

EFFECT OF TORSION ON THE CORROSION RESISTANCE
OF NANOTUBULAR ANODIZED SPIRAL PLATES FOR
FEMORAL FRACTURE FIXATION

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Abstract

The long-term performance of nanotubular anodized spiral plates used for femoral fracture fixation depends on their corrosion resistance in physiological environments. This study investigates the impact of torsion on the corrosion resistance of these implants. Torsion was found to significantly alter the implant's surface properties, affecting its electrochemical behaviour and corrosion resistance. While torsion increased the corrosion potential and electrochemical activity, it compromised the passive oxide layer, leading to reduced corrosion resistance. Electrochemical impedance spectroscopy (EIS) revealed increased solution resistance and decreased polarization resistance post-torsion. These findings provide important insights for designing more durable biomedical implants.

Key words: corrosion resistance, titanium anodization, nanotubular oxide, biomedical implant, surface modification

Introduction. The integration of biomedical engineering and materials science has advanced orthopedic implants, enhancing healing processes and patient outcomes [1]. Anodized spiral plates are promising due to their mechanical strength and biocompatibility [2–4]. These plates provide robust support and stability, essential for aligning and immobilizing fractured bones. The anodization

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process improves surface hardness, wear resistance, and biocompatibility by creating a bio-inert surface, reducing complications such as implant loosening and infection [2, 4, 5].

Helical plates are particularly effective for proximal and middle diaphyseal humeral fractures, allowing stable fixation while avoiding critical anatomical structures [6–8]. However, creating helical shapes from straight plates through mechanical bending can affect their structural integrity and performance, introducing stresses and potential microstructural alterations [9, 10]. Understanding these changes and their impact on corrosion resistance is crucial, as the interaction between mechanical stresses and the body's electrochemical environment can exacerbate corrosion [11, 12].

This study aims to investigate how mechanical bending impacts the corrosion resistance of anodized helical plates for femoral and shoulder fracture fixation.

Experimental. The test subject used for this study was titanium large fragment locking compression distal femur plate (LCP-DF, DePuy Synthes, Zuchwil, Switzerland). Initially, it was cleaned in an ultrasonic isopropanol bath for 30 min, dried, etched in a solution containing 5%vol. hydrofluoric acid (HF) and 10%vol. nitric acid (HNO_3), and air-dried. Then it was electrochemically anodized for 15 min at 100 V, in ethylene glycol bath containing 0.3%wt. ammonium fluoride (NH_4F) and 3%wt. deionized water. The anodization process created a nanotubular oxide layer on the plate's surface. The resulting nanotubular surface of the anodic oxide was examined using a scanning electron microscope (SEM) HIROX SH-5500P.

To evaluate the corrosion properties of the implant specimen before and after mechanical bending, a Corrtest CS350 potentiostat/galvanostat was utilized. The experimental setup featured a three-electrode configuration: a platinum (Pt) counter electrode, a silver/silver chloride (Ag/AgCl) reference electrode, and the test sample as the working electrode. Before testing, the samples were cleaned with isopropanol, rinsed with deionized (DI) water, and air-dried.

After cleaning, the anodized implant plate was immersed in a 3.5 wt% sodium chloride (NaCl) solution for 2 h. The open circuit potential was recorded during this period. Subsequently, potentiodynamic polarization measurements were conducted. The surface area exposed to the NaCl solution was 1 cm^2 . All experiments were performed using freshly prepared solutions and conducted at room temperature to ensure consistency and reliability of the results.

After this initial testing, the nanotubular anodized LCP-DF was subjected to 180 degrees of torsion, and the corrosion resistance testing procedure was repeated. Images of the LCP-DF after 180 degrees of torsion and the microstructure of the nanotubular anodic oxide layer formed at 100 V for 15 min are shown in Fig. 1.

