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Electrochemical machining of 3D printed NiTi alloy: A preliminary study

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Abstract. Electrochemical machining represents a viable approach for enhancing the surface quality of additively manufactured Nitinol components, which typically exhibit excessive roughness. In this study, the electrochemical behavior of Nitinol was examined in chloride- and nitrate-based solutions to evaluate their effectiveness in material removal and surface refinement. Potentiodynamic polarization tests indicated that these solutions facilitate alloy dissolution, with diffusion-controlled kinetics observed at elevated potentials. Preliminary ECM experiments demonstrated that the incorporation of Na_2EDTA into chloride-based solutions increased material removal, likely due to the formation of highly soluble nickel and titanium complexes. Surface analysis revealed that chloride-containing solutions promoted selective nickel dissolution, while the combined chloride-nitrate solution mitigated process selectivity and reduced surface oxidation. These findings underscore the potential of ECM as an effective post-processing technique for improving the surface characteristics of Nitinol components fabricated via additive manufacturing.

Introduction

Shape memory alloys are metallic materials that can "remember" and return to a predefined shape when heated. This property is due to a phase transformation in their crystalline structure, allowing the material to switch from a martensitic phase (at low temperature) to an austenitic phase (at high temperature) [1]

Nitinol, an alloy consisting of approximately 55 wt.% nickel and 45 wt.% titanium, has superior tensile strength, fatigue limits, and corrosion resistance compared to other shape memory alloys. It also exhibits high elongation due to its high tensile strength. Nitinol's shape memory effect remains effective even after more than a million repetitions of shape restoration tests, making it more widely used [2].

Nitinol is applied in high-tech industrial applications such as satellite parts and micro sensors, as well as in medical devices like artificial joints, coronary stents, and orthodontics, due to its excellent biocompatibility [3], another interesting application is the use in automotive industry, particularly in the development of autonomous vehicles [4]. However, traditional machining methods like milling, drilling, and turning are challenging for Nitinol because it retains the characteristics of titanium, leading to difficulties in heat dissipation and internal stress [5]. These issues negatively impact the shape memory effect, prompting research into nontraditional machining methods for Nitinol.

The development of 3D modeling and additive manufacturing technologies has further expanded the use of Nitinol. Additive manufacturing allows the creation of complex products from Nitinol and other materials. This process, also known as 4D printing, involves creating objects that can change shape or properties in response to external stimuli [6].

Additive manufacturing offers advantages such as design flexibility, high material utilization, and environmental benefits. However, it also presents challenges, including the need for optimization of process conditions to ensure product quality.

The most commonly used additive manufacturing techniques for producing NiTi products are laser powder-bed fusion technologies [7].

However, most parts created by 3D additive processes show a relatively rough surface, edges, corners, and discoloration that lower their product quality for further functional industrial applications. The irregular melting of metal powders on the surfaces and localized heat-affected zones via laser irradiation around processed areas are the primary problems in these 3D metal printing processes. Hand-finishing them to create the required surface tolerances and integrity requires highly trained personnel and a lot of time. Moreover, 3D parts with complex structures are difficult or physically impossible to finish [8]. Conventional mechanical machining/polishing processes using micro grits in contact with the work surface are not suitable for these complex-shaped products. Even though several processes for 3D printing are proposed, our point is to propose that the finishing process using electrochemical polishing (ECP) is more efficient considering process time and surface quality . ECP can improve metal surface quality through electrochemical dissolution and leveling processes. Additionally, tool wear consideration or complicated tool design is not necessary in ECP because tools do not contact the work surface. In addition, ECP can be applied to biomedical devices due to its surface smoothing, hydrogen removal and corrosion resistance advantages. ECP can also control various surfaces properties by modifying voltage, electrode gap, and electrolyte temperature [9].

In this work, the electrochemical behavior of nitinol samples produced by laser powder bed fusion was analyzed through potentiodynamic tests using solutions that are environmentally friendly. Additionally, some preliminary electrochemical machining tests were conducted to evaluate the ability of the solutions to remove material.

