
Research article

Assessment of the corrosion resistance of Ti_{49.0}Ni_{51.0} alloy with various microstructures after long-term exposure to biological environments

Elmira Iskhakova^{1,2,*}, Anna Churakova^{1,2} and Evgeniy Vorobiev^{1,2}

¹ Institute of Molecule and Crystal Physics-Subdivision of the Ufa Federal Research Centre of the Russian Academy of Sciences, 151 pr. Oktaybrya, Ufa, 450075, Russia

² Ufa University of Science and Technology, 32 str. Zaki Validi, Ufa, 450076, Russia

* **Correspondence:** Email: elmira.iskhakova.74@mail.ru; Tel: +7-937-481-0429.

Abstract: This article investigated the corrosion properties of a nickel-rich Ti_{49.0}Ni_{51.0} (in at.%) alloy in coarse-grained (CG) and ultrafine-grained (UFG) states in three physiological solutions (0.9% NaCl, Ringer's solution, and Hanks' solution) at 37 °C over 180 days. Gravimetric analysis revealed that the UFG structure exhibits higher corrosion resistance compared to the CG state. According to atomic force microscopy (AFM) data, the increase in surface relief of UFG samples (up to 6 μm) is attributed to the accumulation of phosphate-rich precipitates rather than to degradation. The influence of different microstructures and Ti₃Ni₄ particles on the corrosion resistance in biological media has been established.

Keywords: shape memory alloys; corrosion resistance; coarse-grained structure; ultrafine-grained structure; corrosion rate

1. Introduction

Modern technologies actively utilize materials with unique functional properties, and one of the most interesting among them is titanium nickelide (TiNi) [1,2]. This alloy, which exhibits shape memory effect [3], superelasticity, and high corrosion resistance, has found applications in a wide range of fields, from medicine and aerospace to robotics and microelectronics.

The unique mechanical properties of TiNi and its biocompatibility with living tissues [4,5] have made it one of the most promising materials for medical implants [6–8] and devices. For medical

applications (e.g., stents and endovascular devices), it is important that the austenite finish temperature (A_f) is below body temperature (typically in the range of 20–30 °C), which ensures the superelasticity of the alloy at 37 °C. For other technical applications, an A_f above room temperature may be required. However, the equiatomic TiNi alloy does not demonstrate good stability of functional properties [9,10].

Significant scientific interest lies in the thermomechanical treatment of TiNi alloys, as it allows for purposeful modification of their microstructure and, consequently, regulation of their operational characteristics. For example, aging at certain temperatures can lead to the precipitation of nanosized particles, which enhance strength and shape stability [11–14]. Thus, despite some limitations of equiatomic TiNi, modern methods of composition modification and treatment enable the creation of shape memory alloys that are highly reliable and tailored for specific applications in medicine [15], aerospace, and microelectromechanical systems (MEMS) [16].

The use of titanium nickelide in medical implants requires high corrosion resistance, as material degradation in biological environments can lead to the release of nickel ions [17], causing unwanted immune reactions (toxic, allergic, carcinogenic) and impairment of the functionality of the device [18]. Therefore, research is actively being conducted to enhance the corrosion resistance and biocompatibility of TiNi.

The main protection of TiNi against corrosion is provided by a passive oxide layer of TiO_2 , which forms on the surface and inhibits further oxidation [19–22]. However, in aggressive conditions (low pH or presence of chlorides, such as in physiological saline), local degradation of this layer may occur, leading to pitting corrosion. As shown in [23], electropolishing improves the protective properties of nitinol by reducing the nickel content on the surface and increasing the pitting potential.

To improve the corrosion resistance of nitinol, various treatment methods are employed. In particular, the thermal oxidation of nitinol (50 at.% Ni) in air at temperatures ranging from 300 to 800 °C has been studied in detail [24]. It was found that oxidation at 500 °C results in the formation of a smooth, protective, nickel-free oxide layer (pure TiO_2), which is favorable for biocompatibility. At lower temperatures (300–400 °C), the layer contains nickel, while at higher temperatures (600–800 °C), it is rough and also contains nickel phases. Along with thermal treatment, the microstructure formed during intensive plastic deformation significantly impacts the corrosion resistance of nitinol. In particular, the transition from a coarse-grained (CG) to an ultrafine-grained (UFG) state can alter not only the mechanical properties but also the nature of surface passivation. The literature [5] describes the corrosion properties of coarse-grained nitinol and shows that it passivates well in environments simulating physiological fluids similar to human ones. According to previous research [25], corrosion is most intense in acidic environments in the coarse-grained state (especially at 3 M). The ultrafine-grained structure reduces corrosion in the unaged alloy but increases it in the aged condition (in sulfuric acid).

Thus, the long-term (180 days) corrosion behavior of nitinol with different microstructures under conditions simulating real implant operation, including the evaluation of surface compound accumulation without cleaning, remains insufficiently studied. The present work addresses this gap by conducting a comparative investigation of the corrosion behavior of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy in coarse-grained and ultrafine-grained states in biological media over extended exposure, with particular emphasis on the kinetics of passive film formation and nickel release under static physiological accumulation conditions.

2. Materials and methods

The $\text{Ti}_{49.0}\text{Ni}_{51.0}$ (hereinafter referred to as $\text{Ti}_{49.0}\text{Ni}_{51.0}$, with composition given in at.%) alloy was chosen as the material for the study. The alloy has a body-centered cubic (BCC) lattice ordered in the B2 type and a nickel-enriched Ti_2Ni_3 phase. To obtain the coarse-grained structure (CG, $d \approx 54 \pm 4 \mu\text{m}$), the alloy was quenched in water from 800 °C for 1 h, followed by annealing at 430 °C (aging temperature) for 1, 3, and 10 h. To obtain the UFG state, the alloy was subjected to equal-channel angular pressing (ECAP) followed by heat treatment. The ultrafine-grained microstructure obtained by ECAP with post-ECAP annealing at 430 °C is designated as UFG-I ($d \approx 188 \pm 2 \text{ nm}$), while the ultrafine-grained microstructure obtained by ECAP with preliminary annealing at 450 °C is designated as UFG-II ($d \approx 237 \pm 4 \text{ nm}$). Subsequent aging at 430 °C was performed for UFG-I for 1 and 10 h, while for UFG-II it was performed only for 1 h. Subsequently, the samples were immersed for 180 days in corrosive solutions simulating the biological environment of the body: 0.9% NaCl solution, Ringer's solution (6.5 g NaCl, 0.42 g KCl, and 0.25 g CaCl_2 per 1000 mL of distilled water), and Hanks' solution (8 g/L NaCl; 0.185 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; 0.4 g/L KCl; 0.06 g/L KH_2PO_4 ; 0.1 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; 0.06 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; 0.48 g/L $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; 0.35 g/L NaHCO_3).

The surface of $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy samples was examined before and after corrosion testing. The composition and morphology of the corrosion products on the surface were studied using chemical analysis and atomic force microscopy (AFM). The corrosion rate was determined by gravimetric analysis through periodic weighing of samples at 30-day intervals over a period of 180 days (6 months). The phase composition of the samples before and after corrosion testing was investigated using X-ray diffraction analysis (XRD).

To simulate the real operating conditions of an implant, where corrosion products naturally accumulate on the surface and are not removed, sample weighing after exposure was performed without removing surface deposits. Consequently, the reported gravimetric corrosion rate values (V_{gr}) should be considered as a generalized indicator reflecting the overall mass balance (metal loss and deposit accumulation) and used primarily for the comparative assessment of the effect of structural state under identical conditions.

The gravimetric corrosion rate was calculated using the Eq 1:

$$V_{gr} = \frac{(m - m_0)}{S\tau} \quad (1)$$

V_{gr} : gravimetric corrosion rate ($\text{g}/(\text{m}^2 \cdot \text{h})$); m_0 : initial mass of the sample before the corrosion test (g); m : final mass of the sample after the corrosion test, together with surface deposits (g); S : surface area of the sample (m^2); τ : exposure time (h). The value of V_{gr} is expressed in $\text{g}/(\text{m}^2 \cdot \text{h})$. If $m > m_0$, corrosion products remain on the surface of the sample. If $m < m_0$, the metal undergoes degradation (corrosion damage).

The test samples were disks with a diameter of 12 mm (Figure 1). During the experiment, the samples were placed in an incubator at a temperature of 37 °C.



