were performed in triplicate.

2.2.1. Potentiostatic polarization measurements

Potentiostatic polarization measurements were conducted in an artificial saliva solution over three different time intervals: 1 hour, 24 hours, and 7 days. Prior to each measurement, a relaxation period was allowed for the working electrode potential to reach a stable value. The Nitinol electrode was polarized from -800 mV vs. SCE in the cathodic direction to +600 mV vs. SCE in the anodic direction, at a scan rate of 1 mV/s. The same measurement procedure was applied to the plates that had been subjected to thermal treatment.

The data acquired were subsequently exported to Excel files and further analyzed using Origin 8.5.1 software.

2.2.2. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were carried out at the corrosion potential over a frequency range from 0.01 Hz to 10 kHz, acquiring 10 points per decade. The applied potential was sinusoidal with an amplitude of 10 mV. EIS measurements were performed after immersion times of 1 hour, 24 hours, and 7 days. The same procedure was repeated for the thermally treated plates.

The results obtained were converted into Excel documents and subsequently processed using Origin 8.5.1 software.

3. RESULTS AND DISCUSSION

3.1. Potentiostatic polarization measurements

3.1.1. Influence of exposure time on the electrochemical properties of the tested alloy

The electrochemical behavior of the alloys was monitored over a period of 7 days, with results recorded after 1 hour, 24 hours, and 7 days. The results of potentiostatic polarization measurements recorded under the specified conditions are shown in the form of polarization curves in Figure 1 for Alloy 1, Figure 2 for Alloy 2, and Figure 3 for Alloy 3.

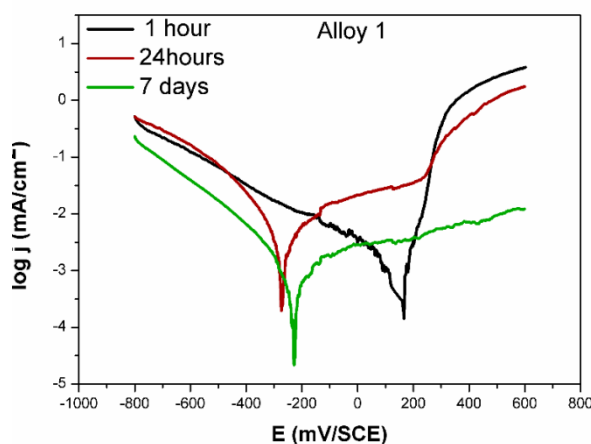


Figure 1. Polarization curves of Alloy 1 recorded after different exposure times to artificial saliva (1 hour, 24 hours, and 7 days)

In order to obtain data on the electrochemical parameters of all alloys, corrosion potential (E_{corr}) and corrosion current density (j_{corr}), the Tafel extrapolation method was applied to the recorded polarization curves, and the obtained average values for corrosion potential (E_{corr}), and corrosion current density (j_{corr}) are shown in Table 2.

Table 2. Electrochemical parameters (corrosion potential and corrosion current density) of the tested alloys after different exposure times to artificial saliva.

	Alloy 1		Alloy 2		Alloy 3	
	E_{corr} (mV)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	j_{corr} ($\mu\text{A}/\text{cm}^2$)
1 hour	153	1.99	143	0.302	-193	0.425
24 hours	-271	8.41	238	0.200	22	0.105
7 days	-229	1.30	20	0.150	-343	2.63

* The average value of the obtained parameters is within the limits of standard deviation of 0.10%-0.25%

As shown in Figure 1 and Table 2, increasing the exposure time of **Alloy 1** to artificial saliva resulted in a substantial cathodic shift of the corrosion potential. After 24 hours, the corrosion potential changed by approximately 400 mV

relative to the initial state, whereas the shift observed after 7 days was small (about 40 mV) compared to the 24-hour value. The corrosion current density decreased over time, as expected, with the lowest value recorded after 7 days of

exposure (Table 2). This behavior suggests that a protective layer gradually forms on the alloy surface.

Upon anodic polarization, a passive current appears, which is generally accepted as evidence of passive film formation on the electrode surface. Exposure time plays a dominant role in the formation of the passive layer on the electrode surface. After 1 hour of exposure, a passive current ($\sim 3 \mu\text{A}/\text{cm}^2$) is observed only at approximately 500 mV. After 24 hours, it appears much earlier, at about -100 mV, and remains stable until roughly 250 mV, after which the passive layer breaks down, and alloy dissolution begins. Following 7 days of exposure, the passive current density is registered at a potential very similar to that after 24 hours (around -100 mV), but it persists up to $+600$ mV, i.e., until the end of the measurement. The passive current density also varies with exposure time, its value decreases from about $25 \mu\text{A}/\text{cm}^2$ (24 hours) to approximately $3 \mu\text{A}/\text{cm}^2$ (7 days). This behavior indicates the formation of a protective layer on the alloy surface, whose protective performance improves over time.

