Study of the Electrochemical Dissolution Behavior of Nitinol Shape Memory Alloy in Different Electrolytes for Micro-ECM Process

Abhijeet Sethi (abhijeet.ab89@gmail.com)
Indian Institute of Technology Kharagpur
https://orcid.org/0000-0001-5134-2017

Biswa Ranjan Acharya
Partha Saha

Research Article

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Abstract

Nickel-Titanium alloy (Nitinol) is an excellent shape memory alloy (SMA) for Micro electro-mechanical systems (MEMS) particularly in biomedical applications owing to its three excellent features like shape memory effect (SME), superelasticity, and biocompatibility. The fabrication of micro features on Nitinol SMAs through conventional machining has been challenging due to its temperature-dependent material transformation properties. Micro electrochemical machining (micro-ECM), a nonconventional machining method for conductive material irrespective of strength and hardness has the potential for microfeature fabrication on Nitinol. This study presents the investigation on electrochemical dissolution behavior of Nitinol in different electrolytes for micro-ECM. The influence of electrolytes on the nature of dissolution of Nitinol has been studied by fabricating microchannels in three levels of parameters containing applied voltage and electrolyte concentration. The first three electrolytes were all aqueous neutral electrolytes i.e. sodium chloride (NaCl), sodium nitrate (NaNO₃), and sodium bromide (NaBr). For profound analysis of dissolution behavior and its influence on machining performance, potentiodynamic polarization (PDP) tests of Nitinol were performed in aqueous NaCl, aqueous NaNO₃, and aqueous NaBr solutions. The PDP tests that are conducted here are cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The three aqueous solutions were utilized for microchannel fabrication in Nitinol through micro ECM in three levels of parameters out of which aqueous NaNO₃ was successful in fabricating microchannel. Then nonaqueous electrolyte of ethylene glycol-based NaNO₃ has been used to fabricate microchannels with lower depth overcut (DOC), width overcut (WOC), and length overcut (LOC) with respect to aqueous NaNO₃ electrolyte.

1. Introduction

Nickel-titanium alloy or NiTi belongs to a class of smart materials that show shape memory effect (SME) and pseudoelasticity and have the composition of Niₓ Ti₁−ₓ, where 0.47 ≤ x ≤ 0.51 [1]. It is popularly known as NITINOL, which is derived from the Nickel titanium naval ordnance factory where it was discovered in the 1960s by William J. Buehler and Fedric Wang [2]. The shape memory effect is the transition of a material from a deformed state to an undeformed state when heated above its transition temperature. The transition is called martensitic transformation which happens due to the solid-state phase transformation where simple cubic austenitic crystal structure transforms to monoclinic martensite crystal structure [3]. Nitinol also exhibits pseudoelasticity otherwise named superelasticity where a large strain can be induced during mechanical loading [4]. NiTi forms a titanium-rich oxide layer on the surface, hence shows excellent biocompatibility [5]. The above three feature i.e. SME, superelasticity and biocompatibility makes NiTi the preferred SMA for MEMS particularly in biomedical applications [6]. These MEMS devices perform significant tasks in a scaled-down miniaturized volume. Sensing and analyzing light and mechanical signals, sequencing biomolecules, mixing, processing, and analyzing the ultra-little volume of chemicals are some of the regular activities realized by these miniaturized machines [7]. The MEMS has various advantages like quick response time (e.g. airbag sensors), usage of less consumables (e.g. Lab-on-a-Chip), high resolution and efficiency (e.g. inkjet printer
The actuators form the fundamental system in the MEMS and SMAs have been now extensively used as a material of choice for actuators. Nitinol MEMS devices such as micro vales, micro pumps, micro grippers, actuated microendoscope, spaces, nerves clamp, tactile displays are some of the examples that have been reported over the last decade [9]. These devices often require the fabrication of micro features on Nitinol SMAs and there are both traditional and non-traditional ways to manufacture these microscale features [10]. Traditional manufacturing processes such as turning [11], milling [12], and drilling [13] and non-traditional machining processes like laser processing [14], electro discharge machining (EDM) [15], abrasive water jet machining (AWJM) [16], chemical etching [17], and electrochemical machining [18–20] have been used in the past for nitinol microfabrication.