Figure 1. Sample before corrosion testing.

3. Results

Figures 2 and 3 show photographs of the surface of the materials under study after six months of exposure in corrosive environments. Since the samples were not cleaned, corrosion products remained on the surface. Local accumulations of corrosion products alternating with areas of relatively clean surface are clearly visible.

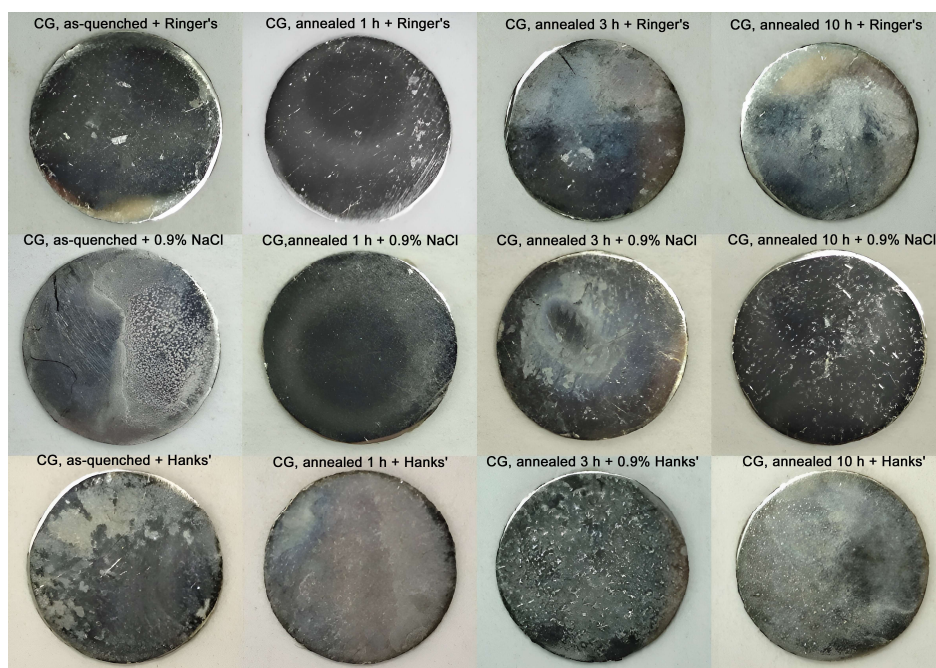


Figure 2. Appearance of samples with coarse-grained structure after six months of exposure in corrosive environments.

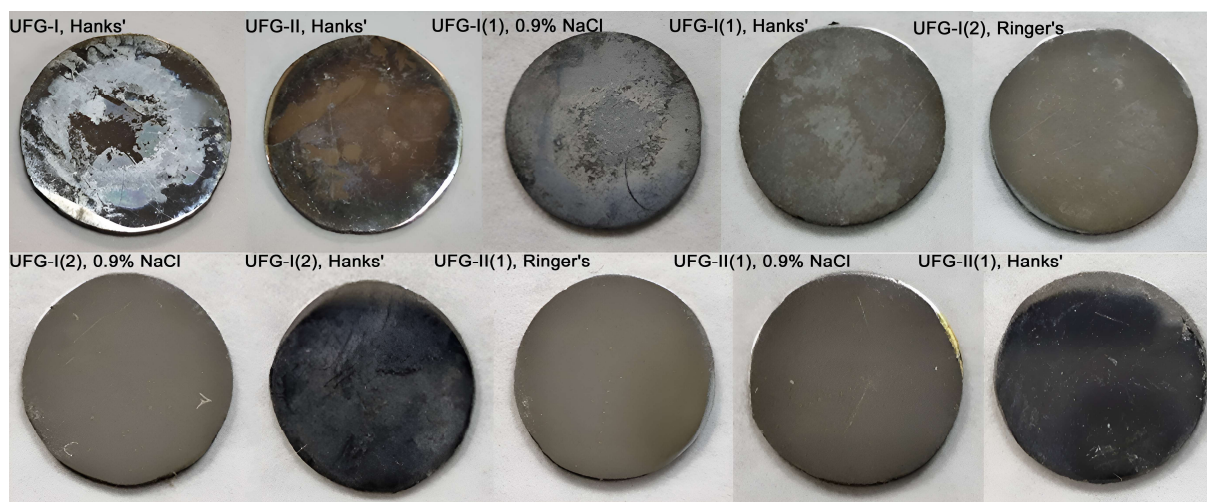


Figure 3. Appearance of samples with ultrafine-grained structure after six months of exposure in corrosive environments.

During the study, data on the corrosion rate of the samples were obtained using gravimetric analysis, and corresponding graphs were plotted based on these data. Figure 4 presents the data on the corrosion rate in the coarse-grained state.

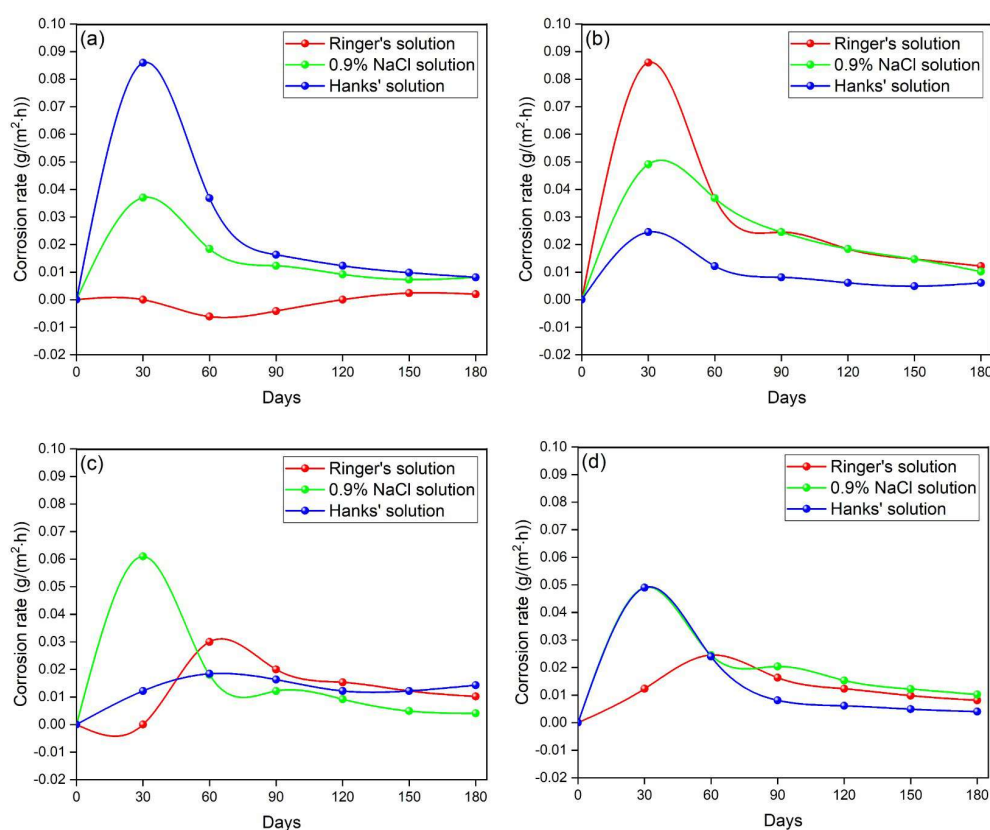


Figure 4. Corrosion rate of samples with coarse-grained structure: (a) quenching (800 °C, 1 h); (b) annealing at 430 °C for 1 h; (c) annealing at 430 °C for 3 h; and (d) annealing at 430 °C for 10 h.

In the first 30 days, an increase in the corrosion rate is observed in nearly all conditions, after which the corrosion rate begins to decrease. The exceptions are the initial state and samples subjected to a 3h annealing in Ringer's solution, where the dynamics are reversed: an initial decrease in the corrosion rate followed by a significant increase. The greatest mass loss, and consequently a more pronounced reduction in the corrosion rate, is characteristic of Ringer's solution. In 0.9% NaCl solution, the corrosion rate is roughly the same across all conditions, reaching 0.04–0.05 g/(m²·h) during the first 30 days, then gradually decreasing to 0.01 g/(m²·h). In Hanks' solution, the highest rate (0.086 g/(m²·h)) is observed in the hardened state. After annealing, the corrosion rate gradually decreases. The best results were obtained after 3 and 10 h of annealing, indicating a positive effect of thermal treatment on corrosion resistance. The corrosion rate in annealed states is significantly lower than that in the initial state.