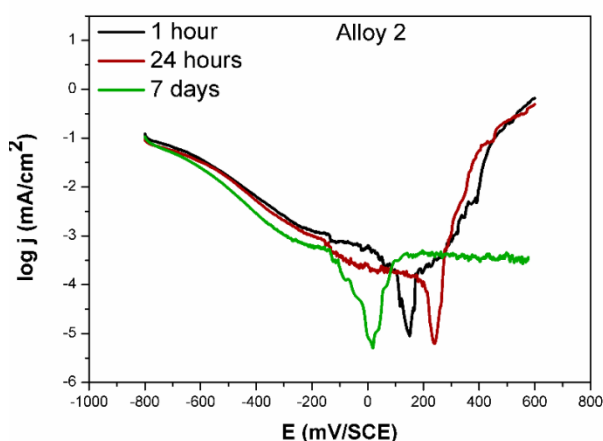


Figure 2. Polarization curves of Alloy 2 at different time intervals

As can be seen from Figure 2 and Table 2, **Alloy 2**, which was thermally treated at 500°C for half an hour prior to electrochemical monitoring exhibits an anodic shift in corrosion potential of approximately 100 mV after 24 hours. After 7 days, however, the corrosion potential shifts toward cathodic values by about 120 mV relative to the initial potential. No significant changes in corrosion current density are observed over any of the monitored time intervals.

Regarding passive current density, it appears only after 24 hours and within a narrow potential range. Stable formation of the passive layer is detectable only after 7 days, at a potential of approximately 110 mV. The passive current

remains stable until the end of the measurement, indicating that a stable protective oxide layer has formed on the alloy surface. This behavior of Alloy 2 suggests that the layer formed during the 30-minute thermal treatment does not initially exhibit pronounced passive properties; however, these properties develop over time, resulting in the formation of a compact passive layer with good protective characteristics.

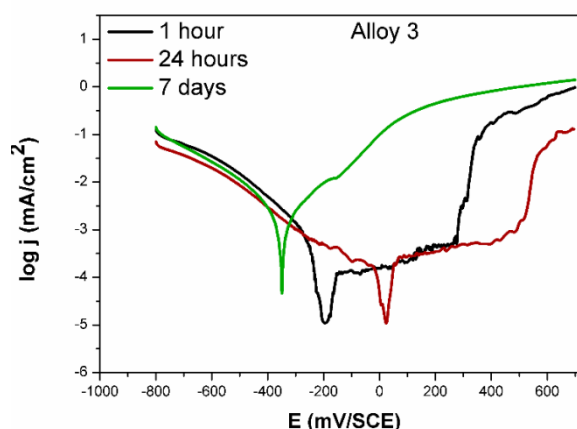


Figure 3. Polarization curves of Alloy 3 at different time intervals

As shown in Figure 3 and Table 2, **Alloy 3** (thermally treated at 500°C for 60 minutes) behaves very similarly to Alloy 2. Specifically, after 24 hours the corrosion potential shifts initially in the anodic direction, whereas after 7 days it shifts toward cathodic values relative to the initial potential.

In the case of Alloy 3, a passive current appears as early as the very beginning of the measurement, indicating that the 60-minute thermal treatment resulted in the formation of a surface layer with good protective performance superior to that achieved after the 30-minute treatment. After one hour of exposure, passive current density is recorded in the potential range from approximately -150 mV to 270 mV; after 24 hours, it appears in the interval from 60 mV to 480 mV; and after 7 days, it is observed at potentials above 60 mV. During the first two measurement intervals, the passive current density remains roughly constant at about $0.4 \mu\text{A}/\text{cm}^2$. However, after 7 days, it increases significantly to approximately $0.7 \text{ mA}/\text{cm}^2$, indicating a marked reduction in the protective properties of the surface layer over the specified period.

3.1.2. Influence of thermal treatment time on the electrochemical properties of the tested alloy

Figure 4 shows the polarization measurement results after 1 hour, Figure 5 after 24 hours, and Figure 6 after 7 days for all tested alloys.

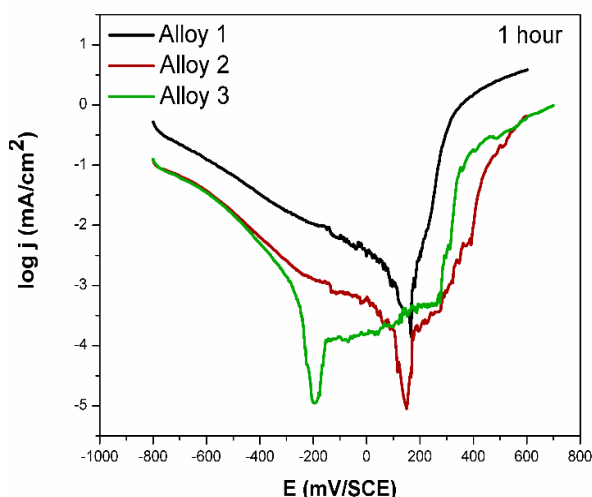


Figure 4. Polarization curves of tested alloys recorded after 1 hour of exposure to artificial saliva

