JCEC
THE JOURNAL OF ENGINEERING AND EXACT SCIENCES

OPEN ACCESS

The Journal of Engineering and Exact Sciences – jCEC, Vol. 09 N. 06 (2023)
journal homepage: https://periodicos.ufv.br/jcec
eISSN: 2527-1075
ISSN: 2446-9416

Effect of chitosan–tungsten composite coating obtained by electrophoretic deposition on the corrosion resistance of Ni–Ti alloy in physiological medium

Efeito do revestimento compósito de Quitosana–tungstênio obtido por deposição eletroforética na resistência à corrosão da liga de Ni–Ti em meio fisiológico

Article Info:
Article history: Received 2023-06-03/ Accepted 2023-07-25 / Available online 2023-08-04
doi: 10.18540/jcecvl9iss6pp16237-01e

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Resumo
As ligas com memória de forma de Ni–Ti (Nitinol) são adequadas para aplicações em biomedicina, como implantes ortodônticos, ortopédicos e cardiovasculares. No entanto, para evitar processos inflamatórios locais, busca-se funcionalizar a superfície na liga de Ni–Ti com materiais bioativos. Revestimentos compósitos à base de quitosana podem ser aplicados para melhorar as propriedades das ligas de Ni–Ti devido às suas excelentes propriedades como, baixa toxicidade, biocompatibilidade, biodegradabilidade e boa capacidade de formação de filme. Neste trabalho, o compósito de quitosana–tungstênio (Quit–W) foi avaliado como revestimento protetor da liga de

Ni–Ti em meio fisiológico (solução de Ringer). Os resultados de morfologia superficial e composição química (MEV e EDX) comprovaram a formação do revestimento compósito formado por uma matriz de quitosana impregnada com nanopartículas de óxido de tungstênio. Os resultados de resistência à corrosão comprovaram a eficiência do revestimento compósito para atuar como uma barreira de proteção entre a superfície do substrato (Ni–Ti) e o meio corrosivo. Portanto, os resultados apontam para um possível candidato de sistema (liga de Ni–Ti revestida com o compósito de Quit–W) adequado para aplicações no setor de implantes ortopédicos.
Palavras-chave: Nitinol. Biomaterial. Revestimento Compósito.

Abstract
Ni–Ti shape memory alloys (Nitinol) are suitable for biomedical applications such as orthodontic, orthopedic, and cardiovascular implants. However, to avoid local inflammatory processes, efforts are being made to functionalize the surface of the Ni–Ti alloy with bioactive materials. Chitosan-based composite coatings can be applied to improve the properties of Ni–Ti alloys due to their excellent properties, such as low toxicity, biocompatibility, biodegradability, and good film-forming ability. In this work, the chitosan–tungsten composite (Chit–W) was evaluated as a protective coating for Ni–Ti alloy in a physiological medium (Ringer's solution). The results of surface morphology and chemical composition (SEM and EDX) confirmed the formation of the composite coating formed by a chitosan matrix impregnated with tungsten oxide nanoparticles. Corrosion resistance results proved the efficiency of the composite coating, acting as a protective barrier between the surface of the substrate (Ni–Ti) and the corrosive environment. Therefore, the results point to a possible system candidate (Ni–Ti alloy coated with Chit–W composite) suitable for applications in orthopedic implants.
Keywords: Nitinol. Biomaterial. Composite Coating.

1. Introduction

Materials applied to living beings (biomaterials) are of great importance in the biomedical area, as a classic example can be mentioned the prostheses applied in the replacement or reconstruction of damaged bone tissues. Depending on the type of biomaterial, different compounds can be used for its manufacture, usually those based on metals or metal alloys, ceramics, polymers, or composites (Lia Fook et al., 2019; Pires, Bierhalz, & Moraes, 2015).

Using non-biological materials such as orthopedic or orthodontic implants in biomedicine is extremely important for modern society. Since materials applied as implants have chemical elements in their constitution that can cause an immune response of the biological system, a concern in recent years has been about the biocompatibility of materials used in biomedicine. Thus, allergies and hypersensitivity reactions at the implant application site can cause it to fail, causing inflammation and unwanted surgical correction processes (Menezes, Freitas, & Gonçalves, 2009; Pires et al., 2015).