Micro-electrochemical machining (micro-ECM) is a promising method for microfeature fabrication due to advantages like defect-free surface generation, negligible tool wear, and capability to machine any conductive material regardless of its strength and hardness [20]. Micro-ECM has been used to manufacture micro features on some of the advanced materials like stainless steel [21], titanium and its alloys [22], nickel alloys [23], tungsten [24], and tungsten carbide [25], etc. Micro-ECM has various potential applications in a wide range of industrial sectors [20]. Micro-ECM can provide an alternative machining method for the fabrication of micro features on Nitinol surface by anodic dissolution. Takashi Mineta performed masked pulsed electrochemical etching of Nitinol with 1 mol l−1 LiCl–ethanol electrolyte to fabricate micro grooves on the surface. He had obtained etched microgrooves with 20 µm in-depth [26]. Ma et al. performed confined etchant layer technique to manufacture intricate 3D microfeatures on Nitinol with an etched pattern having micrometer accuracy. However, the microstructures obtained were having a depth of less than 1 µm [18]. Lee et al. used pulse ECM for the fabrication of micro-grooves on NiTi SMA and studied the parametric influence on the rate of material dissolution and groove depth. They used an electrolyte that generated NaNO2 and tartarate for anodic dissolution, where tartarate prevents the formation of Ni (OH)2 on the surface [19]. Joseph et al. used electrochemical micromachining (EMM) with pulsed DC power supply to machine microstructures of 3 µm depth on NiTi SMA using 1 M methanolic-LiCl [27]. Ao et al fabricated microgrooves on NiTi SMA through EMM with nonaqueous ethylene glycol-based NaCl electrolyte. They have added ethanol to the solution to improve the surface quality of the microstructures and to reduce the formation of oxide films [28]. The above-mentioned investigations promoted the fabrication of microstructures on NiTi SMA through chemical etching and EMM where the process parameters, machining accuracy, and surface integrity have been studied. However, the study of the electrochemical behavior of NiTi in different electrolytes still needs to be further improved.

In the above discussion, it is found that the researchers have worked on electrochemical etching, polishing, and micro features generation by either electrochemical micromachining (EMM) or confined etchant layer technique (CLET). The electrolytes that are used are ethanol-based Lithium Chloride (LiCl) which is costly and hydrofluoric acid (HF) with nitric acid (HNO3) which is toxic in nature. However, there are not many efforts that are aimed at exploring the dissolution behavior of Nitinol in aqueous neutral
solutions which are commercially used in ECM. Therefore, in this paper, a thorough investigation is done to evaluate the performance of aqueous neutral electrolytes like sodium chloride (NaCl), sodium nitrate (NaNO₃), and sodium bromide (NaBr) to find out the effective dissolution of Nitinol in the micro domain by fabricating microchannels. Also, we have explored nonaqueous neutral electrolytes of ethylene glycol and NaNO₃ for their effect on the electrochemical dissolution of Nitinol. For a more profound and comprehensive analysis of the dissolution behavior of Nitinol and its influence on the machining performance, potentiodynamic polarization tests were conducted for both aqueous and nonaqueous electrolytes.

2. Experimental Setup

Experimentation for fabrication of microchannel by micro-ECM was conducted in TTECM-10 (Tabletop type Micro ECM CNC Machine tool) of Synergy nanosystems, Mumbai. The machine consists of a computer, pulsed DC power supply, machining chamber, digital camera, and electrolyte circulation and filtration unit. Figure 1 shows the machine and its components. The machine has the provision of three CNC linear stages in X, Y, and Z-axes. The resolution for each stage is 0.1 µm/step and the control of stepper motors is governed by a computer with the help of Hyper 2GUI software. The machine chamber is provided with horizontal X and Y- motions and the Z- motion is given to the micro tool holder perpendicular to the machining chamber along with the rotational motion. The machine has a power supply that can generate a maximum of 500 kHz frequency voltage pulses for microfabrication purposes. A digital camera is attached to the machine for online monitoring and measurement of micro tools for successive experiments without removing them from the tool holder.