After 1 hour of exposure (Figure 4 and Table 2), Alloys 1 and 2 exhibit similar electrochemical performance, with corrosion potentials close to each other in the anodic region. Alloy 2 shows a slightly lower corrosion current density than Alloy 1. In contrast, Alloy 3 displays a significantly more negative corrosion potential, lower current densities in both the cathodic and anodic regions, and a pronounced passive layer that appears at much more negative potentials and has substantially lower passive current density values compared to Alloys 1 and 2. These observations indicate that a protective layer forms on Alloys 2 and 3 during thermal treatment, with the 60-minute treatment (Alloy 3) producing a protective layer with much better and more stable performance than the 30-minute treatment (Alloy 2).

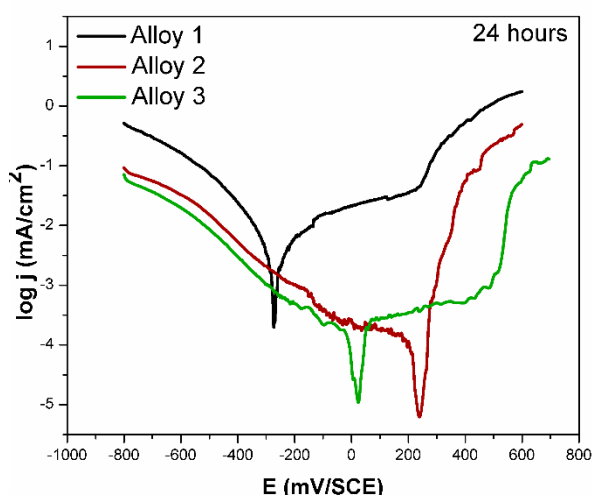


Figure 5. Polarization curves of tested alloys recorded after 24 hours of exposure to artificial saliva

After 24 hours of exposure (Figure 5 and Table 2), Alloys 2 and 3 exhibit similar and significantly more positive corrosion potential than Alloy 1. Passivation is now observed in all three alloys; however, Alloy 1 has a substantially higher passive current density than Alloys 2 and 3. These results indicate that even Alloy 1, which was not thermally treated, forms a passive layer under the influence of the corrosive environment, but at a much slower rate, resulting in a notably higher passive current density compared to the thermally treated Alloys 2 and 3.

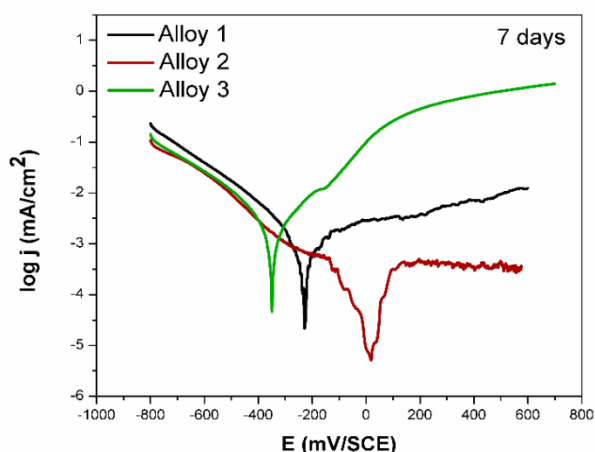


Figure 6. Polarization curves of tested alloys recorded after 7 days of exposure to artificial saliva

After 7 days of exposure (Figure 6 and Table 2), a dominant cathodic shift of the corrosion potential of Alloy 3 is observed, accompanied by a significant increase in its passive current density. For Alloys 1 and 2, the corrosion potentials change less, and the passive current density remains significantly lower than that of Alloy 3. This behavior suggests that Alloy 3 experienced a marked reduction in the protective performance of its formed passive layer, which could be attributed to increased layer permeability or, more likely, to damage of the passive film.

3.2. Electrochemical impedance spectroscopy measurements

3.2.1. Influence of exposure time on the electrochemical properties of the tested alloy

The results of electrochemical impedance spectroscopy measurements of the tested alloys in artificial saliva solution are shown as Bode plots in Figure 7 for Alloy 1, Figure 8 for Alloy 2, and Figure 9 for Alloy 3. The electrochemical behavior of the alloys was monitored over a period of 7 days, whereby the results were recorded after 1 hour, 24 hours, and 7 days, and the obtained average values for total impedance and phase angle are shown in Table 3.