Results and discussion. Open circuit potential (OCP). The OCP curves (Fig. 2) illustrate the open circuit potential (E , in volts) as a function of time (in seconds) for two conditions: "Before torsion" (red line) and "After tor-

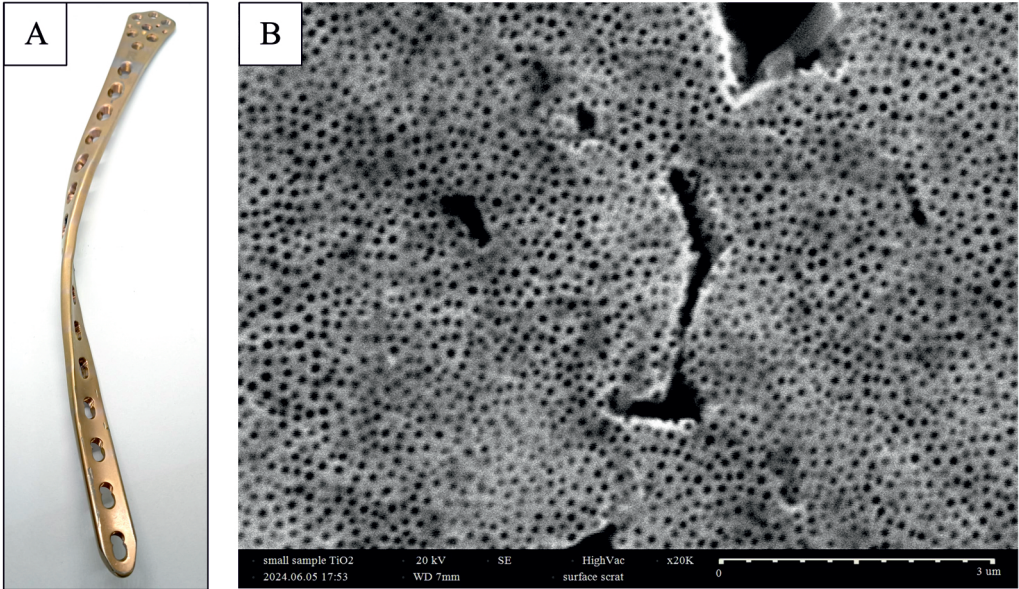


Fig. 1. A: LCP-DF after 180 degrees torsion and B: SEM image showing the microstructure of the nanotubular anodic oxide layer formed at 100 V for 15 min