Materials and methods

For the electrochemical tests, Nitinol samples fabricated via laser powder bed fusion with an energy density of 75 kJ/m^3 were utilized. The samples were cylindrical, with an initial diameter of 1.5 cm and a height of 5 cm, and were subsequently sectioned into smaller cylinders with a height of 0.5 mm. These sections were embedded in cold epoxy resin, and the tests were conducted in six different solutions, as detailed in Table 1.

For the selection of solutions, it should be noted that chlorides and nitrates have proven effective in dissolving nitinol. The addition of Na_2EDTA was made to increase the solubility of the reaction products, as it is known that Na_2EDTA can form very soluble compounds with transition metals [10]. Solutions based on organic acids were also tested, which, according to the literature, react effectively with Nickel and Titanium [11,12].

Potentiodynamic polarization tests were conducted with a PalmSens potentiostat in the range between the open circuit potential and 6V relative to it. Following the potentiodynamic tests, preliminary electrochemical machining tests were carried out. For this purpose, a patch was applied to the samples, leaving only a small part of the metal exposed to the solution a constant potential of 8 V was applied versus a platinum counter electrode for 5 minutes. The comparison between the exposed and unexposed parts allowed for the evaluation of the actual capability of the process to remove material. This analysis was performed using a Leica DCM 3D confocal microscope. The samples treated with chlorides, nitrates, and chlorides plus nitrates, after electrochemical machining tests, were analyzed using the Hitachi TM 3000 electron microscope and EDX analysis using an Oxford Instrument probe.

Table 1 – Employed solutions in electrochemical tests.

	Composition
Solution 1	0.2 M NaCl
Solution 2	0.2 M NaCl + 0.05 M Na_2EDTA
Solution 3	1 M Oxalic Acid
Solution 4	0.5 M Oxalic Acid + 0.5 M Ascorbic Acid
Solution 5	0.5 M NaNO3
Solution 6	0.25 M NaNO3 + 0.25 M NaCl

Results and discussion

The results of the potentiodynamic polarizations for Solutions 1 and 2 are shown in Fig. 1a and Fig. 1b. In solution 1, containing only chlorides, the initiation of localized corrosion is observed at around 0.5 V, while for potential values above 2 V, the kinetics are of a diffusive type.

In Solution 2, the initiation of localized corrosion is less evident, probably due to the inhibitory effect that EDTA exerts against this type of corrosion. Even in this case, for potentials above 2 V, a diffusive regime is observed

The presence of a diffusion-controlled kinetics is particularly significant because the necessary condition to achieve a smoothing effect during a chemical or electrochemical machining process is that the reaction kinetics are limited by the diffusion of products or reagents from the metal surface to the bulk of the solution [13].

