

# Sustainable Electrochemical Machining of Additively Manufactured Nitinol with Deep Eutectic Solvents

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**Abstract.** Additively manufactured Nitinol components often exhibit rough surfaces and defects that affect functional performance. This study investigates the feasibility of electropolishing Nitinol in a deep eutectic solvent (ethaline). Linear sweep voltammetry was used to identify anodic potentials suitable for controlled dissolution, and electropolishing was performed at selected potentials. Surface evolution was analysed by SEM, EDX, optical microscopy, and confocal microscopy. Electropolishing in ethaline effectively reduced surface scratches and produced more homogeneous surfaces without altering alloy composition. Higher applied potentials (12.5 V) resulted in complete removal of surface scratches and visually homogeneous surfaces, whereas lower potentials (6 V) mainly reduced the visibility of surface scratches. Compared to conventional inorganic electrolytes, the process exhibits a lower dissolution rate, offering a safer and more controllable approach.

## Introduction

Shape memory alloys are a class of functional metallic materials capable of recovering a predetermined geometry upon exposure to thermal or mechanical stimuli [1]. This characteristic response, known as the shape memory effect, together with superelasticity, has positioned these alloys as attractive materials for advanced applications. The first documented observations of shape recovery were reported in copper-based alloys in the early twentieth century, but the field gained significant momentum following the development of the nickel titanium alloy Nitinol in the 1960s [2]. This alloy demonstrated a unique combination of stable transformation behaviour, good corrosion resistance, biocompatibility, high recoverable strain, and favourable mechanical performance, which rapidly expanded interest in its scientific and technological potential [3]. These attributes supported the widespread adoption of Nitinol (NiTi) into aerospace components, electronic devices, safety mechanisms, and a wide range of biomedical devices. In particular, cardiovascular stents, orthodontic wires, orthopedic implants, and instruments for minimally invasive procedures have demonstrated the value of Nitinol due to its ability to undergo large reversible deformation while maintaining long-term functional reliability [4].

Despite these compelling advantages, the production and processing of Nitinol remain complex. The shape memory and superelastic responses are highly sensitive to the nickel-to-titanium ratio. Deviations as small as a few tenths of a percent can significantly alter transformation temperatures and mechanical performance [5]. During melting, the volatility of nickel and the high reactivity of titanium complicate control over the final alloy composition, while powder production introduces further challenges related to oxidation, impurity uptake and surface chemistry. Conventional processing routes such as rolling, drawing and tubing are therefore associated with considerable difficulty, and the machining of the alloy is hindered by its ductility, tendency to work harden and complex thermal behaviour [6].

In this scenario, additive manufacturing has emerged as a valuable method to overcome several of these limitations. In particular, Laser Powder Bed Fusion (LPBF) enables the fabrication of dense or porous structures with intricate geometries, internal channels and spatially controlled microstructures [7]. These capabilities have expanded the design space for nickel–titanium components and have

stimulated interest in the production of customised medical devices, actuators, and components for aerospace and robotics applications. Nevertheless, the sensitivity of the alloy to compositional changes and the presence of surface defects generated during melting or powder reuse highlight the importance of surface conditioning after fabrication. Moreover, poor as-built surface quality is a common characteristic of many additive manufacturing processes [8]. Layerwise building, stair stepping on inclined surfaces, partially melted or adhered powder particles, balling phenomena and localized lack of fusion commonly generate rough, irregular topographies and near surface defects across alloys and process variants. These process intrinsic features increase corrosion susceptibility, complicate fatigue and functional performance and therefore demand effective post processing and surface finishing strategies [6].

Surface finishing is essential for controlling corrosion behaviour, improving mechanical performance and managing nickel release, especially in applications involving contact with biological environments [9]. Electropolishing, anodising, chemical etching and hydrothermal treatments have therefore been the focus of extensive research. However, conventional electropolishing solutions, often based on highly concentrated mixtures of hydrofluoric and nitric acids or other strong corrosive agents, present several drawbacks [10]. These include operator safety concerns, stringent handling and disposal requirements, and strong oxidising power that may lead to uncontrolled surface attack. Such limitations have motivated the exploration of more sustainable and controllable electrolytes.