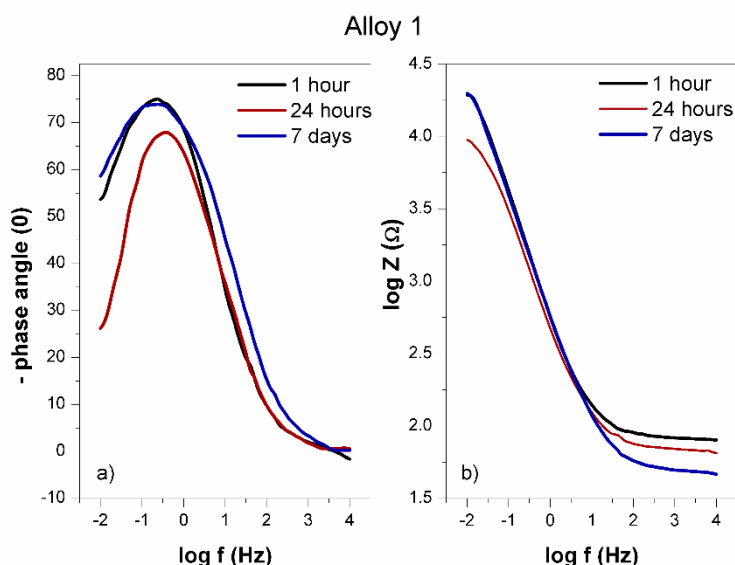


Figure 7. Bode plots of Alloy 1 in artificial saliva solution: a) phase angle vs. frequency; b) impedance modulus vs. frequency

Table 3. Total impedance ($\log Z$) and phase angle values of the tested alloys recorded after different immersion times in artificial saliva

	Alloy 1		Alloy 2		Alloy 3	
	– phase	$\log Z$	–phase	$\log Z$	–phase	$\log Z$
1 hour	75	4.4	78	4.7	78	5.2
24 hours	68	4.0	76	4.8	80	4.7
7 days	74	4.30	76	5.0	60	4.0

*The average value of the obtained parameters is within the limits of standard deviation of 0.10%-0.25%

As shown in Figure 7a and the data in Table 3, **Alloy 1** exhibits only one time constant across all measured time intervals. The maximum phase angle is located in the low-frequency region ($\log f < 1$), ranges between approximately 68° and 75° , and does not change significantly over time. Such behavior is characteristic of a capacitive response, which corresponds to good corrosion resistance of the material [22, 23] and also indicates the presence of a surface layer on the alloy.

The Bode plot of the total impedance of **Alloy 1** (Figure 7b, Table 3) reveals that at low frequencies, the alloy displays a high logarithm of impedance ($\log Z \sim 4\text{--}4.4$), indicating good corrosion properties, i.e., high corrosion resistance [24, 25]. The total impedance of Alloy 1 (Table 3) does not change substantially over time, suggesting that the protective properties of the formed film are maintained throughout the measurement period.

In the medium-frequency range, Figure 7b shows a linear segment of the curve in all time intervals. After fitting this linear portion, slope values between -0.70 and -0.80 were obtained.

These values indicate capacitive behavior of the double layer, consistent with a constant phase element exponent. This further suggests that a layer has formed on the alloy surface in the artificial saliva solution, acting as a type of insulating barrier while remaining partially permeable to ions from the solution [25–27].

As shown in Figure 8a and the data in Table 3, **Alloy 2** also exhibits only one time constant across all measured time intervals. After one hour, the highest phase angle value is observed in the low-frequency region at 0.18 Hz ($\log f = -0.74$), reaching 78° . After 24 hours and 7 days, the maximum phase angle values remain nearly identical, with no significant shift in the frequency of these maximums. The Bode plot of total impedance (Figure 8b) reveals that Alloy 2 also displays a high logarithm of impedance at low frequencies, with $\log Z \sim 4.7\text{--}5$ (Table 3). In the medium frequency range, the linear portions of the curves exhibit slope values between -0.80 and -0.90 . As in the case of Alloy 1, all of the above indicates capacitive behavior of the double layer and confirms the good corrosion properties of Alloy 2 across all time intervals [22, 23, 28].