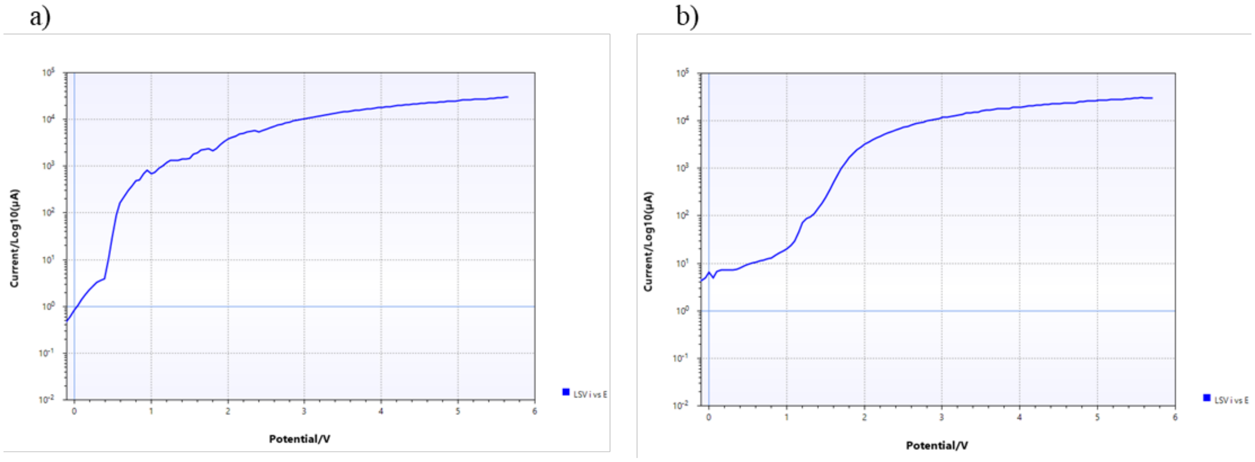

Figure 1 – Potentiodydamic test of: a) NiTi in 0.2M NaCl; b) NiTi in 0.2 M NaCl + 0.05 M Na2EDTA

The polarization curves in Solutions 3 and 4, presented in Fig. 2, although similar to those in chlorides and Na_2EDTA, show a different behavior. In this case, a diffusion-controlled behavior is observed for potentials above 1V. However, the predominant chemical reaction is not the dissolution of the metal but the oxidation of organic acids with significant gas evolution.

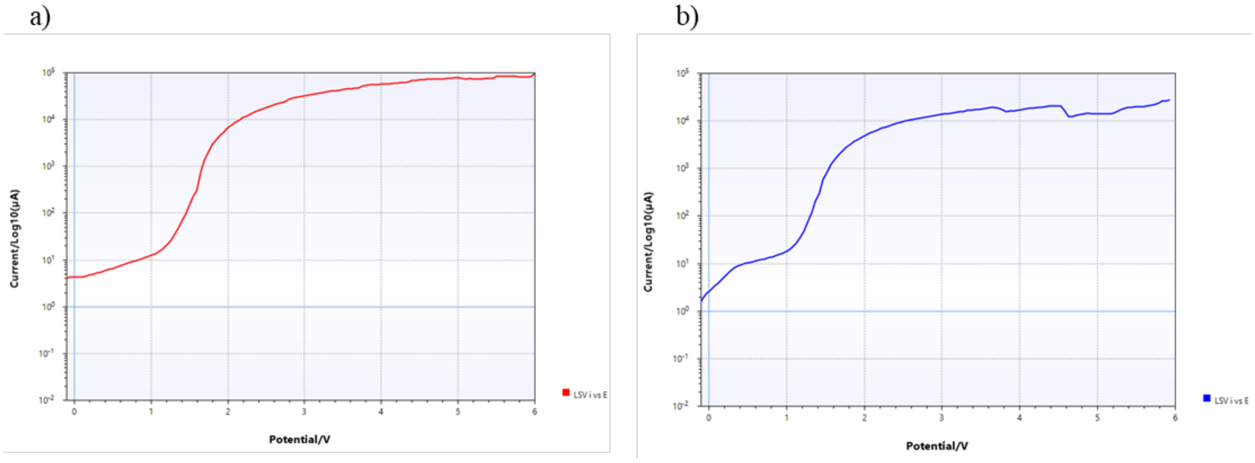

Figure 2 – Potentiodydamic test of: a) NiTi in 1 M Oxalic Acid; b) NiTi in 0.5 M Oxalic Acid +0.5 M Ascorbic Acid

The results of the potentiodynamic tests conducted with nitrate-containing solutions are shown in Fig. 3. Compared to the tests conducted in chlorides, the material behaves passively up to around 1.6 V, followed by transpassivity, and for potentials higher than about 2.2 V, a diffusive behavior is also observed in this case. Furthermore, for Solutions 5 and 6, the measured current values are higher.