The potentiodynamic polarization experiments were conducted in an electrochemical cell having three electrodes with the help of Biologic SP 150 potentiostat as shown in Figure 2. The three electrodes used for the experiments are a reference electrode (saturated Ag/AgCl), an auxiliary electrode (platinum wire), and a working electrode (Nitinol sheet). Every one of the given potentials was determined against the standard hydrogen electrode (SHE). All the electrodes were connected with a PC-controlled potentiostat Biologic SP150. The exposed surface area of the working electrode Nitinol sheet was kept to 1cm².

3. Materials And Methods

For the micro tool fabrication process cylindrical rod of tungsten carbide (WC-Co) having 500 µm diameter has been used. The process is in situ as the TTECM-10 was used for the fabrication process by using the reverse polarity and the same machine was used for the microchannel fabrication by straight polarity without removing the micro tool. The diameter of the cylindrical WC rod is first reduced by electro-discharge grinding (EDG) with a brass block as cathode and WC micro rod as the anode. Then with the help of the wire electrochemical process (WECM), the surface of the fabricated micro tool is improved by taking 250 µm diameter of brass wire as cathode and the EDG fabricated micro tool as the anode. There are two micro tools been used in the microchannel fabrication through the micro ECM process. The
images of the micro tool obtained through a scanning electron microscope (SEM) have been given in Figure 3.

For this study commercial Nitinol (52% Ni and 48% Ti) sheets of 1mm thickness were used. For microchannel fabrication in micro-ECM, the samples were ultrasonically cleaned using acetone. For potentiodynamic polarization (PDP) analysis the samples were prepared on a Buehler-Phoenix 4000 machine through grinding and polishing using SiC papers down to 2500 grit and diamond pastes (9, 3, then 1 µm) from Struers. After that ultrasonic cleaner has been used to clean the samples with acetone and deionized water. The prepared samples for microchannel fabrication through the micro ECM process and PDP tests are shown in Figure 4 along with their surface composition obtained from energy dispersive spectroscopy (EDS) analysis.

The electrolytes were used for the possibility of electrochemical dissolution of Nitinol by trying to generate micro channels applying mask-less micro-ECM technique are aqueous neutral solutions of NaCl, NaNO₃, and NaBr. Also, ethylene-based nonaqueous electrolytes were studied for their effect on the electrochemical dissolution of Nitinol. The electrolytes and their concentrations used for both the fabrication of microchannel as well as PDP tests are given in Table 1.

The layer-by-layer material removal by scanning method was employed to fabricate a micro channel of 2 mm length on the surface of a 1 mm thick Nitinol sheet. The microchannels were fabricated with a downward feed of 0.1 µm/sec and a scanning feed of 0.5 µm/sec with 5 µm layer thickness. A total depth of 10 µm is given for microchannel fabrication with 5 µm layer thickness. The Schematic view of microtool movement during the generation of the microchannel is given in Figure 5. The experiments were conducted in three levels of parameters with each level containing a combination of electrolyte concentration and applied voltage. The three-level of parameters are low levels containing 0.1 M concentration and 8 V applied voltage, mid-level with 0.15 M concentration and 12 V applied voltage, and high level of parameter with 0.2 M concentration and 16 V applied voltage whereas other parameters were kept constant for each level (Table 2).

Further, the effect of electrolytes on the accuracy of the fabricated microchannel was evaluated based on width overcut, depth overcut, and length overcut. The schematic showing width, depth, and length of a microchannel are given in Figure 6. Width overcut (WOC) is the excess material removed across the width of the micro channel is calculated as

\[
\text{Width overcut} = \frac{(\text{Width} - \text{Tool Diameter})}{2}
\]

\[
\text{Depth Overcut (DOC)} = H_2 - H_1
\]

\[
\text{Length Overcut (LOC)} = L_2 - L_1
\]
### Table 1
Electrolytes with their concentration for Micro-ECM and PDP test

| S. No. | Description                                      | Molar Concentration (M) | Micro-ECM | PDP Test |
|--------|--------------------------------------------------|-------------------------|-----------|----------|
| 1      | Sodium Chloride (NaCl)                           | 0.1, 0.15, 0.2          | 0.1       |          |
| 2      | Sodium Nitrate (NaNO₃)                           | 0.1, 0.15, 0.2          | 0.1       |          |
| 3      | Sodium bromide (NaBr)                            | 0.1, 0.15, 0.2          | 0.1       |          |
| 4      | Ethylene glycol and Sodium Nitrate (EG + NaNO₃)  | 0.1, 0.15, 0.2          | 0.1       |          |