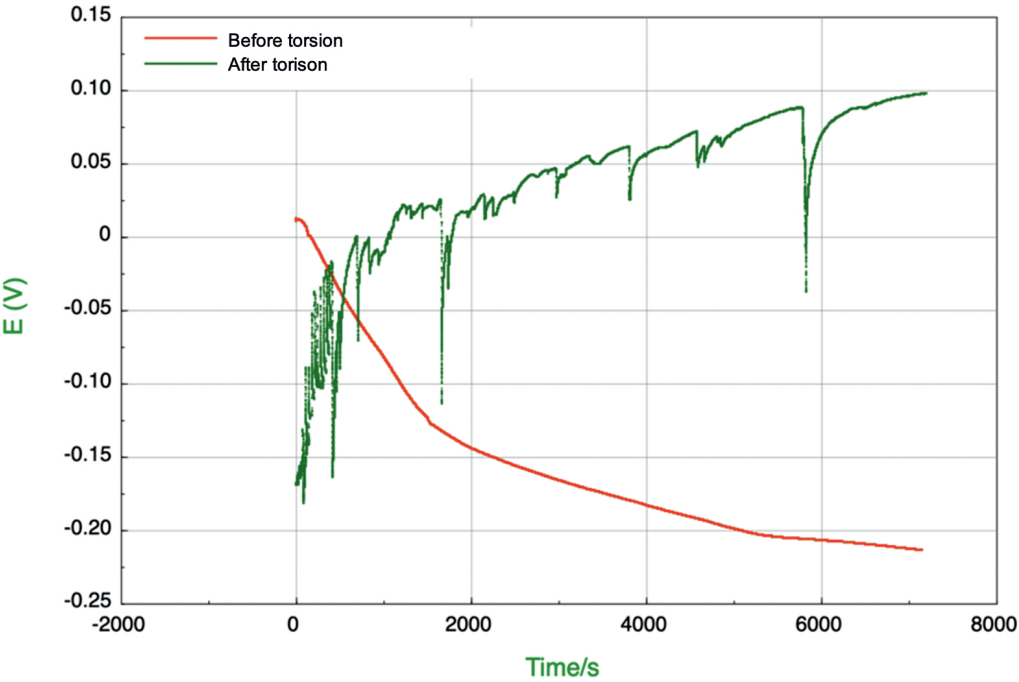
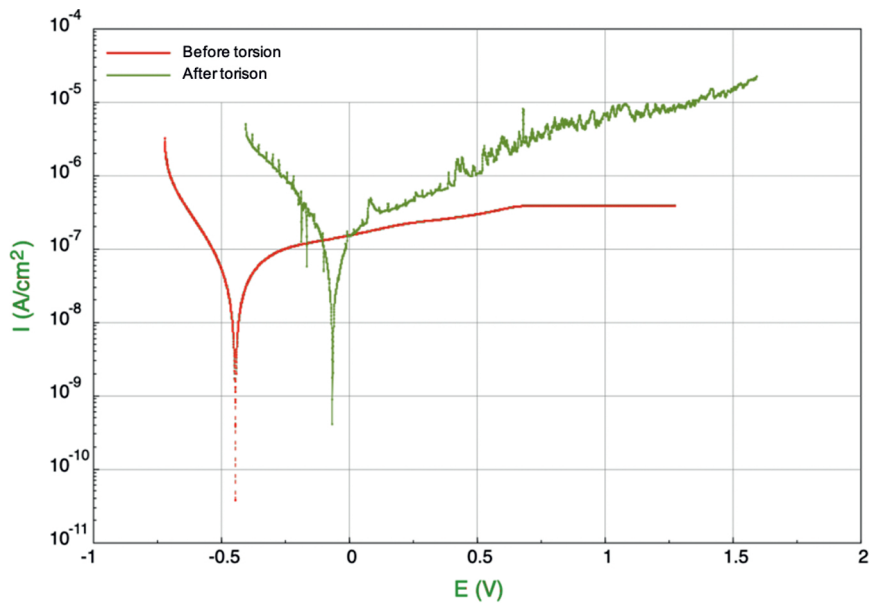


Fig. 2. OCP curves of the tested implant before and after torsion

sion” (green line). Initially, the potential before torsion starts at approximately 0.01 V, showing minimal fluctuations and gradually stabilizing around -0.21 V. Conversely, the potential after torsion begins at around -0.17 V, exhibiting significant initial fluctuations before stabilizing slightly above 0.09 V. Over the long term, the potential before torsion remains relatively stable. In contrast, the potential after torsion stabilizes around 0.1 V, suggesting that the surface properties have altered due to the torsion. The initial fluctuations in the post-torsion dataset likely indicate active surface reactions. The eventual stabilization of both curves suggests the formation of a stable passive layer.

Potentiodynamic polarization. The Tafel plot provides insights into the corrosion behaviour of a material by illustrating the relationship between the electrode potential (E , in volts) and the logarithm of the current density (I , in A/cm^2). From the data in Fig. 3 we can infer several conclusions regarding the corrosion characteristics before and after torsion.