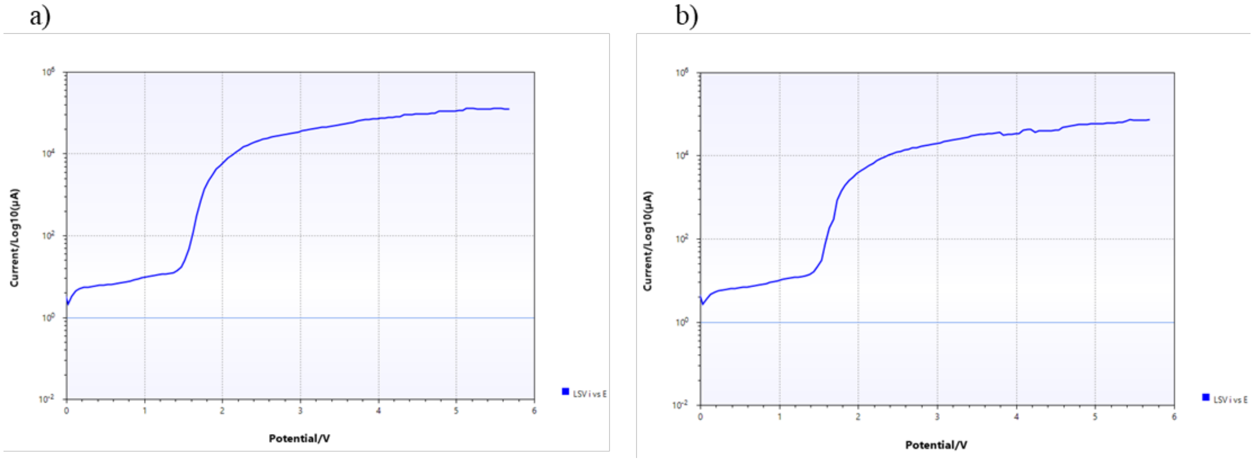

Figure 3 – Potentiodydamic test of: a) NiTi in 0.5 M $NaNO_3$; b) NiTi in 0.25 M $NaNO_3$ + 0.25 M NaCl

Following those results, preliminary electrochemical machining tests were conducted only with Solutions 1, 2, 5 and 6. The ability of Solutions 1 and 2 to remove material is demonstrated in Fig. 4. The profiles clearly show a depression in the central area corresponding to the part of the metal exposed to the solution, while the ends of the profile correspond to the area covered by the patch mentioned earlier. The central depression related to the test with Na_2EDTA appears deeper compared to the solution with chlorides only, this initial analysis seems to indicate that the presence of Na_2EDTA promotes material removal, likely through the formation of highly soluble compounds of nickel and titanium.