Next, let us consider the corrosion rate graphs for the ultrafine-grained state (Figure 5).

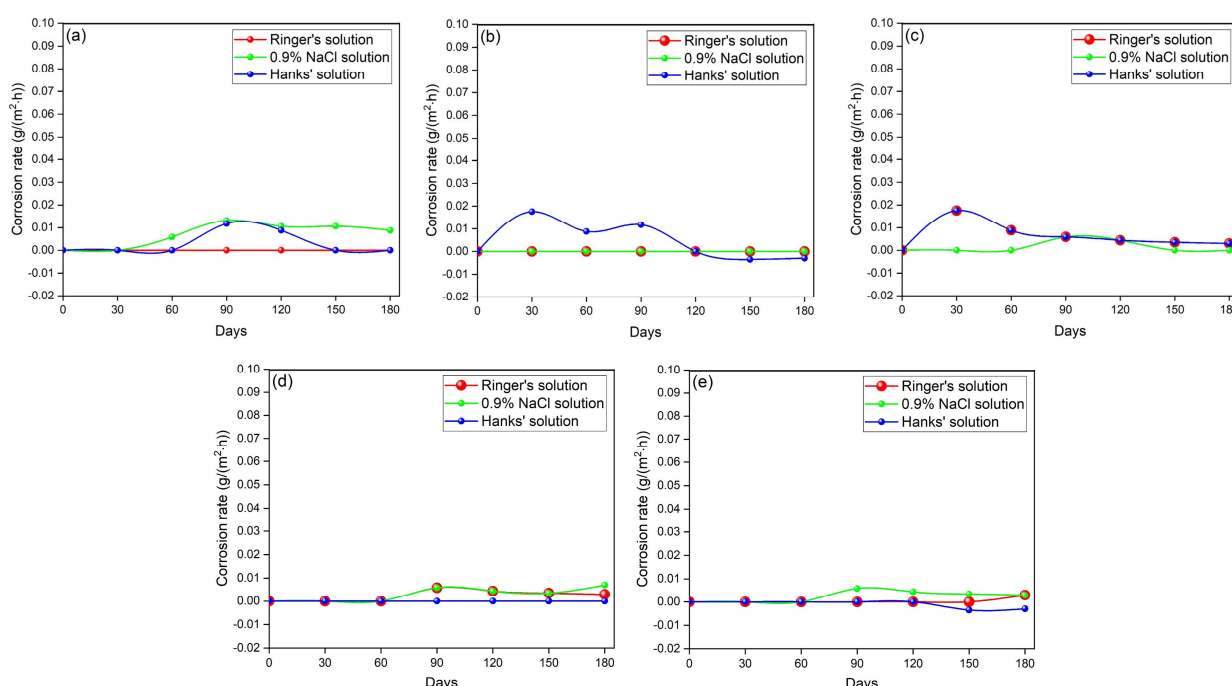


Figure 5. Corrosion rate of samples with ultrafine-grained structure: (a) quenching + ECAP; (b) ECAP + annealing at 430 °C for 1 h; (c) ECAP + annealing at 430 °C for 10 h; (d) annealing at 450 °C for 1 h + ECAP; and (e) annealing at 450 °C for 1 h + ECAP + annealing at 430 °C for 1 h.

The corrosion resistance of the alloy is determined by the corrosion rate. The research results demonstrate that the corrosion rate of the UFG alloy, compared to the CG alloy, changes minimally or not at all. In the UFG state, the best results were shown by the alloy in the as-received condition with preliminary annealing, where the corrosion rate over 30 days was nearly zero in almost all solutions. In 0.9% NaCl solution, the corrosion rate of the UFG-I alloy after 1 and 10 h of annealing remained unchanged over 180 days. In Hanks' solution, the most noticeable changes in corrosion kinetics were observed for the ultrafine-grained UFG-I alloy, where the corrosion process exhibits moderate growth both in the initial period (the first 30 days) and on the 90th day. According to the obtained data, the most corrosion-resistant alloy is Ti_{49.0}Ni_{51.0} with an ultrafine-grained structure.

In order to reveal the effect of long-term exposure in biological media on the phase composition of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy, XRD was performed. Figures 6 and 7 show the obtained XRD patterns for the coarse-grained and ultrafine-grained states after exposure for 180 days.

Prolonged exposure of the samples (in the CG state) for 180 days did not lead to significant changes in the phase composition of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy. However, in samples subjected to annealing for 3 and 10 h followed by exposure to Hanks' solution, XRD revealed the appearance of a low-intensity peak characteristic of the crystalline structure of 0.9% NaCl. This indicates a slight surface deposition of sodium chloride under these conditions, while the main matrix of the alloy retains its original phase composition. In the UFG-I state, an intense 0.9% NaCl peak was recorded after one month, which significantly decreased to a weakly expressed level after 180 days. In the UFG-I(1) and UFG-I(2) states, intense sodium chloride peaks were observed not only in Hanks' solution but also, in some cases, in Ringer's solution and 0.9% NaCl solution, indicating the specific corrosion behavior of these structural states in physiological media of different compositions.

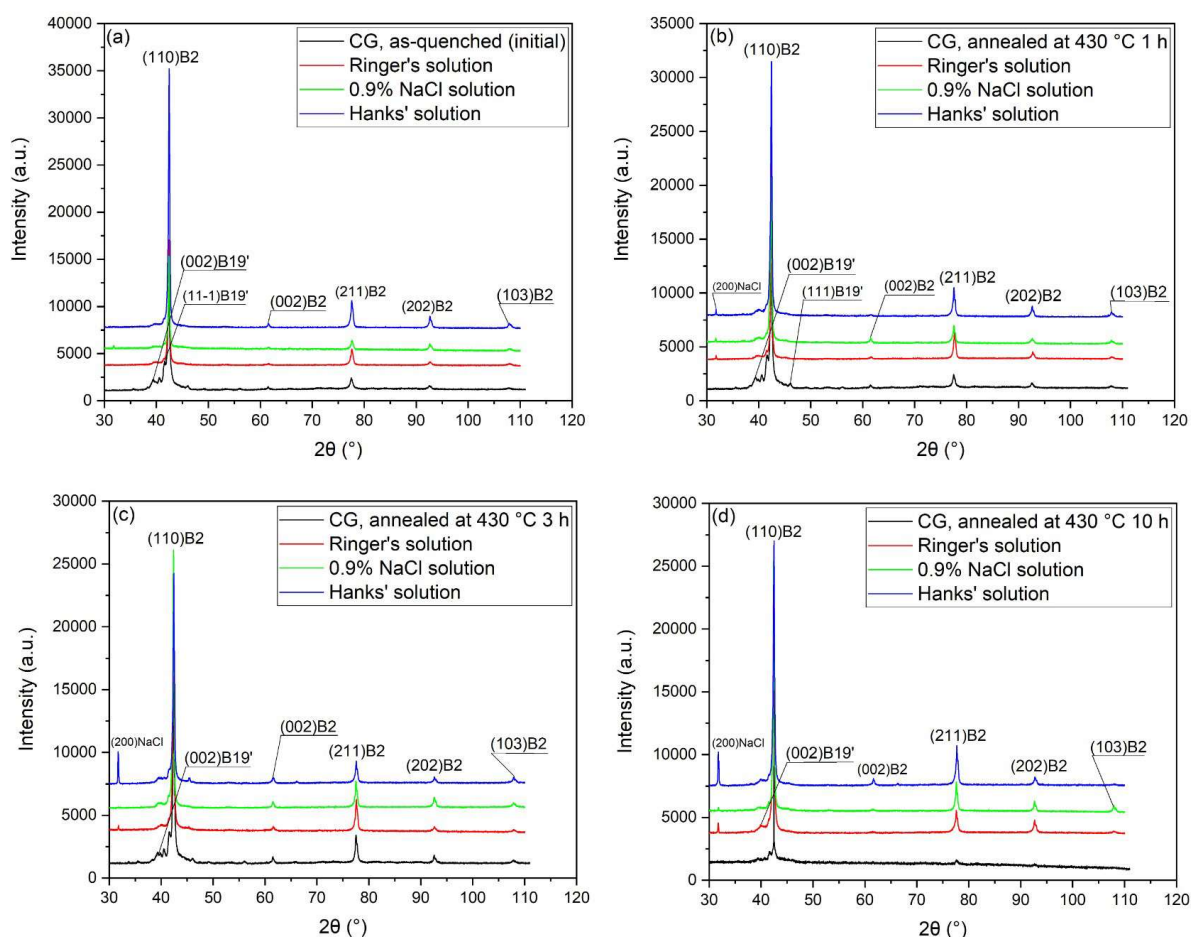


Figure 6. XRD patterns of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy after exposure to corrosive environments: (a) as-quenched; (b) after annealing at 430 °C for 1 h; (c) after annealing at 430 °C for 3 h; and (d) after annealing at 430 °C for 10 h.