Deep eutectic solutions (DES) have emerged as promising candidates for more environmentally responsible metal finishing [11]. These liquids are formed by combining a hydrogen bond donor and a hydrogen bond acceptor, resulting in eutectic mixtures with reduced melting points, low volatility, low toxicity, and high electrochemical stability. DES-based electrolytes have been successfully employed for the electropolishing of metals such as nickel and stainless steels, producing smoother and more homogeneous surfaces while reducing environmental impact and extending electrolyte lifetime. Since Nitinol is composed of both nickel and titanium, for which DES-based electropolishing has already demonstrated effectiveness, applying DES electrolytes to NiTi is expected to combine the benefits observed for both constituents, enabling more uniform surface finishing, reduced surface defects, and improved corrosion stability, while avoiding the drawbacks of conventional acid-based electrolytes. For these reasons, the present work aims to assess the feasibility of electropolishing additively manufactured NiTi using the deep eutectic solvent ethaline, composed of choline chloride and ethylene glycol. Linear sweep voltammetry (LSV) was employed to identify suitable anodic potentials for controlled dissolution, followed by electropolishing experiments performed within the selected potential range. Surface morphology and topographical evolution were then evaluated using scanning electron microscopy, optical microscopy, and confocal microscopy.

## Materials and Methods

Additively manufactured nickel titanium samples were produced by laser powder bed fusion using pre-alloyed NiTi powder. The chemical composition of the alloy was selected to ensure near-equiatom nickel-to-titanium ratio, in order to promote stable shape memory and superelastic behaviour. The fabricated specimens were sectioned to 10 x 0.5 mm cylinders, and mechanically polished with abrasive paper.

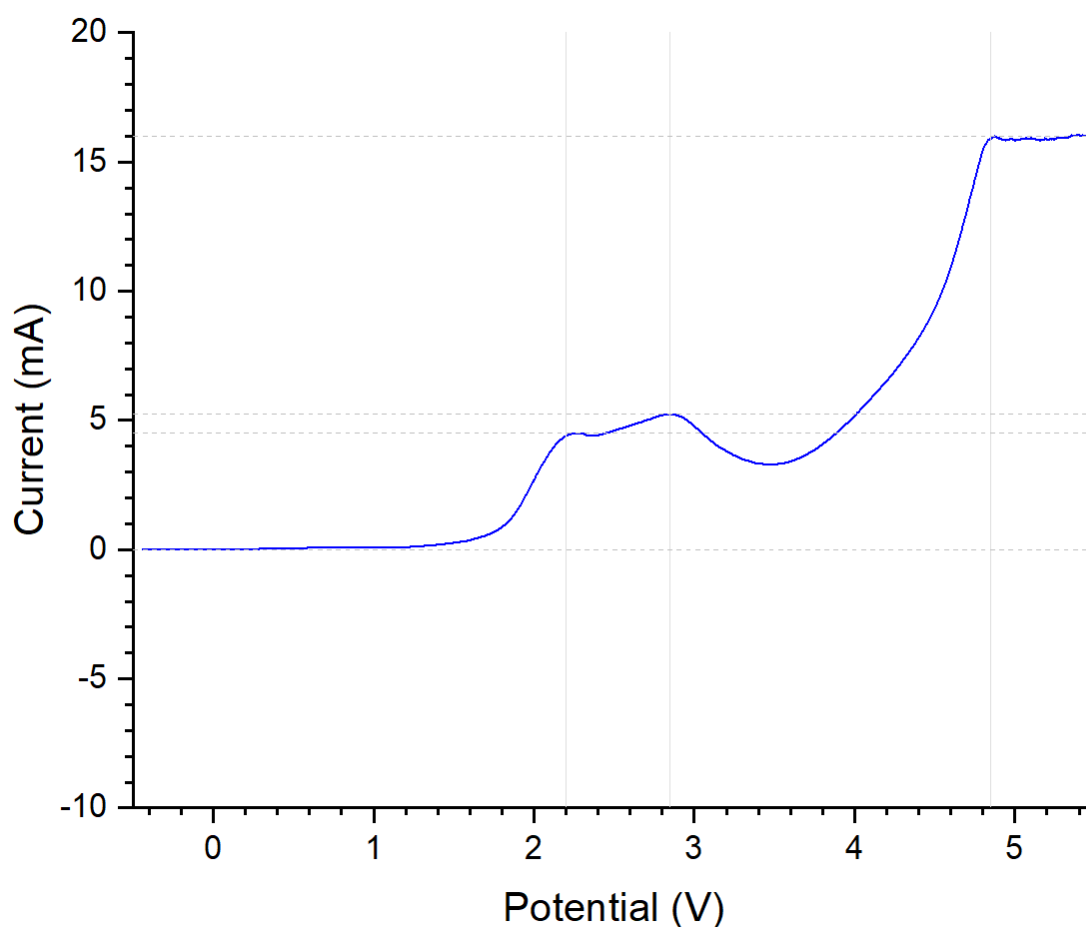
Electrochemical experiments were conducted using a conventional three-electrode cell configuration. The NiTi specimens acted as the working electrode, while a platinum electrode was employed as the counter electrode. An Ag/AgCl electrode containing 0.1 M KCl in acetonitrile was used as the reference electrode. The electrolyte consisted of the deep eutectic solution known as ethaline, prepared by mixing choline chloride and ethylene glycol at a molar ratio of 1:2. The mixture was heated under stirring until a homogeneous and transparent liquid was obtained.