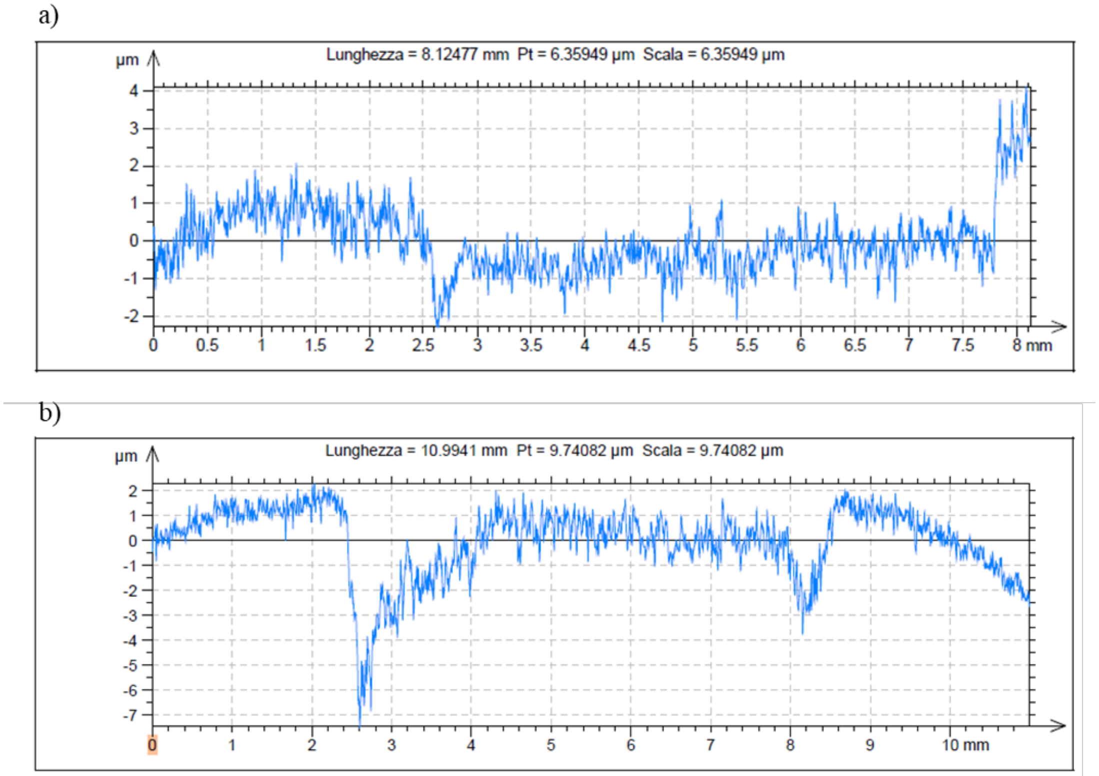

Figure 4 – Profile of treated sample in a) NaCl 0.2 M; b) NaCl 0.2 M+ 0.05 M Na_2EDTA. The lower height in the middle indicates material removing.

However, further measurements are needed to confirm this result. The 3D reconstruction of the surfaces after the electrochemical machining test (shown in Fig. 5) also supports this observation

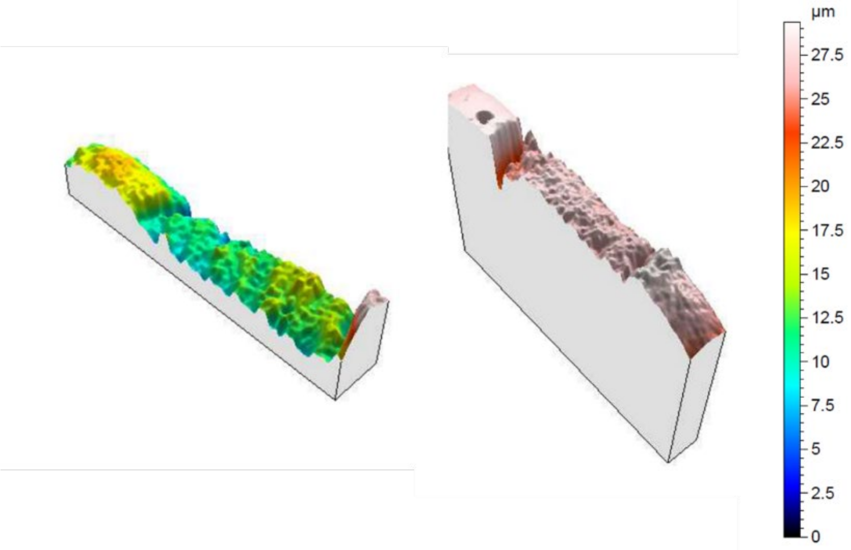

Figure 5 – 3D reconstruction of surface after preliminary electrochemical machining test. Left 0.2M NaCl, right 0.2 M NaCl + 0.05 M Na_2EDTA

Further information on the effects of the treatments is provided by the SEM EDX analysis. It is observed that the treatment in chlorides alone (Fig. 6) produces an oxidized surface with a prevalence of titanium oxide, which means that the treatment is selective towards nickel. This result can be explained by the fact that titanium in aqueous chloride solution does not form soluble compounds, and the oxidizing conditions of electrochemical machining promote the formation of oxides

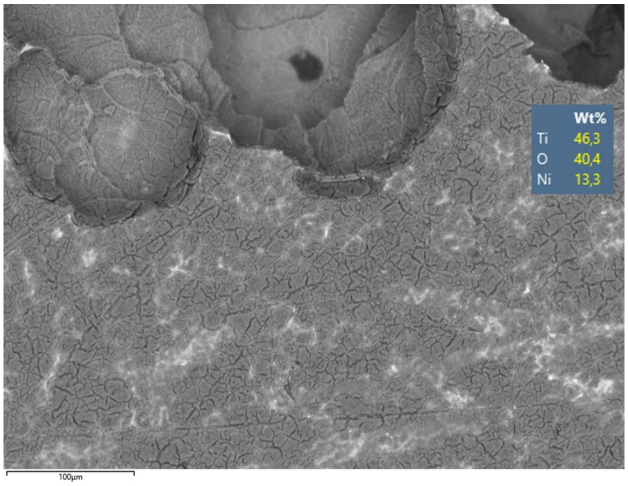

Figure 6 – Appearance and composition of the surface after treatment in the chlorides solution.