Before torsion	After torsion
ba (mV) = 942.34	ba (mV) = 445.59
bc (mV) = 258.53	bc (mV) = 239.62
i0 (Amps/cm ²) = 7.1916E-08	i0 (Amps/cm ²) = 1.4731E-07
E0 (Volts) = -0.44387	E0 (Volts) = -0.064109
Corrosion rate(mm/a) = 0.00084367	Corrosion rate(mm/a) = 0.0017281
Residual = 7.0015E-09	Residual = 4.0026E-12

Fig. 3. Polarization curves and data of the tested implant before and after torsion

Before torsion, the anodic Tafel slope (b_a) was 942.34 mV, which significantly decreased to 445.59 mV after torsion. This reduction indicates that the material's anodic reaction kinetics have become more favourable, suggesting a modification in the material's surface that facilitates anodic processes. The cathodic Tafel slope (b_c) also decreased slightly from 258.53 mV to 239.62 mV, indicating a minor change in the cathodic reaction kinetics.

The exchange current density (i_0), which represents the rate of electrochemical reactions at equilibrium, increased from $7.1916\text{E}-08$ A/cm² to $1.4731\text{E}-07$ A/cm² after torsion. This increase suggests heightened electrochemical activity post-torsion, possibly due to changes in surface morphology or the removal of a protective film.

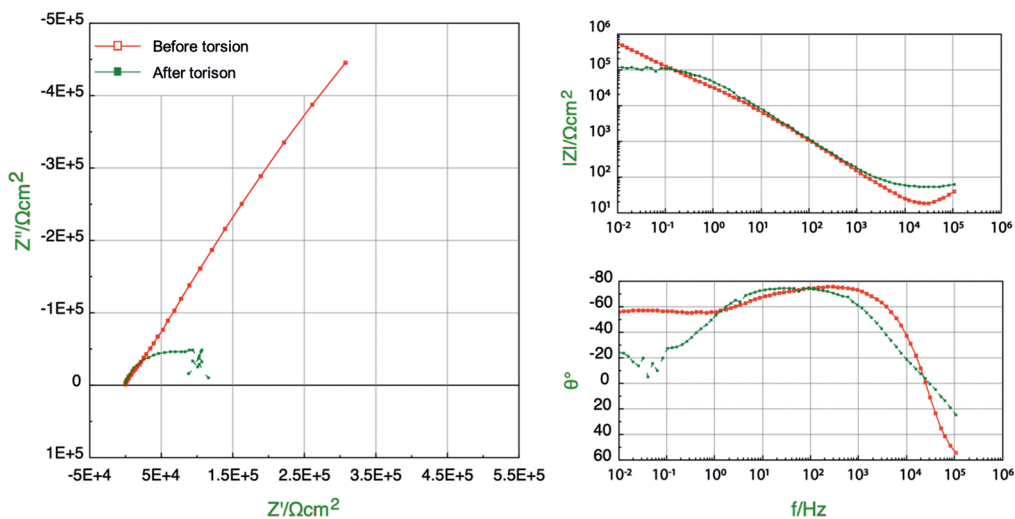
The corrosion potential (E_0) shifted from -0.44387 V before torsion to -0.064109 V after torsion, indicating an improvement in the material's corrosion resistance. A more positive corrosion potential generally signifies better resistance to corrosion. However, the corrosion rate increased from 0.00084367 mm/a to 0.0017281 mm/a after torsion, suggesting that despite the improved potential, the overall corrosion process has accelerated. This paradox may be due to torsion compromising the integrity of the nanotubular anodic oxide layer and exposing more reactive sites on the material's surface, thereby increasing its susceptibility to corrosion.

Overall, torsion appears to have altered the material's surface properties, enhancing its electrochemical activity and shifting the corrosion potential to more positive values. However, this also led to an increased corrosion rate, likely due to the exposure of more reactive sites on the material's surface.

Electrochemical impedance spectroscopy (EIS). Additionally, the corrosion testing is complemented by EIS analysis, with the results displayed in Fig. 4. The Nyquist and Bode plots provide significant insights into the corrosion behaviour of a biomedical implant before and after torsion.

The Nyquist plot, which graphs the imaginary part of the impedance against the real part, reveals an almost straight line before torsion. This indicates a high overall impedance, suggesting that the implant's surface has a strong and stable passive layer, leading to better corrosion resistance. However, after torsion, the plot shows a small semicircle, reflecting a decrease in overall impedance. This reduction suggests that mechanical stress has compromised the protective nanotubular oxide layer, thereby reducing the implant's corrosion resistance.