### Table 2
Micro-ECM process parameter set up for micro channel generation on Nitiol

| Sl No | Process Parameter     | Nature | Low level | Mid-level | High Level |
|-------|-----------------------|--------|-----------|-----------|------------|
| 1     | Electrolyte Concentration | variable | 0.10 M    | 0.15 M    | 0.20 M     |
| 2     | Applied Voltage        | variable | 8 V       | 12 V      | 16 V       |
| 3     | Pulse Frequency        | Fixed   | 500 kHz   |           |            |
| 4     | Pulse on time          | Fixed   | 1 µs      |           |            |
| 5     | Pulse off time         | Fixed   | 1 µs      |           |            |
| 6     | Tool RPM               | Fixed   | 500 rpm   |           |            |

### 4. Results And Discussions

#### 4.1 Effect of aqueous neutral electrolytes on anodic dissolution of NITINOL

One of the major problems related to the electrochemical dissolution of Nitinol is surface oxidation in atmospheric conditions. When exposed to a medium containing oxygen Nitinol forms a passive oxide film on its surface [28]. The EDS study reveals the same which can be found out in Figure 4(a). Electrolyte containing aqueous sodium chloride (NaCl) was the first electrolyte to be used for electrochemical dissolution of Nitinol by the micro-ECM process. It can be seen from Figure 7 that the color of the electrolytic solution has turned yellow and the formation of black-colored sludge has been observed. This black sludge is formed due to the particles which arise out from the local pitting of oxide film that is quickly formed due to the aqueous nature of electrolyte [22]. In all aqueous solutions, we have found the changing of electrolyte color and formation of sludge on the surface of the material.

In the case of aqueous NaCl solution, it can be seen that from figure 8 (a)-(c) at all levels of parameters a solid sludge layer is developed on the machined surface. EDS analysis of the sludge layer is given in
Table 3 which shows the presence of Titanium, Nickel, and Oxygen at all level parameters. Thus, in the case of aqueous NaCl solutions, the sludge generated during machining contains the oxides of both Titanium and Nickel. In the case of aqueous NaNO₃, it could be observed from figure 8 (d)-(f) that the volume of sludge attached to the surface is low and the EDS data from Table 3 shows the amount of oxygen is low in comparison to NaCl. Further experiments were conducted with the aqueous electrolyte of NaBr. In this case, also due to the aqueous nature of the electrolyte a large amount of sludge is generated and the EDS study of sludge shows a high percentage of oxygen is present due to the formation of Titanium and Nickel oxide during the machining process.

After cleaning the workpiece, the SEM images have been taken and are given in Figure 9. From Figure 9(a) it can be seen that in the case of aqueous NaCl solution at low-level parameter a channel is fabricated with an average depth achieved is 46.78 µm. However, in the case of mid-level and high-level parameters, the anodic dissolution of Nitinol is uncontrolled with an uneven and irregular surface. Thus, in aqueous sodium chloride solution for mid-level and high-level parameters, the channel fabrication was not successful. In the case of an aqueous NaNO₃ solution, a controlled dissolution can be seen at all levels of parameters (Figure 9 (d)-(f)). The channel depth of the machined surface obtained is 120.95 µm, 157.56 µm, and 316.92 µm for a low, mid, and high level of parameters respectively. However, in the case of aqueous NaBr at all levels of parameters, the channel fabrication was not successful. From figure 9 (g)-(i) it can be observed that there is uncontrolled and uneven dissolution and large pitting areas have been formed at a mid and high level of parameters. Thus, the aqueous sodium bromide electrolyte was not successful in machine Nitinol through micro-ECM. The 3D profiles were obtained for all the microchannels through a non-contact surface profilometer and the 3D profile of the microchannel fabricated in NaNO₃ electrolyte with 0.2 M and 16 V parameters is given in Figure 10. Figure 11 represents the relationship between the average surface roughness (Ra) of the machined surface and the level of process parameters for NaCl, NaNO₃, and NaBr electrolyte. In the case of NaNO₃ for the high level of the parameter, the lowest surface roughness of 0.848 µm has been obtained confirming a better uniform dissolution of Nitinol. Thus, aqueous sodium nitrate (NaNO₃) is the better electrolyte for the anodic dissolution of Nitinol.
Table 3
EDS data of sludge growth on the specimen for different electrolyte condition under three level of parameters