Treatment in nitrate solution (Solution 5) also produces an oxidized surface (see Fig. 7) however, the selective effect towards nickel is less pronounced. This can be explained by the greater solubility of titanium in nitrate solutions. Additionally, it should be noted that titanium is more easily oxidizable than nickel, so the oxide layer that inevitably forms during electrochemical machining will be richer in titanium.

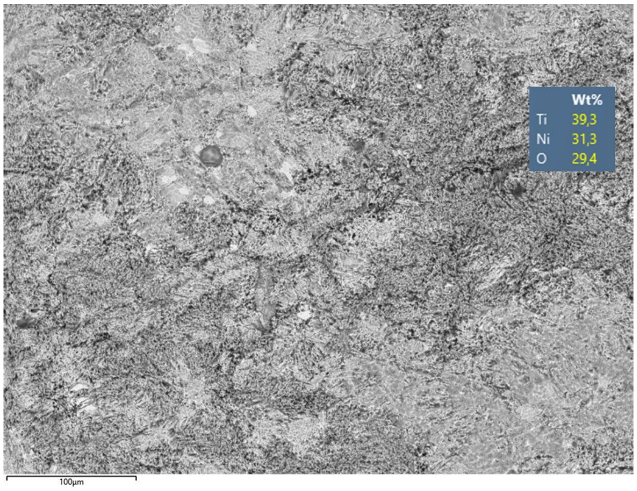

Figure 7 – Appearance and composition of the surface after treatment in the nitrates solution.

Fig. 8 shows the surface of Nitinol after treatment in Solution 6. On the left side, the surface appears similar to that treated in a solution containing only nitrates, and the surface composition is very similar to that shown in Fig. 7. On the right side of the image, however, a significantly less oxidized area is observed, with a Ni/Ti ratio closer to that of the starting alloy

It is evident that the synergistic effect of nitrates and chlorides leads to a less selective removal of the material by balancing the oxidation and solubilization processes of nickel and titanium.

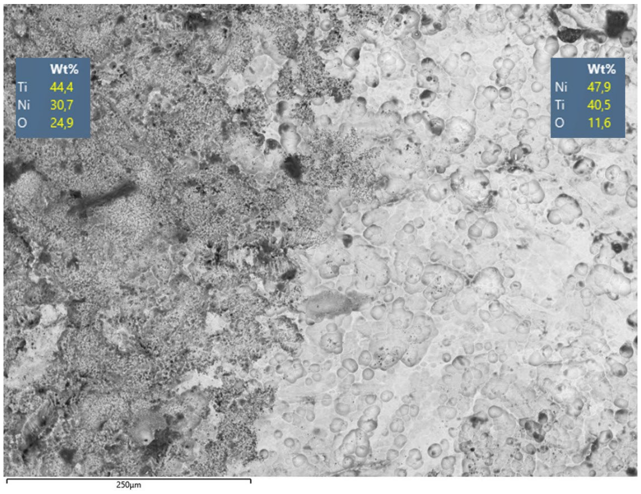

Figure 8 – Appearance and composition of the surface after treatment in the chlorides plus nitrates solution.

Conclusions

The preliminary experiments conducted in this work have demonstrated that electrochemical machining is an applicable process for nitinol. In particular, chloride, nitrates and chlorides plus nitrates solutions are capable of dissolving the alloy. The addition of Na_2EDTA to chlorides solution, through the formation of highly soluble compounds of nickel and titanium, seems to increase material removal. Solutions based on organic acids were not effective, as these acids are not stable at the potentials typical of an electrochemical machining process and decompose forming gas without material removal.