The Bode plot, which illustrates impedance magnitude and phase angle as functions of frequency, reinforces these findings. Prior to torsion, the impedance magnitude is elevated across all frequencies, and the phase angle remains relatively stable and more negative, particularly in the low to mid-frequency range. This stability indicates a well-formed passive layer that enhances corrosion resistance. After torsion, the impedance magnitude decreases, signalling reduced corrosion resistance. The phase angle also exhibits greater fluctuation and becomes less



Equivalent circuit		Before torsion			After torsion		
Element	Freedom	Value	Error	Error%	Value	Error	Error%
Rs	Free+	24.463	2.4007	9.8136%	52.84	1.5496	2.9326%
CPE-T	Free+	8.5617E-06	5.7121E-7	6.6717%	3.8951E-06	1.4184E-7	3.6416%
CPE-P	Free+	0.77347	1.1789E-2	1.5242%	0.85035	5.8728E-3	0.69063%
Rp	Free+	6.7345E+05	1.1109E+5	16.495%	1.1511E+05	3215.1	2.7931%

Fig. 4. EIS of the tested implant before deformation and after deformation

negative, suggesting alterations in surface properties and a destabilized passive layer.

Overall, these plots demonstrate that torsion has negatively impacted the corrosion resistance of the biomedical implant. Before torsion, the higher impedance and stable phase angle reflect a robust and effective passive oxide layer, providing strong protection against corrosion. Following torsion, the diminished impedance and variable phase angle indicate a compromised passive layer, which leads to decreased corrosion resistance. This mechanical disruption of the oxide layer renders the implant more vulnerable to corrosive environments. Consequently, while the implant initially displayed good corrosion resistance, mechanical stress has impaired its protective properties, highlighting the need for further research to improve the mechanical robustness of the anodic oxide to ensure the long-term durability of biomedical implants under mechanical stress.

The equivalent circuit used to model the electrochemical behaviour of the biomedical implant is a simple Randles circuit. This circuit consists of three primary components: solution resistance (R_s), constant phase element (CPE),

and polarization resistance (R_p). The R_s component represents the resistance of the electrolyte solution, accounting for the ion transport in the 3.5% NaCl solution used for corrosion testing. The CPE is used instead of a pure capacitor to model the non-ideal capacitive behaviour of the implant's surface, accounting for surface roughness and inhomogeneities. The R_p component represents the polarization resistance, which is indicative of the corrosion resistance of the implant.

In this study, fitting the EIS data to this equivalent circuit allows for quantification of the implant's electrochemical behaviour before and after torsion. The key parameters obtained from the fit are R_s and R_p . Before torsion, the solution resistance R_s is measured at 12.9 ohms, reflecting the ionic conductivity of the NaCl solution. After torsion, R_s increases to 16.7 Ω , suggesting changes in the solution properties, possibly due to interactions with the altered implant surface. More critically, the polarization resistance R_p significantly decreases from 21.1 k Ω before torsion to 2.3 k Ω after torsion. This marked reduction in R_p indicates a substantial decline in the implant's corrosion resistance due to the mechanical stresses imposed by torsion. The decrease in R_p highlights the compromised integrity of the passive oxide layer, rendering the implant more susceptible to corrosive attack in physiological environments.

Conclusions. This study demonstrates that torsion significantly alters the surface properties and corrosion resistance of nanotubular anodized spiral plates used for femoral fracture fixation. While torsion improved corrosion potential and electrochemical activity, it compromised the passive oxide layer, reducing corrosion resistance. EIS analysis confirmed increased solution resistance and decreased polarization resistance post-torsion. These findings underscore the need for further research to enhance the mechanical robustness of the passive layer, ensuring the long-term durability of biomedical implants under mechanical stress.

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