Despite the acceptable biocompatibility of the Ni–Ti alloy, suitable for applications in biomedicine, the physiological environment may favor the formation of infections associated with bacterial adhesion or the release of nickel ions due to corrosion or mechanical weakening during the process of using the implant orthopedic or orthodontic, and may cause allergy in individuals sensitive to nickel and, consequently, implant failure. Thus, using coatings to functionalize the surface and thus improve the strength of the Ni–Ti alloy in a physiological environment becomes an interesting alternative to be investigated (Liu et al., 2019; Shabalovskaya, Rondelli, & Rettenmayr, 2009).

The use of chitosan-based coatings (a naturally occurring polysaccharide obtained by deacetylation of chitin) for applications in biomedicine has gained prominence in recent years due to its excellent biocompatible properties, such as low toxicity, antibacterial activity, and biodegradability (Avcu et al., 2019). In addition, chitosan has functional groups (–OH and $–NH_2$) in its chemical structure suitable for functionalization with organic and/or inorganic materials and the formation of films and composites (Silva, Cunha, Hotza, & Machado, 2021; Yi et al., 2005;

Zhitomirsky, 2006). Therefore, the objective of this work was to evaluate the corrosive performance of the system formed by the shape memory alloy of Ni–Ti coated with the chitosan–tungsten composite (Chit–W) in a physiological medium and, in this way, to expand the application possibilities of the newly developed Chit–W composite (Oliveira, de Santana, & Wanderley Neto, 2020).

2. Experimental

2.1 Chemicals

Chitosan (average viscosimetric molar mass of 1.6 x 10^5 g/mol and 75-88% deacetylated) (Stopilha, Xavier-Júnior, De Vasconcelos, & Fonseca, 2019) from Polymar LTDA, Sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) from NEON Commercial, Glacial acetic acid from Dinâmica LTDA and Sodium hydroxide from NEON Commercial were used as received for preparation of electrolytic suspension, using distilled water as solvent.

2.2 Obtaining the composite coating (Chit–W)

The electrolytic suspension used for the deposition of the chitosan–tungsten composite coating was prepared according to our previous work (Oliveira et al., 2020). In summary: 0.5 g/l of chitosan was dissolved in acetic acid (1 %), with magnetic stirring for 24 h at room temperature of 25 ± 2 °C to obtain an electrolytic suspension of chitosan, followed by the addition of 1 mM of sodium tungstate, with magnetic stirring for another 1 h at the same temperature. The pH of the electrolyte suspension was adjusted to 5.5 using NaOH solution (1 M).

The electrophoretic deposition of the composite coating was carried out in a conventional electrochemical station adapted with two electrodes: a substrate made of shape memory alloy Ni–Ti (Nitinol), used as a cathode for coating deposition, embedded in Acrylic type resin, featuring an active area of 1.30 cm² for deposition, positioned 10 mm away from a 316L stainless steel plate used as an anode. The Ni–Ti alloy was obtained by the assisted casting method, following the procedure described in the literature (Da Cruz Gomes et al., 2021; Montenegro et al., 2020), in short: sources of high-purity Ti and Ni metals (99.5%) are used in the casting process, using a crucible of copper in an inert atmosphere of argon in the smelting chamber. For finishing the Ni–Ti electrodes, the rectangular tablet obtained in the foundry process was segmented by electroerosion. Subsequently, a surface finish of the electrodes was carried out through a chemical pickling process for 15 min using a pickling solution (3 ml of hydrofluoric acid, 30 ml of nitric acid, and 67 ml of water – Standard ASTM B600-11) and then immersed in distilled water. After surface finishing, the electrodes were submitted to thermal treatments of 850 °C for 1 h (homogenization) and 500 °C for 2 h (annealing), both in an inert nitrogen atmosphere and naturally cooled to room temperature. Annealing is used to stabilize transformation temperatures and eliminate internal stresses related to the solidification process.