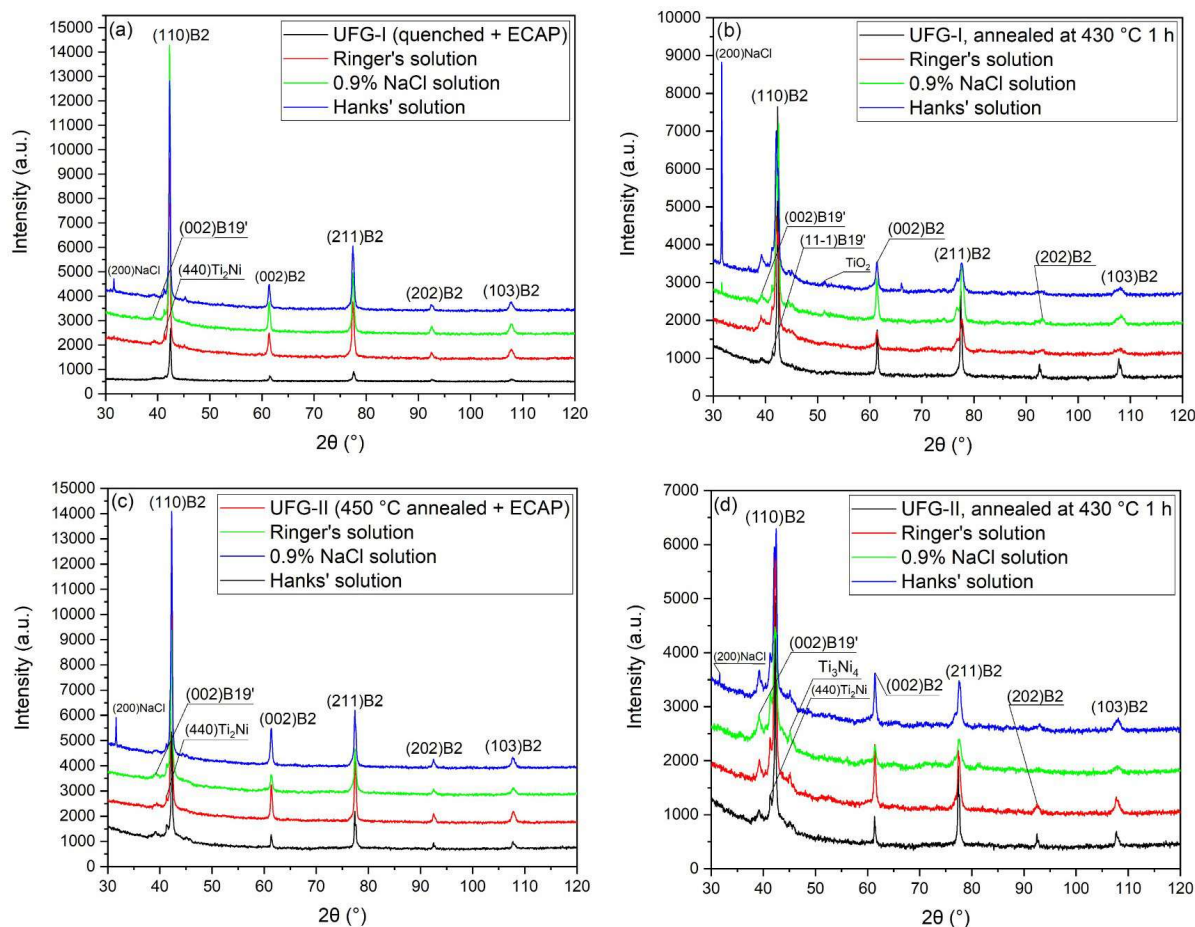


Figure 7. XRD patterns of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy after exposure to corrosive environments: (a) as-received UFG-I; (b) UFG-I after annealing at 430 °C for 1 h; (c) as-received UFG-II; and (d) UFG-II after annealing at 430 °C for 1 h.

An investigation of the surface relief of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy before and after corrosion tests was also carried out. The results obtained by AFM are presented in Figures 8 and 9.

While studying the effect of heat treatment and corrosive media on the surface relief of coarse-grained samples, it was found that the relief before corrosion testing ranged from 0.56 (after quenching) to 0.71 μm (after 10 h of annealing). After six months of exposure to corrosive media, multidirectional changes in relief were observed. In the quenched samples, the greatest increase in surface relief was caused by the 0.9% NaCl solution (from 0.91 to 2 μm) and Ringer's solution (up to 1.8 μm), whereas in Hanks' solution, a decrease in relief to 0.51 μm was recorded instead. The increased surface relief observed by AFM after immersion (up to 4.2 μm for CG and 6 μm for UFG) is primarily attributed to the accumulation of mineralized apatite/phosphate layers, as confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis. Rather than indicating severe surface degradation, this accumulation may serve as a physical barrier that passivates the surface and reduces the release of toxic Ni^{2+} ions. This is consistent with the qualitative Ni^{2+} detection results, which showed significantly less nickel release in the UFG state despite higher AFM relief values [26]. After annealing for 1 h in 0.9% NaCl solution, the microrelief reached up to 0.40 μm , while in Hanks' solution, it increased sharply to 1.8 μm . After 3 h of annealing, the maximum values (up to 2.6 μm) were recorded in Ringer's solution, indicating high activity of this medium for the given heat

treatment. The greatest variability in surface relief was observed after annealing for 10 h. In Hanks' solution, the relief height reached $4.2\text{ }\mu\text{m}$, indicating intense corrosion, whereas in Ringer's solution and 0.9% NaCl, the changes were less pronounced (ranging from 0.64 to 2.6 and $1.05\text{ }\mu\text{m}$, respectively). Thus, corrosion resistance strongly depends both on the heat treatment regime and the composition of the medium.

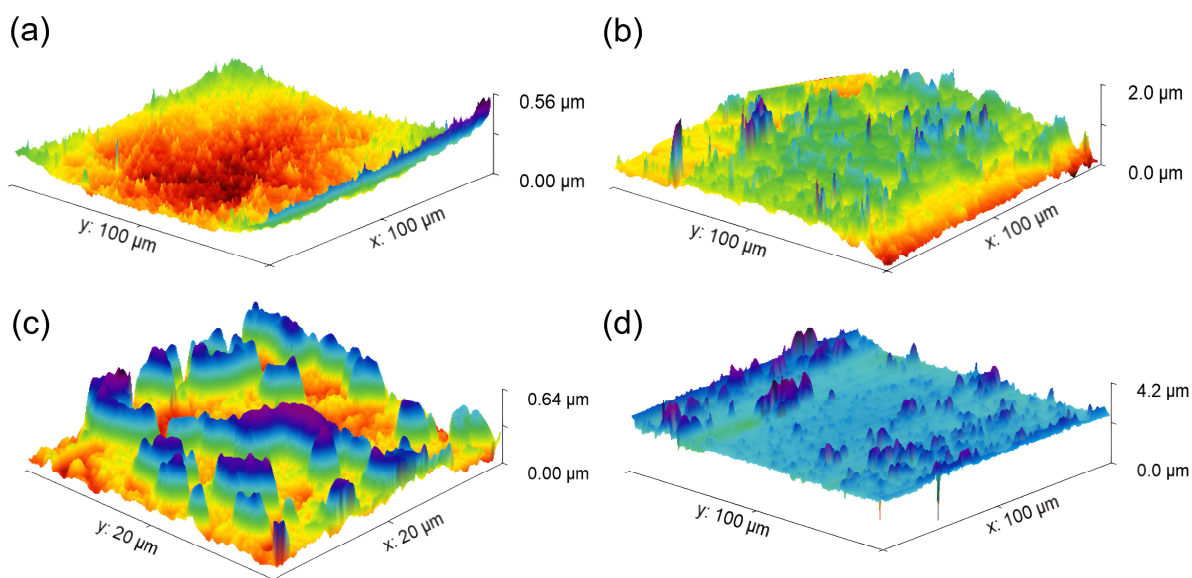


Figure 8. Surface relief of the CG $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy before and after corrosion testing: (a) as-quenched, initial state; (b) as-quenched, after exposure to 0.9% NaCl; (c) annealed at $430\text{ }^{\circ}\text{C}$ for 10 h, after exposure to Ringer's solution; and (d) annealed at $430\text{ }^{\circ}\text{C}$ for 10 h, after exposure to Hanks' solution.