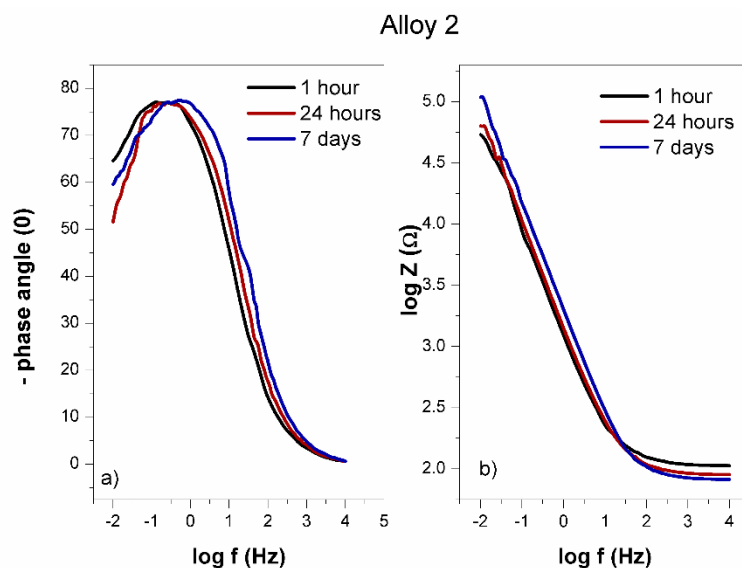


Figure 8. Bode plots of Alloy 2 in artificial saliva solution: a) phase angle vs. frequency; b) impedance modulus vs. frequency

From Figure 9a and the data shown in Table 3, it can be seen that after one hour of contact with artificial saliva, **Alloy 3** exhibits a high phase angle value of 78° in the low frequency region. After 24 hours, there is a slight increase in the phase angle to 80° and a modest shift toward lower frequencies, indicating that the performance of the layer formed during thermal treatment does not change significantly over this period. After 7 days, a substantial decrease in the phase angle is observed, down to 60°, occurring at frequencies like those recorded after 1 hour of measurement.

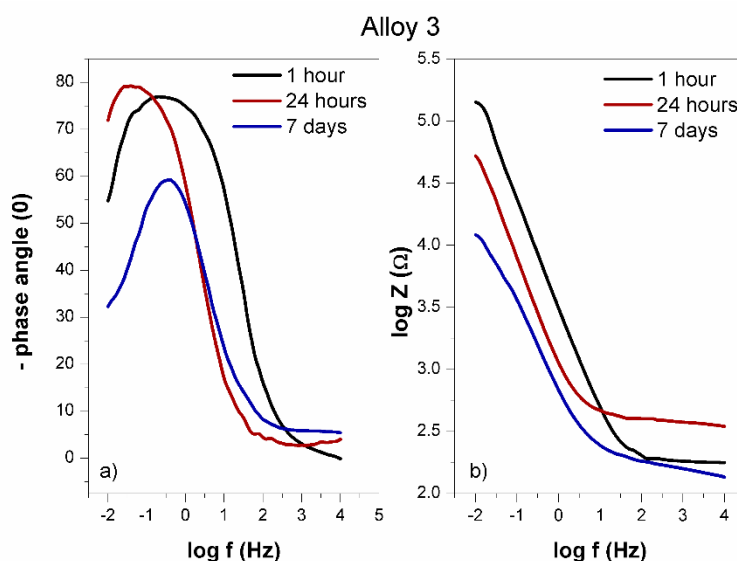


Figure 9. Bode plots of Alloy 3 in artificial saliva solution: a) phase angle vs. frequency; b) impedance modulus vs. frequency

The Bode plot of total impedance (Figure 9b, Table 3) reveals that Alloy 3 exhibits a high logarithm of impedance at low frequencies ($\log Z \sim 4\text{--}5.2$), indicating good corrosion resistance under the given conditions[22, 23, 28]. In the medium-frequency range, Figure 9b shows, as with the previous alloys, a linear segment of the curve across all time intervals. After fitting this linear portion, a slope value of -0.88 was obtained after 1 hour, which decreased to -0.79 after 7 days. These values indicate capacitive behavior of the double layer and simultaneously suggest that a protective layer has formed on the alloy surface; however, the performance of this layer degrades over the tested period.

3.2.2. Influence of thermal treatment time on the electrochemical properties of the tested alloy

The Bode plots for all analyzed alloys, measured after 1 hour, 24 hours, and 7 days, are presented together in Figures 10, 11, and 12, respectively.

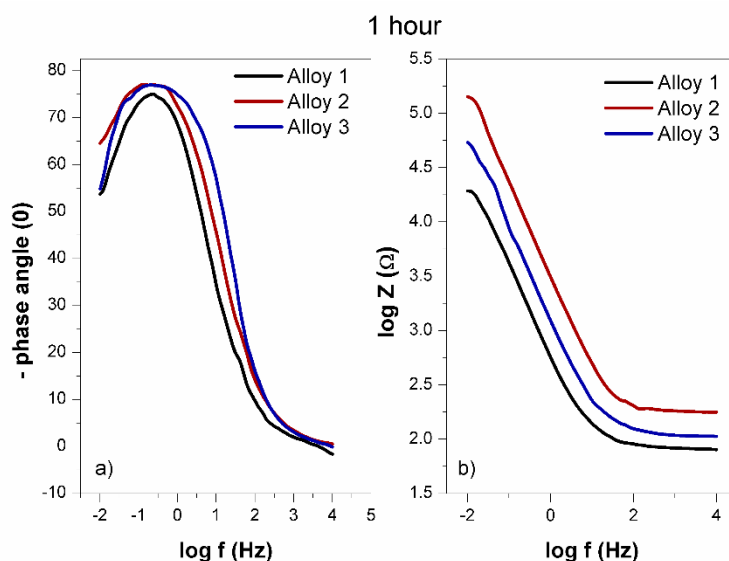


Figure 10. a) Bode phase angle plot after 1 hour; b) Bode impedance plot after 1 hour