Before the deposition process, the surface of the working electrode was mechanically polished using abrasive sandpaper in a decreasing grain size of 80–1200#, followed by polishing using diamond paste (1μm) and washing in ethanol for 10 min. in an ultrasonic bath. The deposition was performed using potentials of 5, 7.5, and 10 V (the potential was controlled using an AUTOLAB potentiostat/galvanostat, model PG STAT 302N), connected to the NOVA software version 2.1.4 for system control, for 10 min. at room temperature (25 ± 2 °C).

2.3 Characterization of materials

The surface morphology of the composite coatings and the uncoated Ni–Ti substrate was evaluated by Scanning Electron Microscopy (SEM) with a TESCAN microscope (model VEGA 3SBH). The chemical composition of the coatings was performed by Energy Dispersive X-rays (EDS) using an OXFORD detector (model X-ACT IE150) coupled to the SEM to confirm the formation of the Chit–W composite coating.

2.4 Corrosion tests

To evaluate the corrosion resistance of the system formed by the Ni–Ti shape memory alloy coated with the chitosan–tungsten composite (Chit–W), the techniques of Potentiodynamic Polarization (PP) and Electrochemical Impedance Spectroscopy (EIS) were conducted in a conventional three-electrode system: the system formed by the Ni–Ti alloy coated with the Chit–W composite acting as a working electrode (1.30 cm^2), a platinum counter electrode, and a saturated calomel electrode as reference. The corrosion tests were carried out using an AUTOLAB potentiostat/galvanostat (model PG STAT 302F) connected to the NOVA software version 2.1.4 for system control and data processing obtained by PP and EIS.

Corrosion tests were performed in a physiological medium (Ringer's solution: NaCl - 8.6 g/l, $CaCl_2 \cdot 2H_2O$ - 0.33 g/l, KCl - 0.30 g/l) (Pang, Casagrande, & Zhitomirsky, 2009), at a temperature of 37 ± 2 °C. Polarization (PP) tests were performed using a sweep range of ± 0.3 V from open circuit potential (OCP, stabilization for 1 h) and a velocity of 1 mV/s. The impedance tests (EIS) were performed on the OCP with an amplitude of 0.01 V and a sweep range of 0.01 Hz to 100 kHz.

3. Results and Discussion

3.1 Surface morphology and chemical composition

Figure 1 shows the Ni–Ti alloy's surface micrographs and chemical composition results (EDS and EDS maps). The surface morphology and EDS map (for tungsten distribution) for the chitosan–tungsten composite coating that showed the highest corrosion resistance (Tab. 1) are shown in Figure 2.