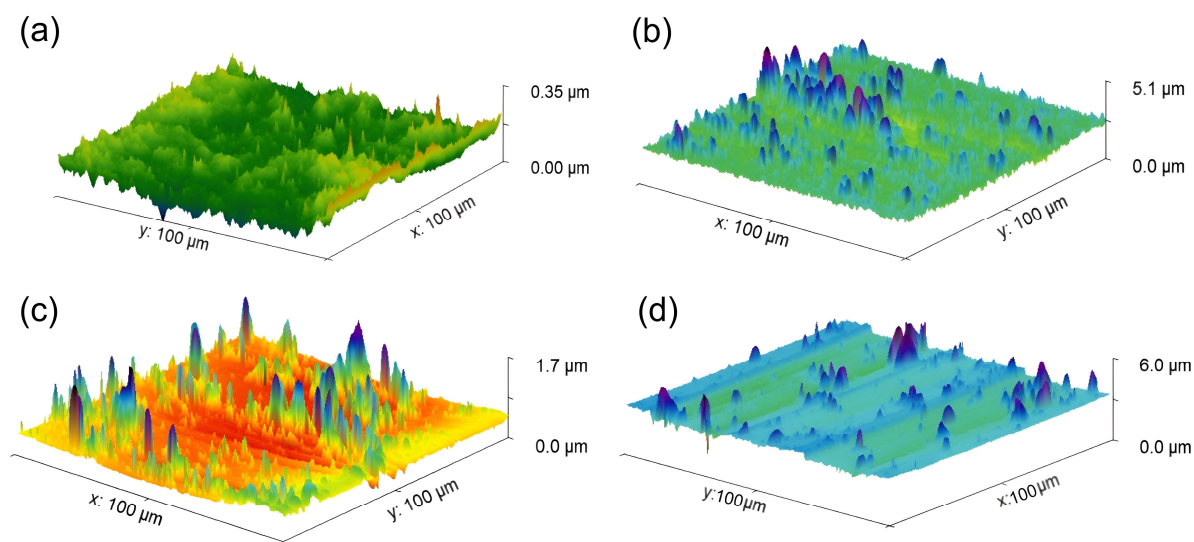


Figure 9. Surface relief of the UFG $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy before and after corrosion testing: (a) UFG-II, initial state; (b) UFG-I, after exposure to Hanks' solution; (c) UFG-II, after exposure to Ringer's solution; and (d) UFG-II (annealed at $430\text{ }^{\circ}\text{C}$ for 1 h), after exposure to Hanks' solution.

Investigation of the surface relief of samples with an ultrafine-grained microstructure showed the following results. After corrosion tests, the most active effect was demonstrated by Hanks' solution, causing an increase in relief up to 5.1 μm for UFG-I and 6 μm for UFG-II(1), while samples UFG-I(2) and UFG-II showed relatively stable values of approximately 1.3 μm . In Ringer's solution, most samples exhibited an increase in the range of 1.4–2.1 μm , except for UFG-II(1), where the relief height was 0.5 μm . In 0.9% NaCl solution, the values ranged from 0.4 μm for UFG-II(1) to 2 μm for UFG-I(1). Of particular interest is the behavior of sample UFG-II(1), which showed simultaneously low relief in Ringer's solution and 0.9% NaCl solution, and the highest relief in Hanks' solution. The obtained data indicate that optimal corrosion resistance is achieved in the state with pre-annealing at 450 °C (UFG-II), while additional annealing at 430 °C can either improve (UFG-I(2)) or worsen (UFG-II(1)) surface stability depending on the corrosive environment. The observed patterns highlight the complex nature of the interaction between the structure, heat treatment of the material, and corrosion mechanisms in different solutions.

4. Discussion

EDX of the surface of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy showed that corrosion products are present on the alloy surface in all studied structural states and in all corrosive media. These include the main alloy components (Ti, Ni) and elements present in the solutions. The formation and local accumulation of these products (oxides, chlorides, phosphates) on the surface lead to an increase in surface relief (as previously demonstrated by AFM images). Figure 10 shows, as an example, the results for Hanks' solution, illustrating this trend.

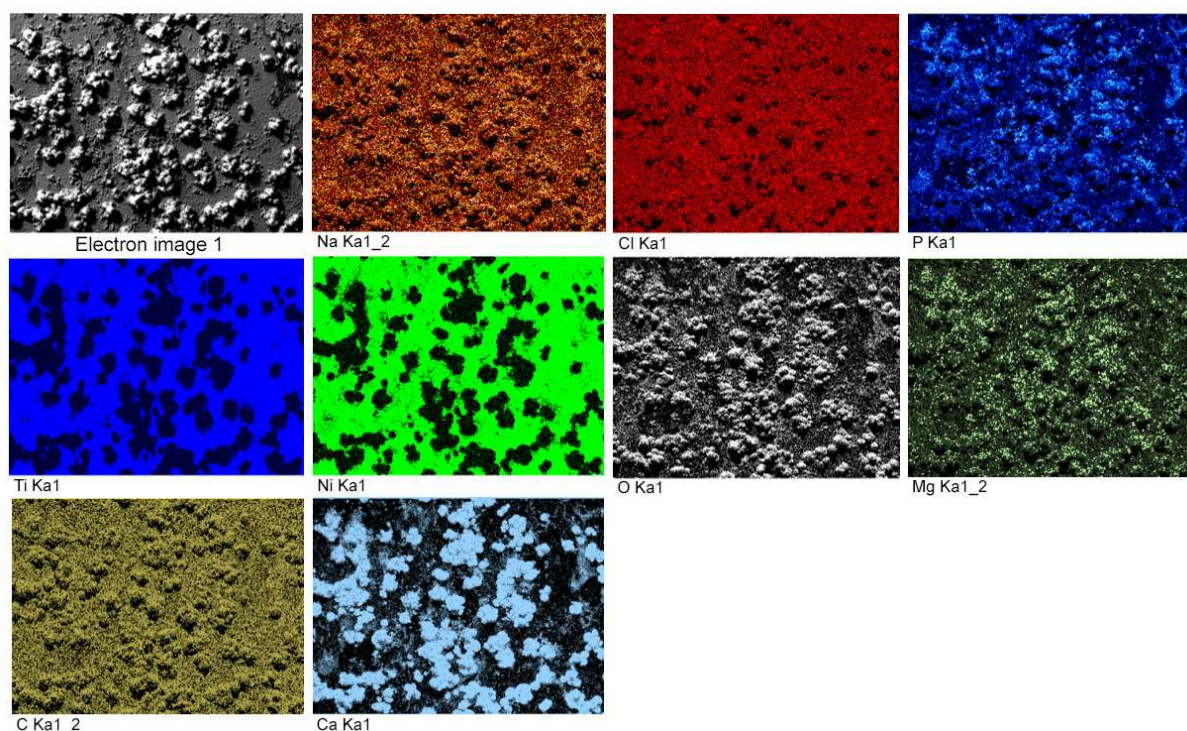


Figure 10. Results of EDX mapping of the surface of the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy in the ultrafine-grained UFG-II state after exposure to Hanks' solution for 180 days.

The main alloy components (Ti, Ni) are uniformly distributed on the surface according to scanning electron microscopy (SEM) analysis. The elements of the corrosive environment (Na, Ca, Mg, P, O) are present throughout the entire studied area (Figure 11, Table 1), indicating the formation of a surface film containing chloride, phosphate, and hydroxide compounds. Local inhomogeneities in the distribution of Ca, P, and Mg point to uneven deposition of corrosion products [27], which contributes to the formation of surface relief [26].