Potentiodynamic polarization tests have shown that the dissolution kinetics in Solutions 1 and 2 are governed by diffusion for potentials above 2V. This result is particularly interesting in the perspective of using the electrochemical machining process for smoothing components made by additive manufacturing, as diffusion-limited kinetics is a necessary condition for a smoothing effect to occur.

The analysis of the surfaces after electrochemical machining treatment shows a certain degree of oxidation, with a prevalence of titanium oxide for Solutions 1 and 5. Additionally, in these two solutions, the process is selective towards nickel. The combined action of nitrates and chlorides (Solution 6) decreases the selectivity of the process and the degree of surface oxidation.

Aknowledgement

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References

[1] Mohd Jani J, Leary M, Subic A, Gibson MA. A review of shape memory alloy research, applications and opportunities. Mater Des 2014;56:1078–113. https://doi.org/https://doi.org/10.1016/j.matdes.2013.11.084

[2] Chaudhari R, Vora JJ, Parikh DM. A Review on Applications of Nitinol Shape Memory Alloy BT - Recent Advances in Mechanical Infrastructure. In: Parwani AK, Ramkumar PL, Abhishek K, Yadav SK, editors., Singapore: Springer Singapore; 2021, p. 123–32.

[3] Billah T, Aquib TI, Dey K. A review on surface modification of NiTinol for biomedical applications. J Mater Sci 2024;59:19340–79. https://doi.org/10.1007/s10853-024-10273-8

[4] Barik L, Samal S, Behera A, Rajak DK, Pruncu CI. On the replacement of steel by NITINOL as coupling agent in automobile shaft. ISSS J Micro Smart Syst 2021;10:87–102. https://doi.org/10.1007/s41683-021-00075-4

[5] Guo Y, Klink A, Fu C, Snyder J. Machinability and surface integrity of Nitinol shape memory alloy. CIRP Ann 2013;62:83–6. https://doi.org/https://doi.org/10.1016/j.cirp.2013.03.004

[6] Mohol SS, Sharma V. Functional applications of 4D printing: a review. Rapid Prototyp J 2021;27:1501–22. https://doi.org/10.1108/RPJ-10-2020-0240

[7] Elahinia M, Shayesteh Moghaddam N, Taheri Andani M, Amerinatanzi A, Bimber BA, Hamilton RF. Fabrication of NiTi through additive manufacturing: A review. Prog Mater Sci 2016;83:630–63. https://doi.org/https://doi.org/10.1016/j.pmatsci.2016.08.001

[8] Mani G, Porter D, Grove K, Collins S, Ornberg A, Shulfer R. Surface finishing of Nitinol for implantable medical devices: A review. J Biomed Mater Res Part B Appl Biomater 2022;110:2763–78. https://doi.org/https://doi.org/10.1002/jbm.b.35112

[9] Kim US, Park JW. High-Quality Surface Finishing of Industrial Three-Dimensional Metal Additive Manufacturing Using Electrochemical Polishing. Int J Precis Eng Manuf Technol 2019;6:11–21. https://doi.org/10.1007/s40684-019-00019-2

[10] Scherillo F, Astarita A, Prisco U, Squillace A. Selective electrochemical machining of the steel molds in hot isostatic pressing of Ti6Al4V powder. Mater Manuf Process 2018;33:1587–93. https://doi.org/10.1080/10426914.2018.1424905

[11] Figueroa CA, Sileo EE, Morando PJ, Blesa MA. Dissolution of Nickel Oxide in Oxalic Acid Aqueous Solutions. J Colloid Interface Sci 2001;244:353–8. https://doi.org/https://doi.org/10.1006/jcis.2001.7862

[12] Mukherjee A, Raichur AM, Modak JM. Dissolution studies on TiO2 with organics. Chemosphere 2005;61:585–8. https://doi.org/https://doi.org/10.1016/j.chemosphere.2005.02.059

[13] Kim DE, Suh NP. Chemical Smoothing of Rough Metal Surfaces. J Eng Ind 1992;114:421–6. https://doi.org/10.1115/1.2900693