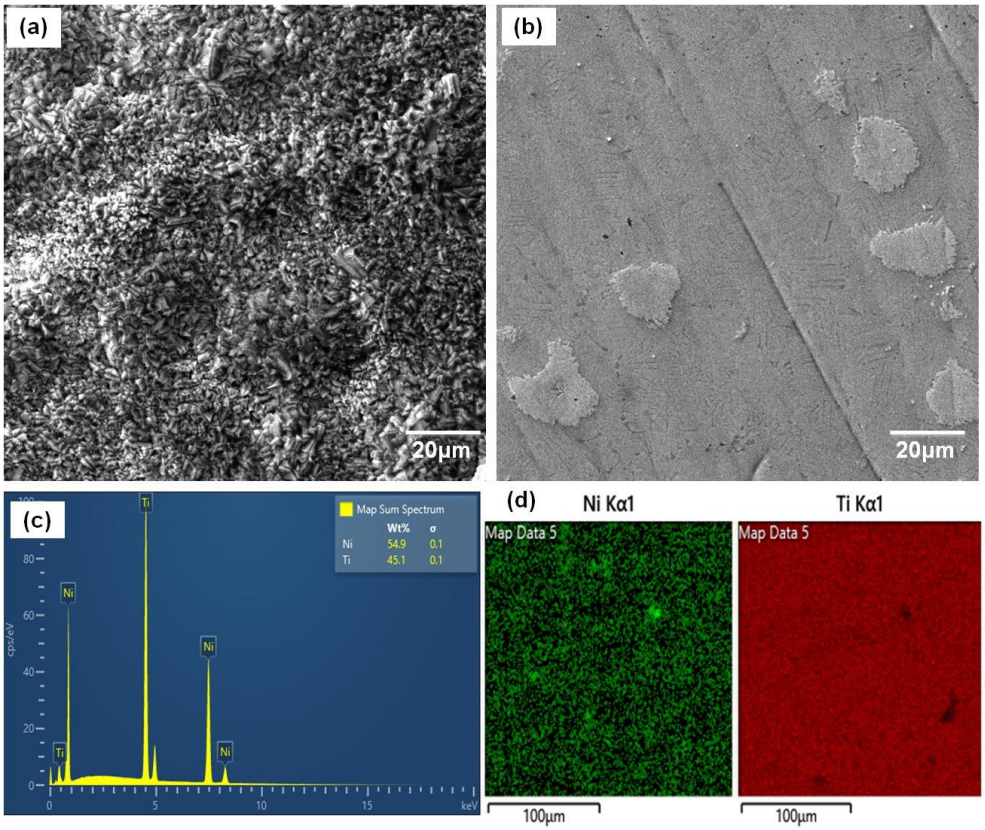

Figure 1– SEM of the Ni–Ti alloy surface (1000X magnification): (a) before polishing and (b) after polishing. (c) chemical composition and (d) EDS maps.

A rough surface is observed for the surface of the Ni–Ti alloy before mechanical polishing (Fig. 1a). The surface of the Ni–Ti alloy (Fig. 1b) becomes more homogeneous after polishing. Mechanical polishing is necessary to remove the natural oxide layer formed on the surface of the Ni–Ti alloy after processing and ensure proper adhesion of the composite coating. The chemical composition result (Fig. 1c) shows that the obtained alloy presented a weight composition of approximately 55 wt.% of Ni and 45 wt.% of Ti, proving the efficiency of the Ni–Ti alloy production method for biomedical applications (Nitinol). Furthermore, a homogeneous distribution of Ni and Ti metals on the surface of the alloy is observed (Fig. 1d).

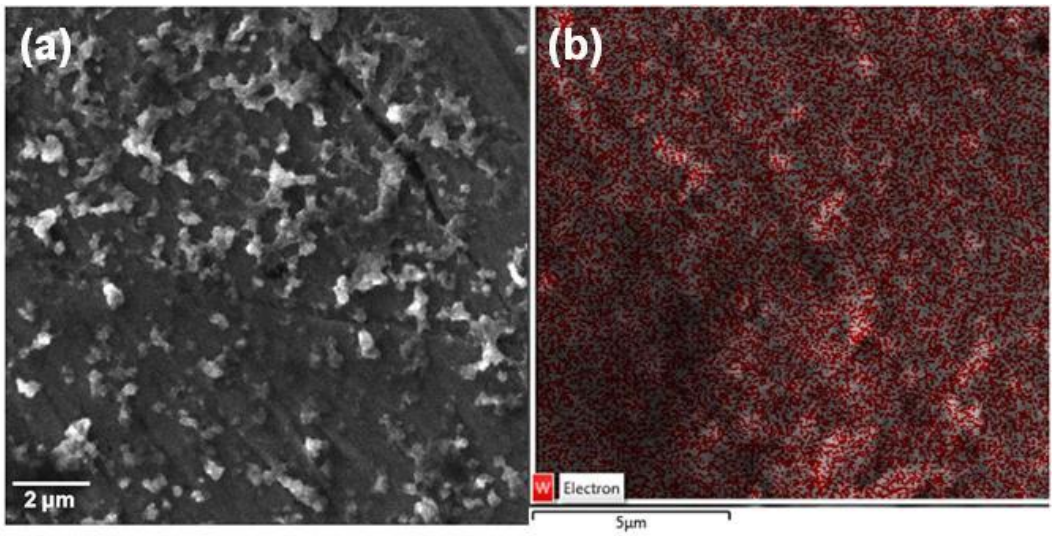

Figure 2 – (a) SEM and (b) EDS map (W) of the surface of the chitosan–tungsten composite coating (10000X magnification) obtained at 5 V and pH 5.5.