Linear sweep voltammetry (LSV) was performed to investigate the anodic behaviour of the alloy and to identify potential regions associated with controlled material dissolution. Based on the voltammetric response, electropolishing experiments were carried out at selected anodic potentials within the diffusion-limited current regime. The treatment duration was fixed at 1 h for all conditions to allow a direct comparison of surface evolution as a function of the applied potential.

Surface morphology was examined by scanning electron microscopy. Optical surface inspection was performed using a Hirox digital microscope, while surface topography and roughness evolution were evaluated by confocal microscopy. Compositional analysis of the surface after treatment was carried out by energy dispersive spectroscopy to assess potential changes in alloy chemistry induced by the electrochemical process.

### Results and Discussion

In order to evaluate the electrochemical behaviour and, consequently, to assess the feasibility of an electrochemical material removal process, LSV tests were performed, as shown in Fig. 1.



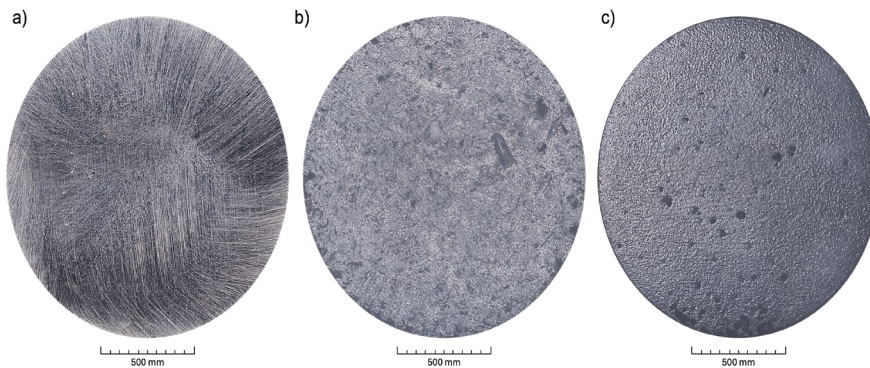
**Fig. 1.** LSV curve of additively manufactured NiTi in ethaline.

The potential range investigated spanned between  $-0.5$  V and the potential of the AgCl 0.1 M KCl reference electrode in acetonitrile. It can be observed that, starting from 1.8 V, an initial increase in current occurs, culminating in a peak at around 2.1 V. Subsequently, the current exhibits a weakly increasing trend up to a second peak located at approximately 2.9 V. At higher potentials, around 5 V, a diffusion-limited current plateau is established. In this type of electrochemical measurement, the observed current peaks are generally associated with specific electrochemical reactions occurring at the electrode surface. One plausible interpretation is that these two peaks are associated with the dissolution of titanium, as reported in the literature [11]. The dissolution peak of nickel, expected around 0.5 V [12], is not observed, likely due to a surface enrichment in titanium on the NiTi alloy. The surface is covered by a native nanometric oxide layer, and between the two constituent metals, titanium is more readily oxidized, which dominates the electrochemical response.