As shown in Figure 10, after **1 hour** of measurement, all alloys exhibit similar behavior, with very close maximum phase angle and total impedance values. However, Alloy 3 displays slightly better electrochemical properties related to corrosion resistance, while Alloy 1 shows slightly worse ones. This behavior can be attributed to the good corrosion properties of all alloys over this short exposure period.

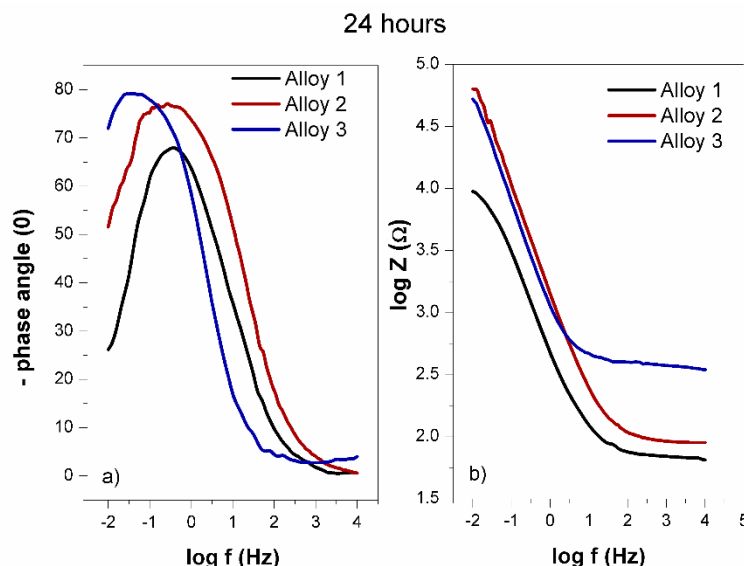


Figure 11. a) Bode phase angle plot after 24 hours; b) Bode impedance plot after 24 hours

After **24 hours** of measurement (Figure 11), oscillations in the behavior of the alloys become apparent. Alloy 3 still exhibits the highest phase angle (80°) and total impedance, recorded at the lowest frequency of 0.02 Hz, while Alloy 1 continues to show the lowest values. At this time point, however, the differences among the alloys are much more pronounced (Table 3). These differences can be interpreted as a consequence of the lack of a compact protective passive layer on Alloy 1, which had not been thermally treated prior to exposure. Similar to the measurements taken after 24 hours, the alloys displayed certain deviations in their electrochemical behavior following 7 days of exposure.

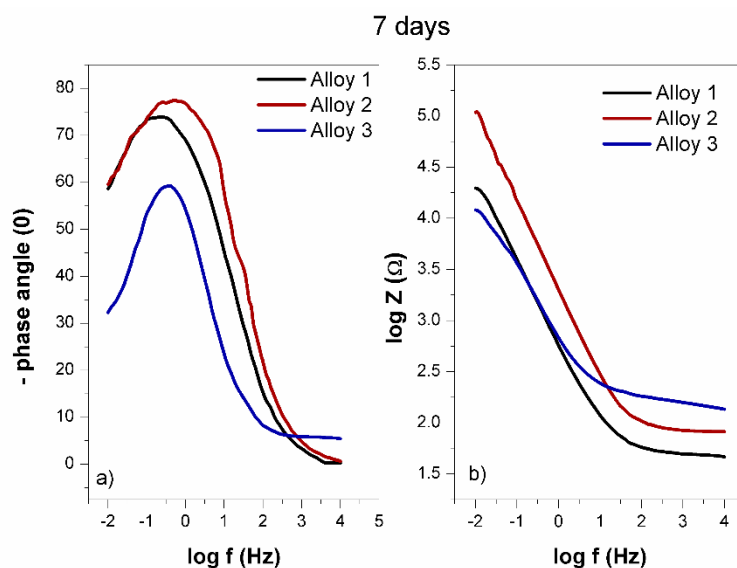


Figure 12. a) Bode phase angle plot after 7 days; b) Bode impedance plot after 7 days

After **7 days** of measurement (Figure 12), the highest phase angle value (76° at 0.40 Hz) and the highest total impedance (Table 3) were recorded for Alloy 2. In this time period, Alloy 1 no longer lags far behind, indicating that a protective layer is slowly forming on its surface, achieving increasingly good protective properties.