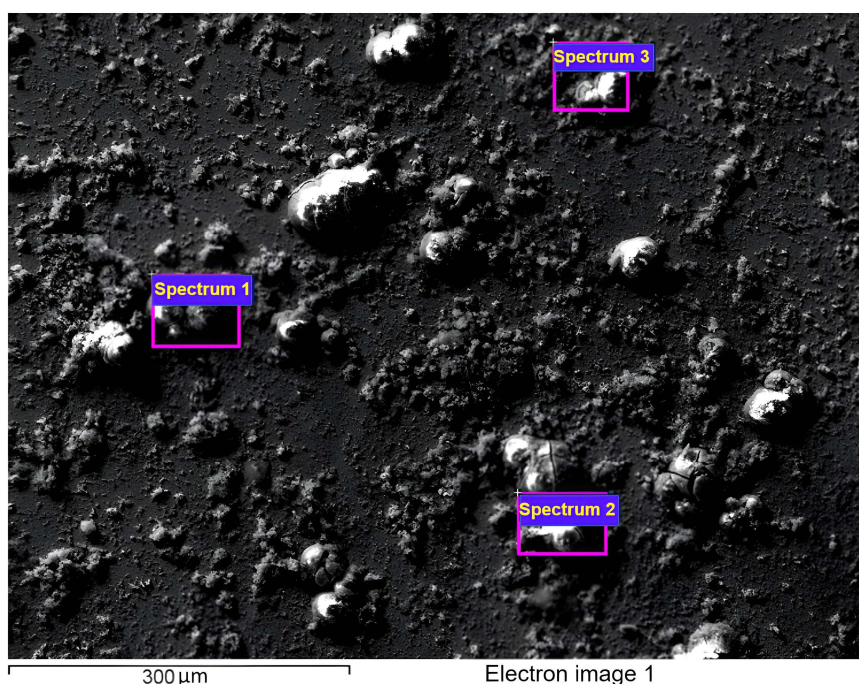


Figure 11. SEM micrograph showing the locations of the EDX point analysis (spectra 1–3).

Table 1. EDX analysis results (wt.%) of the selected points.

Spectrum	Stat.	C	O	Na	Mg	P	Cl	K	Ca	Ti	Ni	Total
Spectrum 1	Yes	3.81	39.89	2.18	2.84	8.23	1.06	0.20	19.93	9.28	12.57	100.00
Spectrum 2	Yes	4.78	41.13	2.32	3.17	10.53	1.36	0.19	22.75	5.87	7.90	100.00
Spectrum 3	Yes	3.62	35.56	2.57	3.44	10.44	1.26	—	14.15	13.13	15.83	100.00

Surface analysis revealed the presence of various corrosion products, the formation of which can be described by the following reactions. The breakdown of the passive TiO_2 film in chloride-containing media is initiated by chloride ions displacing oxygen from defective sites on the oxide surface. This local interaction leads to the formation of soluble Ti–chloride complexes and the thinning of the protective film, which creates sites for pitting initiation. The subsequent dissolution of the nickel-rich sub-layers proceeds through galvanic coupling between the exposed metallic phases, resulting in localized corrosion and nickel ion release [28]. This mechanism is consistent with the point-defect model of passive film breakdown, which is widely accepted for understanding localized corrosion of nitinol in biological environments. In Ringer’s solution, in addition to the above-mentioned products, Ca^{2+} ions present in the solution react with hydroxide and dissolved

carbon dioxide, depositing calcium carbonate on the surface: $\text{Ca}^{2+} + 2\text{OH}^- + \text{CO}_2 \rightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$. In Hanks' solution, which contains phosphates and sulfates, the nature of the corrosion products changes significantly. Ni^{2+} ions are bound by phosphates into sparingly soluble nickel phosphate: $3\text{Ni}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Ni}_3(\text{PO}_4)_2\downarrow$. The Ca^{2+} and Mg^{2+} ions present in Hanks' solution form protective phosphate layers: $\text{Ca}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4\downarrow$ and $\text{Mg}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{MgHPO}_4\downarrow$. In addition, bicarbonates promote the deposition of carbonates: $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3\downarrow$. Phosphate ions adsorb onto defects in the oxide film, forming phosphate complexes that stabilize TiO_2 and block chloride access. As a result, a dense multilayer deposit forms in Hanks' solution, consisting mainly of nickel, calcium, and magnesium phosphates, as well as calcium carbonate, which suppresses further nickel ion release.

TiNi alloys are prone to the release of toxic nickel ions during corrosion, which limits their application in medical implants [29]. In this regard, the present study assessed the intensity of nickel ion release from the TiNi alloy. For qualitative determination, upon addition of a solution containing Ni^{2+} , a red complex of nickel dimethylglyoximate is formed (a characteristic feature of the analytical chemistry of nickel). This method was used as a semi-quantitative comparative approach to visually assess the relative intensity of nickel release between different structural states. While the method does not provide absolute Ni^{2+} concentrations (mg/L), it enables a clear and reproducible comparison: intense pink coloration indicates significant nickel release, whereas its absence or weakness indicates suppression of nickel dissolution: $\text{NiCl}_2 + 2\text{C}_4\text{H}_8\text{N}_2\text{O}_2 + 2\text{NH}_4\text{OH} \rightarrow (\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Ni}\downarrow + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$.

Among the three studied media, the most aggressive toward the nitinol surface was 0.9% NaCl solution, followed by Ringer's solution, while Hanks' solution was the least aggressive. In 0.9% NaCl, due to the high chloride concentration, intense degradation of the oxide film, pitting corrosion, and noticeable nickel ion release (pink precipitate) are observed. In Ringer's solution, the presence of calcium ions partially reduces the aggressiveness of chlorides through the deposition of carbonates/phosphates, which create a barrier. In Hanks' solution, which contains HPO_4^{2-} phosphates and sulfates, surface damage is minimal, nickel release is virtually absent, and the oxide film remains stable.

Figure 12 shows the solutions that had been in contact for 6 months with samples with a coarse-grained microstructure.

During qualitative reactions for nickel ions (Ni^{2+}) using dimethylglyoximate, a pink precipitate formed in all solutions, indicating a low Ni^{2+} content [30]. The highest corrosion activity of nickel was observed after quenching and after annealing for 1 and 3 h. Longer annealing (10 h) reduced the release of Ni^{2+} , which may be associated with the formation of a more stable structure.

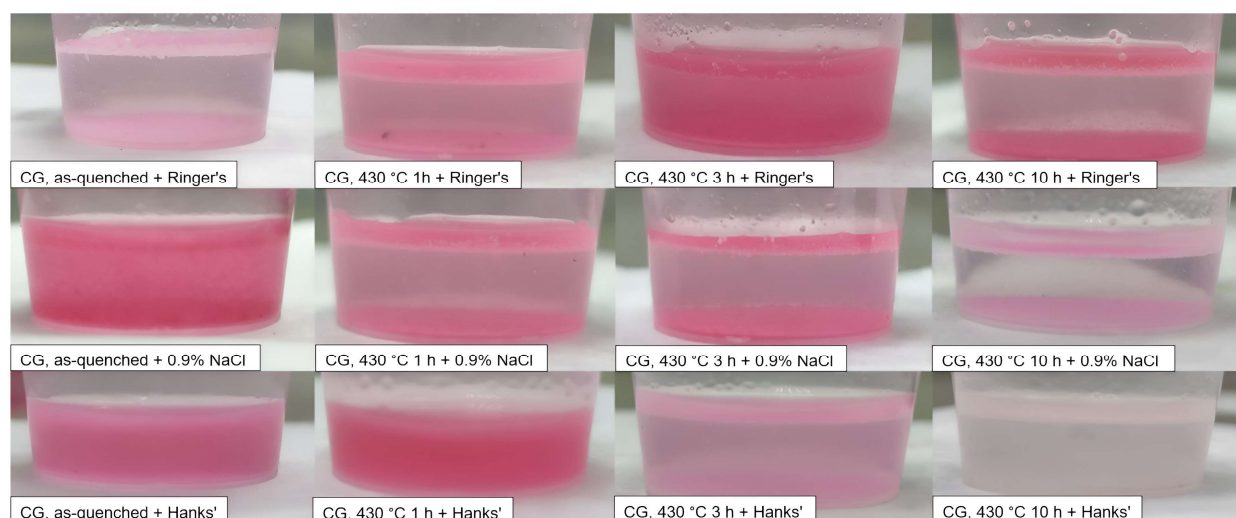


Figure 12. Reactions of nickel ion release in the CG state.