Based on these results, the dissolution experiments were carried out at potentials where the diffusion-limited current regime is fully developed. Accordingly, the applied potentials were set to 6

V and 12.5 V. In future studies, supported by more detailed analyses, it will be possible to identify the specific chemical reactions corresponding to these peaks.

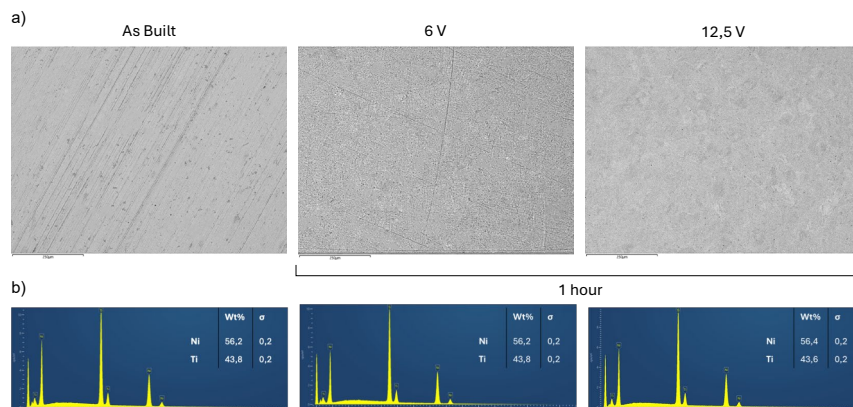
As shown in Fig. 2, at both selected dissolution potentials, a modification of the surface morphology is observed when compared to the initial sample treated only by abrasive paper polishing.



**Fig. 2.** HIROX macrographs of additively manufactured NiTi surfaces: a) as-built condition; b) specimen after electrochemical dissolution at 6 V for 1 h; c) specimen after electrochemical dissolution at 12.5 V for 1 h.

In particular, a reduction in the visibility of surface scratches can be observed, while the porosity detected on the surface can be ascribed to pores originating from the additive manufacturing process, which were exposed as a result of material removal. The exposure of intrinsic additive manufacturing pores following electropolishing is a relevant outcome with potential implications for both mechanical and biological performance. From a fatigue perspective, surface-connected pores may act as stress concentrators and crack initiation sites, potentially reducing fatigue life compared to fully dense or sealed surfaces. However, compared to the as-built condition, electropolishing removes sharp surface asperities and partially melted particles, which are also known to promote early crack initiation. The net effect on fatigue performance is therefore expected to depend on the balance between pore exposure and surface smoothing. In terms of biocompatibility, surface-exposed porosity may have a dual role. While increased surface area and micro-scale porosity can promote cell adhesion and osseointegration in certain biomedical applications, open pores may also influence corrosion behaviour and nickel ion release. Consequently, the suitability of the electropolished surface state should be evaluated in relation to the specific functional requirements of the intended application.

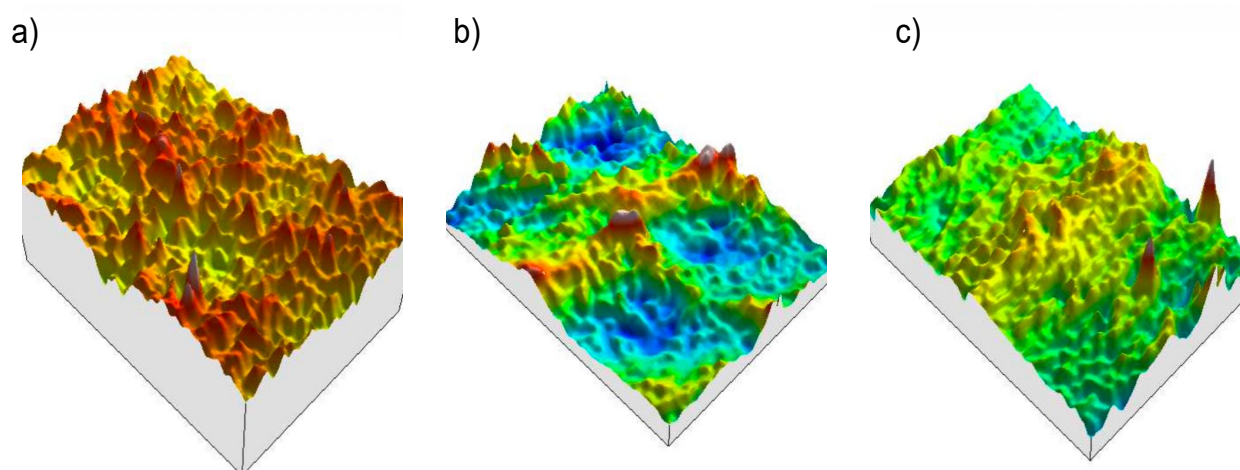
A more detailed analysis by scanning electron microscopy (SEM), shown in Fig. 3a, indicates that after a treatment duration of 1 h at an applied potential of 6 V, a significant reduction in surface scratches is achieved, although they are not eliminated. By contrast, under the same treatment time, complete elimination of polishing-induced scratches and a markedly more uniform surface morphology are observed at an applied potential of 12.5 V.