In contrast, Alloy 3, which exhibited the best performance after 1 hour and 24 hours shows the lowest values of both phase angle and total impedance after 7 days. This is a clear indication of a significant weakening of corrosion resistance. The cause of this deterioration may be damage to the film, whether it is accidental or resulting from cracking due to inhomogeneity or excessive thickness of the layer. This phenomenon is planned to be investigated in our further work.

Analysis of the EIS results enabled the selection of an appropriate equivalent electrical circuit to describe the electrochemical response of the Ti-Ni alloy investigated in artificial saliva solutions. Since the impedance spectra (Figures 7-9) exhibited non-ideal capacitive behavior, a constant phase element (Q) was incorporated into the equivalent circuit instead of an ideal capacitor. The corresponding double-layer capacitance (C_{dl}) was subsequently calculated from the constant phase elements using the conventional relationship reported in the literature [23, 25]. The experimental impedance data were successfully fitted using the equivalent circuit $R_s (R_p Q_{dl}) (R_f C_f)$ for all samples, with the exception of Alloy 1 after 1 h of immersion, for which the simplified $R_s (R_p Q_{dl})$ circuit provided the best fit (Figure 13).

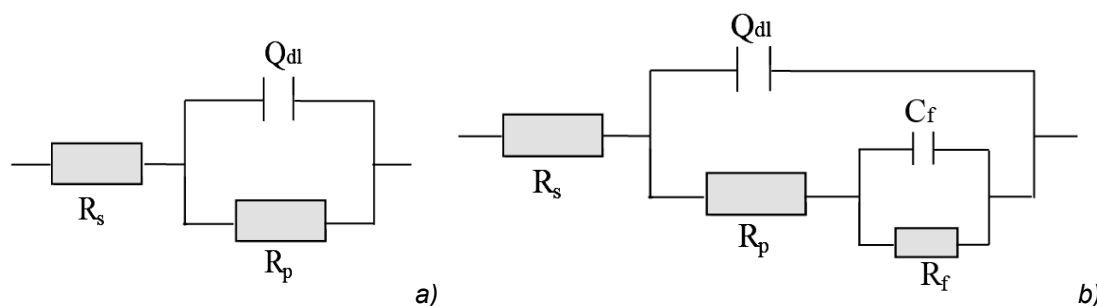


Figure 13. Equivalent circuit for the tested alloys a) Alloy 1 after 1 hour, b) all tested Alloys after 1 hours (except Alloy 1), 24 hours and 7 days

The electrochemical parameters obtained from the fitting procedure are summarized in Table 4. These include the solution resistance (R_s), polarization resistance (R_p), double-layer capacitance (C_{dl}), passive film resistance (R_f), passive film capacitance (C_f), and the constant phase element exponent (n), all of which were determined from the EIS measurements.

Table 4. EIS parameters of the investigated Ti-Ni alloys at different immersion times in artificial saliva

	R_s (Ωcm^2)	R_p ($\text{k}\Omega\text{cm}^2$)	C_{dl} (mF/cm^2)	n	R_f ($\text{k}\Omega\text{cm}^2$)	C_f (mF/cm^2)	$\chi^2 \cdot 10^3$
Alloy 1							
1 hour	10	50.0	17.2	0.84	---	---	1.2
24 hour	10	12.0	6.49	0.81	10	9.0	2.6
7 days	10	71.5	8.79	0.86	18	2.0	2.2
Alloy 2							
1 hour	10	200	5.73	0.89	50	1.8	1.1
24 hour	10	195	2.63	0.88	50	3.0	4.6
7 days	10	190	2.84	0.88	50	5.0	3.2
Alloy 3							
1 hour	10	1000	2.20	0.88	100	10	4.0
24 hour	120	700	75.5	0.90	80	30	1.4
7 days	120	15.5	675	0.73	15	150	4.5

*The average value of the obtained parameters is within the limits of standard deviation of 0.10%-0.25%

The electrochemical parameters derived from the fitting of the EIS data provide quantitative support for the main conclusions established from the polarization measurements and the analysis of the Bode plots.

As previously discussed, the results presented in Table 4 indicate that the corrosion resistance of **Alloy 1** improves with increasing immersion time, as evidenced by the increase in polarization resistance (R_p) and the decrease in double-layer capacitance (C_{dl}). This behavior can be attributed to the formation and stabilization of a protective passive film on the alloy surface. The protective characteristics of the passive film improve with immersion time, as evidenced by the increase in film resistance (R_f) and the corresponding decrease in film capacitance (C_f).

At the beginning of the immersion period, **Alloy 2** exhibited significantly higher corrosion resistance than Alloy 1, as indicated by its higher polarization resistance (R_p) and lower double-layer capacitance (C_{dl}) and presence of film on surface (R_f and C_f). This behavior can be attributed to the protective surface film formed during the heat treatment. An important observation is that these electrochemical characteristics remained essentially unchanged throughout the immersion period, as no significant variations were observed in the values of R_p , R_f , C_{dl} , and C_f . A slight increase in film capacitance (C_f) with immersion time was detected, suggesting a minor increase in the concentration of ionic species within the passive film.