The results of the 180-day contact of the solutions with the samples with an ultrafine-grained structure are shown in Figure 13.

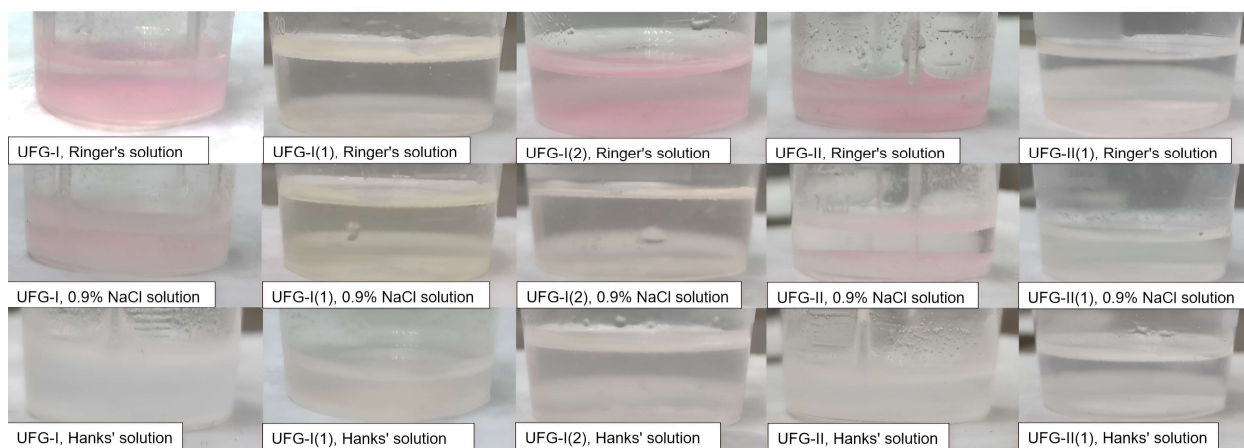


Figure 13. Reactions of nickel ion release in the UFG state.

In contrast to the solutions with coarse-grained samples, where intense coloration and precipitate formation were observed, no visible changes were observed in the solutions with UFG samples. After 6 months of contact, all solutions retained their original color, and signs of precipitate formation were practically absent. This indicates a lower corrosion rate and nickel release under these conditions. A barely noticeable light pink precipitate is most often observed in Ringer's solution, which indicates its increased corrosion activity with respect to nickel.

The corrosion behavior of titanium nickelide in the studied media is determined by the chloride-to-phosphate ratio. The influence of the biological medium composition is ambiguous. On the one hand, chloride ions, possessing high penetrating ability, initiate the depassivation of the oxide film and promote the development of pitting corrosion. On the other hand, the presence of phosphate ions (in Hanks' solution) significantly changes the picture: phosphates act as inhibitors,

adsorbing on the TiO_2 surface and accelerating the formation of a protective layer similar to apatite. Thus, the corrosion resistance of TiNi in a given medium is determined by the balance between the damaging action of Cl^- and the passivating effect of PO_4^{3-} .

Although the XRD patterns (Figures 6 and 7) do not show pronounced superlattice reflections corresponding to nano-sized Ti_3Ni_4 precipitates, this does not indicate the absence of this phase. The lack of clear peaks can be attributed to two main reasons. First, as reported in the literature [31,32], the Ti_3Ni_4 peaks in the 2θ range of $\sim 39\text{--}43^\circ$ overlap with those of the B19' martensitic phase and the $\text{Ti}_4\text{Ni}_2\text{O}_x$ oxide phase, making their unambiguous identification from standard powder diffraction patterns extremely difficult. Second, quantitative phase analysis indicates that the Ti_3Ni_4 phase content in the studied states is relatively small, which is insufficient to produce clearly resolved reflections against the intense matrix peaks. Direct evidence of the presence of nano-sized Ti_3Ni_4 precipitates in similar alloys has been obtained by transmission electron microscopy [33], confirming that the absence of clear peaks on standard diffractograms does not necessarily indicate the absence of this phase. In the present work, aging at 430°C is likely to result in the formation of nano-sized Ti_3Ni_4 precipitates, however, their small volume fraction and possible localization near grain boundaries prevent unambiguous identification using standard XRD patterns.

The increased corrosion resistance of the UFG state is likely associated with the formation of a denser and more uniform passive layer on the surface [34]. The larger total length of grain boundaries may accelerate titanium diffusion to the surface, thereby promoting faster passive layer formation. However, this interpretation remains hypothetical, since no local electrochemical measurements (e.g., scanning electrochemical microscopy or microprobe potential analysis) were performed in the present work. Alternative mechanisms, including changes in internal stress distribution, surface oxide composition, or the kinetics of passive film formation, cannot be excluded and require further investigation. Nevertheless, regardless of the exact mechanism, the experimental data unambiguously demonstrate that the UFG state significantly suppresses nickel release compared to the CG state, which is the key practical finding of this study.

It should be noted that the relationship between grain size and corrosion resistance in titanium alloys is not always monotonic. Studies on Ti-6Al-4V and other titanium-based alloys [35,36] have shown that grain refinement does not uniformly improve corrosion resistance. In some cases, an intermediate grain size may exhibit optimal performance due to the competing effects of grain boundary density, dislocation structure, and surface chemistry. However, direct extrapolation of these findings to the TiNi system should be made with caution, since the corrosion behavior of nitinol is strongly influenced by the specific composition, the presence of Ni-rich precipitates, and the unique nature of its passive oxide layer. The present study was limited to two extreme structural states (CG $\sim 54\ \mu\text{m}$ and UFG $\sim 0.2\ \mu\text{m}$), and the investigation of intermediate grain sizes remains an important direction for future work to fully understand the evolution of corrosion properties in this alloy system.

5. Conclusions

The results of this study demonstrate that under the investigated conditions—in 0.9% NaCl, Ringer's solution, and Hanks' solution (at pH ~ 7.4 and 37°C), for the $\text{Ti}_{49.0}\text{Ni}_{51.0}$ alloy subjected to the specific thermomechanical treatment regimes employed in this work—the ultrafine-grained state exhibits higher corrosion resistance than the coarse-grained state. This is evidenced by lower

generalized gravimetric mass changes, differences in surface relief, and significantly suppressed nickel ion release in the UFG state. The precipitation of Ti_3Ni_4 particles during aging in the coarse-grained state slightly increases the corrosion resistance, whereas in the ultrafine-grained state, it does not cause significant changes. These findings are valid for the specific alloy composition, processing conditions, and experimental parameters used in this study.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

Acknowledgments

The authors express gratitude to the Collective Use Center “Nanotech” (Ufa University of Science and Technology) for providing the opportunity to conduct research using its available equipment.

Author contributions

Conceptualization: E.I. and A.C.; methodology: E.I.; investigation: E.I. and E.V.; formal analysis: E.I.; writing—original draft preparation: E.I.; writing—review and editing: E.I. and A.C.; supervision: A.C. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

References

1. Khachin VN, Pushin VG, Kondratyev VV (1992) *Titanium Nickelide: Structure and Properties*, Moscow: Nauka.
2. Otsuka K, Wayman CM (1998) *Shape Memory Materials*, Cambridge: Cambridge University Press.
3. Huang WM, Ding Z, Wang CC, et al. (2010) Shape memory materials. *Mater Today* 13: 54–61. [https://doi.org/10.1016/S1369-7021\(10\)70128-0](https://doi.org/10.1016/S1369-7021(10)70128-0)
4. Shabalovskaya SA (2002) Surface, corrosion and biocompatibility aspects of Nitinol as an implant material. *Biomed Mater Eng* 12: 69–109.
5. Ryhänen J, Niemi E, Serlo W, et al. (1997) Biocompatibility of nickel-titanium shape memory metal and its corrosion behavior in human cell cultures. *J Biomed Mater Res* 35: 451–457. [https://doi.org/10.1002/\(SICI\)1097-4636\(19970615\)35:4%3C451::AID-JBM5%3E3.0.CO;2-G](https://doi.org/10.1002/(SICI)1097-4636(19970615)35:4%3C451::AID-JBM5%3E3.0.CO;2-G)
6. Cui ZD, Chen MF, Zhang LY, et al. (2008) Improving the biocompatibility of NiTi alloy by chemical treatments: An *in vitro* evaluation in 3T3 human fibroblast cell. *Mater Sci Eng C* 28: 1117–1122. <https://doi.org/10.1016/j.msec.2007.05.006>
7. Figueira N, Silva TM, Carmezim MJ, et al. (2009) Corrosion behaviour of NiTi alloy. *Electrochim Acta* 54: 921–926. <https://doi.org/10.1016/j.electacta.2008.08.001>