**Fig. 3.** a) SEM images of additively manufactured NiTi surfaces before and after electropolishing at 6 V and 12.5 V for 1 h; b) EDX spectra of the electropolished NiTi surfaces.

The dissolution process is homogeneous, and no dealloying phenomena are observed, as evidenced by the spectra in Fig. 3b, which indicate that the surface composition of the alloy remains unchanged after the treatment. It should also be noted that, when compared with electrochemical machining processes carried out in conventional inorganic electrolytes [9], the present treatment exhibits a markedly lower dissolution rate. From an industrial perspective, the lower dissolution rate observed in ethaline-based electropolishing may represent both a limitation and an opportunity. While longer processing times could reduce throughput compared to conventional inorganic electrolytes, the enhanced process controllability and reduced aggressiveness may be advantageous for components requiring precise dimensional tolerances.

With regard to the evolution of surface morphology, the results of the confocal microscopy analyses are shown in Fig. 4.



**Fig. 4.** Confocal microscopy images of additively manufactured NiTi surfaces: a) as-built condition; b) after electrochemical dissolution at 6 V for 1 h; c) after electrochemical dissolution at 12.5 V for 1 h.

After electrochemical treatment, the surface appears more homogeneous when compared to the as-built condition. For the dissolution performed at 6 V, pores associated with the additive manufacturing process become more evident than in the as-built sample. This behaviour can be attributed to the preferential erosion of surface asperities, since charge accumulation is enhanced at protruding features, leading to a more efficient removal of peaks. At this potential, a treatment duration of 1 h is insufficient for the dissolution process to progress towards a more pronounced surface homogenization.

As regards the surface roughness, similar values are measured before and after treatment. The as-built sample exhibits a Sa value of 2.88  $\mu\text{m}$ , while values of 2.65  $\mu\text{m}$  and 2.58  $\mu\text{m}$  are measured after treatment at 6 V and 12.5 V, respectively. These results indicate that the treatment is particularly effective for scratch removal, while only a modest reduction in overall surface roughness is achieved.

## Conclusion

In this study, the feasibility of electropolishing additively manufactured NiTi using a deep eutectic solution based on choline chloride and ethylene glycol was investigated. The effects of the applied potential on surface morphology and composition were systematically analysed. The main results of the work can be summarized as follows:

- LSV highlighted distinct anodic features associated with the electrochemical reactions of the alloy constituents and enabled the identification of a diffusion limited current regime suitable for electropolishing.

- Electropolishing in ethaline induced a clear modification of the surface morphology compared to the mechanically polished reference condition. Surface scratches originating from abrasive finishing were significantly reduced at 6 V and fully eliminated at 12.5 V after 1 h of treatment.
- Porosity observed after treatment was attributed to intrinsic pores from the additive manufacturing process that became exposed as a result of material removal.
- The dissolution process was homogeneous and no dealloying phenomena were detected, with surface composition remaining unchanged after treatment.
- The dissolution rate was lower than that typically reported for electrochemical machining in conventional inorganic electrolytes, which has implications for process scalability and industrial application.
- Confocal microscopy analysis confirmed enhanced surface homogeneity after electropolishing, while indicating that the treatment primarily promotes scratch removal rather than a significant reduction in areal surface roughness parameters.

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