Alloy 3 exhibited substantially superior corrosion resistance compared with the other two alloys, as evidenced by its significantly higher polarization resistance (R_p) and passive film resistance (R_f). However, after 24 h of immersion, both the polarization resistance (R_p) and film

resistance (R_f) decreased, in agreement with the polarization measurements. This degradation became more pronounced after 7 days of immersion, as evidenced by a further decline in R_p and R_f , accompanied by a significantly pronounced increase in the double-layer capacitance (C_{dl}) and film capacitance (C_f). These changes indicate the progressive deterioration of the protective surface film and a corresponding reduction in the corrosion resistance of the alloy with prolonged exposure. The observed reduction in the corrosion resistance of Alloy 3 may have resulted from several factors, including stress accumulation, oxide cracking, excessive oxide growth, local nickel enrichment, and passive film instability. Based on the available electrochemical data, however, it is not possible to identify the predominant mechanism responsible for the observed behavior.

Based on the overall electrochemical results, it can be concluded that the 30 min heat treatment provides the investigated alloy with the highest corrosion resistance under the tested conditions and throughout the examined immersion period in artificial saliva solution.

4. CONCLUSION

In this study, the electrochemical behavior of a Nitinol alloy in artificial saliva solution was investigated using electrochemical methods: Potentiostatic polarization measurements and electrochemical impedance spectroscopy.

Based on the analysis of the results obtained, the following conclusions can be drawn:

Potentiostatic polarization measurements

- The electrochemical activity of all alloys depends on both the exposure time to artificial saliva and the duration of their thermal treatment.

- A passive current density, which is generally accepted as evidence of passive film formation on the electrode surface, was observed for all tested alloys and its characteristics are largely determined by the prior thermal treatment of the alloy.
- Longer thermal treatment (60 minutes) promotes the formation of a protective layer within a shorter time frame, and the protective ability of the layer is superior but only in a short time interval. In contrast, the layer forms much more slowly on the alloy that did not receive any thermal treatment, but the protected performance lasts longer.

Electrochemical impedance spectroscopy

- All tested alloys exhibit capacitive behavior, and the results indicate the presence of a protective layer on the surface of each of them.
- All tested alloys show high total impedance and phase angle values across all time intervals (except Alloy 3 after 7 days), indicating good corrosion properties, i.e., high corrosion resistance.
- The electrochemical parameters obtained by the fitting process also confirm that Alloy 1 (non-thermally treated) require longer exposure time to develop enhanced corrosion resistance, most likely through the gradual formation of a protective film on its surface.
- The best initial protective performance is observed for Alloy 3, which was exposed to high temperature for the longest duration (60 minutes). However, after 7 days, the protective properties of Alloy 3 weakened significantly.
- Overall, the obtained results indicate that the 30 minutes heat treatment yields the optimum corrosion performance of the investigated Ti-Ni alloy under the applied experimental conditions and during the entire immersion period in artificial saliva solution.

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IZVOD

ELEKTROHEMIJSKO PONAŠANJE MODIFIKOVANE Ti-Ni LEGURE U RASTVORU VEŠTAČKE PLJUVAČKE

Savremeni ljudi se sve više susreću sa situacijama u kojima telesne tečnosti poput znoja, pljuvačke, limfe ili krvi dolaze u privremeni ili produženi kontakt sa metalnim predmetima. Ovo se dešava sa stomatološkim materijalima, ortopedskim implantatima, protezama i modnim nakitom i može pokrenuti različite elektrohemijske procese. Takvi procesi imaju dvostruke posledice: mogu promeniti strukturu i svojstva metala, a istovremeno izazvati štetne reakcije u susednom ljudskom tkivu. Legure titanijum nikla (TiNi) su među najčešće korišćenim materijalima kako za modne dodatke, tako i za razne implantate (stomatološke i ortopedske). Uprkos mnogim povoljnim svojstvima, TiNi legure imaju veliki nedostatak: joni nikla, oslobođeni tokom elektrohemijske reakcije između legure i ljudskih elektrolita, sve su odgovorniji za alergijske reakcije kod sve većeg broja pojedinaca. Iz tog razloga, postoji značajno interesovanje za pronalaženje načina da se spreči ili minimizira oslobađanje jona nikla iz legure. Shodno tome, ova studija se fokusirala na praćenje elektrohemijskih karakteristika termički modifikovane TiNi legure. Elektrohemijsko ponašanje termički modifikovane NiTi legure procenjeno je u rastvoru veštačke pljuvačke kao funkcija vremena izlaganja.

Ključne reči: legura Ti-Ni; elektrohemijska svojstva; veštačka pljuvačka

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