8. Duerig TW, Pelton AR, Stöckel D (1999) An overview of nitinol medical applications. *Mater Sci Eng A* 273–275: 149–160. [https://doi.org/10.1016/S0921-5093\(99\)00294-4](https://doi.org/10.1016/S0921-5093(99)00294-4)
9. Otsuka K, Ren X (2005) Physical metallurgy of Ti–Ni-based shape memory alloys. *Prog Mater Sci* 50: 511–678. <https://doi.org/10.1016/j.pmatsci.2004.10.001>
10. Potekaev AI, Klopotov AA, Matyunin AN, et al. (2011) The influence of phase hardening on premartensitic states and on martensitic transformation in multicomponent alloys Ti(Ni, Co, Mo) with shape memory effects. *Inorg Mater Appl Res* 2: 387–394. <https://doi.org/10.1134/S2075113311040083>
11. Wang X, Verlinden B, Kustov S (2017) Multi-stage martensitic transformation in Ni-rich NiTi shape memory alloys. *Funct Mater Lett* 10: 1740004. <https://doi.org/10.1142/S1793604717400045>
12. Karbakhsh Ravari B, Nishida M (2013) *In situ* SEM studies of the transformation sequence of multistage martensitic transformations in aged Ti-50.8 at.% Ni alloys. *Philos Mag* 93: 2279–2296. <https://doi.org/10.1080/14786435.2013.769070>
13. Zhou N, Shen C, Wagner MFX, et al. (2010) Effect of Ni₄Ti₃ precipitation on martensitic transformation in Ti–Ni. *Acta Mater* 58: 6685–6694. <https://doi.org/10.1016/j.actamat.2010.08.033>
14. Zhang J, Cai W, Ren X, et al. (1999) The nature of reversible change in *M_s* temperatures of Ti–Ni alloys with alternating aging. *Mater Trans JIM* 40: 1367–1375. <https://doi.org/10.2320/matertrans1989.40.1367>
15. Yahia LH, Rayes F, Warrak AO (2009) Regulation, orthopedic, dental, endovascular and other applications of Ti–Ni shape memory alloys, In: Yoneyama T, Miyazaki S, *Shape Memory Alloys for Biomedical Applications*, Cambridge: Woodhead Publishing, 306–326. <https://doi.org/10.1533/9781845695248.2.306>
16. Chaudhary K, Haribhakta VK, Jadhav PV (2024) A review of shape memory alloys in MEMS devices and biomedical applications. *Mater Today Proc.* <https://doi.org/10.1016/j.matpr.2024.04.105>
17. Sussman EM, Shi H, Turner PA, et al. (2022) Nitinol release of nickel under physiological conditions: Effects of surface oxide, pH, hydrogen peroxide, and sodium hypochlorite. *Shap Mem Superelasticity* 8: 98–106. <https://doi.org/10.1007/s40830-022-00364-3>
18. Močnik P, Kosec T (2021) A critical appraisal of the use and properties of nickel–titanium dental alloys. *Materials* 14: 7859. <https://doi.org/10.3390/ma14247859>
19. Huang HH, Chiu TH, Lai HC, et al. (2003) Corrosion resistance of stressed NiTi and stainless steel orthodontic wires in acid artificial saliva. *J Biomed Mater Res A* 66: 829–839. <https://doi.org/10.1002/jbm.a.10463>
20. Shabalovskaya SA, Anderegg J, Van Humbeeck J (2008) Critical overview of Nitinol surfaces and their modifications for medical applications. *Acta Biomater* 4: 447–467. <https://doi.org/10.1016/j.actbio.2008.01.013>
21. Churakova AA, Iskhakova EI, Vorobyev EV (2025) Features of corrosion-mechanical strength of TiNi alloy under various structural states in biological solutions. *Bull Russ Acad Sci Phys* 89: 412–416. <https://doi.org/10.1134/S1062873824710213>
22. Ma K, Zhang R, Sun J, et al. (2020) Oxidation mechanism of biomedical titanium alloy surface and experiment. *Int J Corros* 2020: 1678615. <https://doi.org/10.1155/2020/1678615>

23. Thierry B, Tabrizian M, Trepanier C, et al. (2000) Effect of surface treatment and sterilization processes on the corrosion behavior of NiTi shape memory alloy. *J Biomed Mater Res* 51: 685–693. [https://doi.org/10.1002/1097-4636\(20000915\)51:4<685::AID-JBM17>3.0.CO;2-S](https://doi.org/10.1002/1097-4636(20000915)51:4<685::AID-JBM17>3.0.CO;2-S)
24. Firstov GS, Vitchev RG, Kumar H, et al. (2002) Surface oxidation of NiTi shape memory alloy. *Biomaterials* 23: 4863–4871. [https://doi.org/10.1016/s0142-9612\(02\)00244-2](https://doi.org/10.1016/s0142-9612(02)00244-2)
25. Churakova AA, Kayumova EM (2023) Corrosion behavior and surface analysis of Ni-rich TiNi alloy. *Nanoindustry* 16: 208–219. <https://doi.org/10.22184/1993-8578.2023.16.3-4.208.219>
26. Cheng Y, Cai W, Zheng YF, et al. (2005) Surface characterization and immersion tests of TiNi alloy coated with Ta. *Surf Coat Technol* 190: 428–433. <https://doi.org/10.1016/j.surfcoat.2004.03.051>
27. Soltan AAM, Esen İ, Kara SA, et al. (2023) Examination of the corrosion behavior of shape memory NiTi material for biomedical applications. *Materials* 16: 3951. <https://doi.org/10.3390/ma16113951>
28. Pound BG (2016) Galvanic corrosion of nitinol under deaerated and aerated conditions. *J Biomed Mater Res Part B* 104B: 1322–1327. <https://doi.org/10.1002/jbm.b.33474>
29. Korshunov AV, Lotkov AI, Kashin OA, et al. (2015) Influence of surface modification of nitinol with silicon using plasma-immersion ion implantation on the alloy corrosion resistance in chloride-containing solutions. *Bull Tomsk Polytech Univ Geo Assets Eng* 326: 114–123.
30. Chemist's Handbook 21. Available from: <https://chem21.info>.
31. Kim JI, Liu Y, Miyazaki S (2004) Ageing-induced two-stage R-phase transformation in Ti–50.9 at.%Ni. *Acta Mater* 52: 487–499. <https://doi.org/10.1016/j.actamat.2003.09.032>
32. Fan G, Zhou Y, Chen W, et al. (2006) Precipitation kinetics of Ti₃Ni₄ in polycrystalline Ni-rich TiNi alloys and its relation to abnormal multi-stage transformation behavior. *Mater Sci Eng A* 438–440: 622–626. <https://doi.org/10.1016/j.msea.2006.02.066>
33. Wang HZ, Zhao YD, Ma YH, et al. (2020) Effect of low-energy proton on the microstructure, martensitic transformation and mechanical properties of irradiated Ni-rich TiNi alloy thin films. *Int J Miner Metall Mater* 27: 538–543. <https://doi.org/10.1007/s12613-019-1893-7>
34. Amirkhanova NA, Valiev RZ, Adasheva SL, et al. (2006) The investigation of corrosion and electrochemical properties of Ni-Ti alloys in large and ultra-fine grained states. *Vestn UGATU* 7: 143–146.
35. Li X, Dong YC, Dan ZH, et al. (2019) Corrosion behavior of ultrafine grained pure Ti processed by equal channel angular pressing. *Acta Metall Sin* 55: 967–975. <https://doi.org/10.11900/0412.1961.2019.00010>
36. Xiang R, Huang J, Yu X, et al. (2025) Effect of pulse frequency on the microstructure and corrosion behavior of Ti-6Al-4V alloy fabricated by pulse arc remelting method. *Surf Coat Technol* 507: 132159. <https://doi.org/10.1016/j.surfcoat.2025.132159>



AIMS Press

© 2026 the Author(s), licensee AIMS Press. This is an open access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>)