The formation of a rough chitosan–tungsten composite coating on the surface of the substrate is observed (Fig. 2a). Note also a homogeneous distribution of tungsten on the surface of the composite coating (Fig. 2b). These results prove the effectiveness of the electrophoretic deposition technique (EPD) in the formation of the chitosan–tungsten composite coating.

The coating formation can be attributed to the cathodic neutralization mechanism, already well established in the literature to explain the formation of chitosan-based coatings (Fig. 3) (Avcu et al., 2019). In summary, the positively charged chitosan macromolecules, through the protonation of their amino groups, are attracted to the cathode surface by electrophoresis where they are deposited through the neutralization of these amino groups by hydroxyl ions arising from the decomposition reaction of the water used in the preparation of the electrolytic suspension and, in this way, are adhered to the surface of the substrate (Avcu et al., 2019; Zhitomirsky, 2006). In the formation of composite coatings, chitosan acts as a matrix where other substances (organic and/or inorganic) can be anchored or impregnated through intermolecular interactions (hydrogen bonds, in the case of organic molecules) or complexation processes, for example, in the formation of composites with metals and other inorganic materials (Oliveira et al., 2020; Oliveira, de Santana, & Wanderley Neto, 2021; Zhitomirsky, 2006).

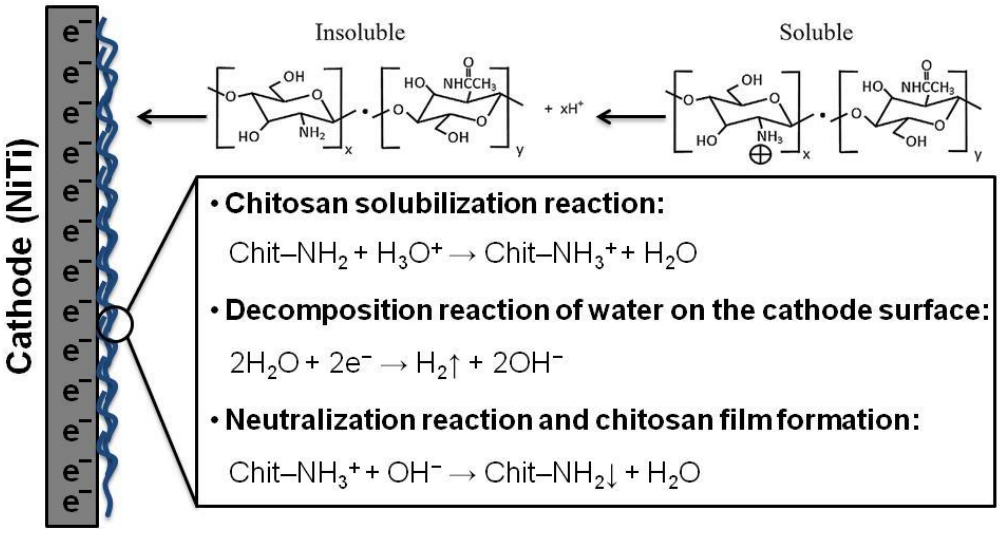

Figure 3 – Illustration of the electrophoretic deposition mechanism of chitosan-based composite coatings. Adapted from (Avcu et al., 2019; Oliveira et al., 2020).

3.2 Corrosion test results

Corrosion results for polarization resistance (R_p), corrosion current density (j_{corr}) and corrosion potential (E_{corr}), obtained from Polarization curves (Fig. 4a), using the technique of extrapolation of Tafel's lines, are presented in Table 1.

Table 1 – Corrosion results for Ni–Ti alloys coated with Chit–W composite coatings, obtained in a simulated physiological medium (Ringer's solution) at 37 ± 2 °C.

Potential (V)	E_{corr} (V)	R_p (Ω.cm²)	j_{corr} (A/cm²)
5	-0.357	16630	9.777×10^{-6}
7.5	-0.439	8497.6	5.517×10^{-5}
10	-0.431	5723	3.372×10^{-5}

The Potentiodynamic Polarization (PP) curves and the Electrochemical Impedance Spectra (EIS) for the systems formed by the Ni–Ti alloy coated with the Chit–W composite coating are shown in Figure 4.

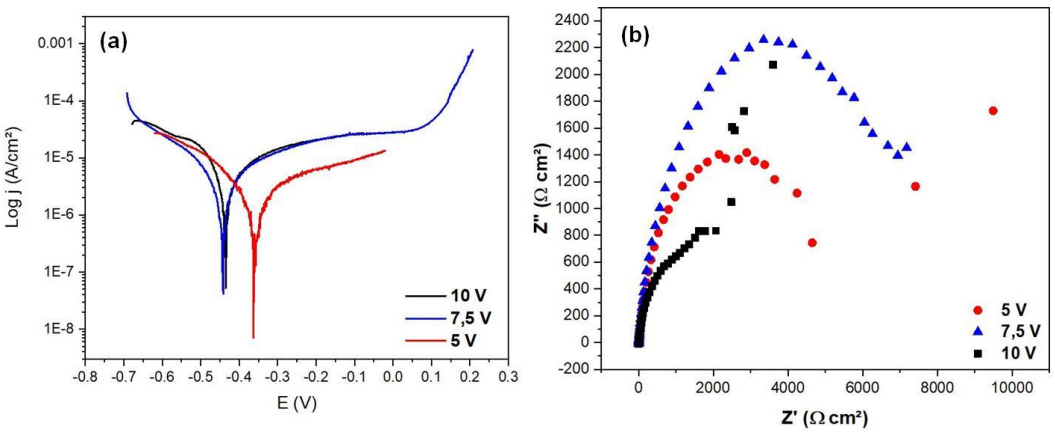

Figure 4 – Corrosion results for Ni–Ti alloys coated with Chit–W composite coatings, obtained in simulated physiological medium (Ringer's solution) at 37 ± 2 °C: (a) Polarization Curves and (b) Impedance Diagrams (Nyquist).

It can be observed in the corrosion results (Tab. 1 and Fig. 4) that the system formed by the Ni–Ti alloy coated with the Chit–W composite obtained under experimental conditions of 5 V and pH 5.5 showed the highest resistance in simulated physiological medium (Ringer's solution, at 37 ± 2 °C), as it showed the highest polarization resistance (R_p: 16630 Ω.cm²) and the lowest corrosion current density (j_{corr}: $9.777x10^{-6}$ A/cm²), in addition to a shift in the corrosion potential to nobler values compared to the other systems. Results confirmed by the EIS results (Fig. 1b). It is also observed that there were no significant changes in the anodic branch of the PP curves, indicating that the composite coating did not significantly affect the corrosion mechanism of the substrate (Ni–Ti alloy). Furthermore, it is noted that the impedance diagrams are depressed, which indicates a heterogeneous surface for the Chit–W coatings, and showed dispersion in the low-frequency region for the coatings obtained at 5 and 10 V (Oliveira, de Almeida, et al., 2021; Oliveira et al., 2020; Oliveira et al., 2021).

4. Conclusion

The surface characterization results (SEM and EDS) confirmed the achievement of the composite coating of chitosan–tungsten (Chit–W) by the electrophoretic deposition technique and applied to functionalize the surface of the alloy with the shape memory of Ni–Ti (Nitinol). Electrochemical corrosion results (PP and EIS) showed that the composite coating could act as a protective barrier between the corrosive medium (Ringer's saline solution) and the Ni–Ti alloy's surface, thereby increasing the system's resistance. The system formed by the Ni–Ti alloy coated with the Chit–W composite obtained under conditions of 5 V and pH 5.5 showed the highest polarization resistance (16630 Ω.cm²) and the lowest corrosion current density ($9.777 x10^{-6}$ A/cm²), in addition to having a nobler corrosion potential (–0.357 V) among the systems evaluated in this work. Therefore, the results show that the system formed by the Ni–Ti alloy coated with the Chit–W composite has potential application in the orthopedic sector. Future work will evaluate the biocompatibility and possible antibacterial activity of the system.

Acknowledgements

The authors appreciate the financial support from National Council for Scientific and Technological Development – CNPq/Brazil (grant number: 150263/2022-8).

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