| Electrolyte | Parameters | Element Weight (%) |
|-------------|------------|---------------------|
|             |            | Ti      | Ni      | O       |
| NaCl        | 0.1 M, 8 V | 36.37   | 32.78   | 30.84   |
|             | 0.15 M, 12 V | 26.55  | 17.52   | 55.92   |
|             | 0.20 M, 16 V | 31.67  | 25.40   | 42.94   |
| NaNO₃       | 0.1 M, 8 V | 38.15   | 40.91   | 20.00   |
|             | 0.15 M, 12 V | 23.43  | 27.15   | 42.92   |
|             | 0.20 M, 16 V | 36.69  | 36.98   | 26.33   |
| NaBr        | 0.1 M, 8 V | 34.84   | 20.19   | 44.97   |
|             | 0.15 M, 12 V | 21.99  | 34.57   | 43.44   |
|             | 0.20 M, 16 V | 26.07  | 35.12   | 38.81   |

4.2 Potentiodynamic Polarisation Analysis

For in-depth analysis of electrochemical dissolution behavior and its effect on machining performance, potentiodynamic polarization (PDP) tests of Nitinol were performed in aqueous NaCl, aqueous NaNO₃, and aqueous NaBr solutions. The PDP tests that are conducted here are cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

CV is one of the most popular methods for the quantitative analysis of an electrochemical reaction. CV gives data on redox reactions, adsorption processes, and heterogeneous electron transfer reactions [29]. This technique also locates the rapid changes of redox potentials of electroactive species in a solution. During the CV process, the potential of the stationary working electrode is scanned using a triangular waveform. The resulting current due to the electrochemical reaction at the electrode-electrolyte interface is then recorded by the potentiostat. The current response then plotted as a function of applied potential is called a cyclic voltammogram. The LSV procedure is a standard electrochemical technique however only a forward scan is performed with comparison to both forward and backward scan in CV.

The first cyclic voltammogram of Nitinol in aqueous NaCl solution was recorded between 0 V to 2 V (SCE) with 5 repetitive cycles at a scan rate of 20 mV/sec at room temperature. The cyclic voltammogram of Nitinol in 0.1 M aqueous NaCl solution is given in Figure 12. It is apparent from Figure 12 (a) in cycle 1 the current density increases rapidly as the potential increases from 0 V. However, at 0.8 V the rate of increase in current density decreases. This may be due to the passivation of the working electrode as Nitinol forms an oxide layer in an aqueous solution. At 1.6 V the current density again starts to rise.
quickly and linearly indicating the passive oxide film breakdown and initialization and propagation of pitting. The maximum current density achieved is 13.33 mA cm\(^{-2}\). On the contrary, the reverse potential sweep shows a hysteresis loop for pitting current and then decreases rapidly until it is suppressed at a specific repassivation potential. Above this potential, the pit initiation occurs and below this, there is no pitting [30]. The voltammogram shows that in the reverse scan the current density is higher with respect to the forward scan which is due to the reduction of the remaining oxide film on the electrode surface. In cycle 2 (Figure 12 (b)) the current density decreases after 0.79 V indicating the passivation of Nitinol and again the current density linearly increases after 1.6 V breaking the passivation layer and a maximum current has been achieved is 9.25 mA. From Figure 12 (f) it can be observed that in subsequent cycling up to cycle 5 the maximum current density gradually decreases. This can be reasoned upon successive cycling; the oxide film turns out to be more protective as the passive layer formed during the forward scan stayed unreduced during the reverse scan [31]. The passive layer formation has been confirmed through EDS analysis of the surface (Figure 13) after the completion of CV.

Figure 14 shows the cyclic voltammogram of Nitinol in 0.1 M aqueous NaNO\(_3\) solution measured between 0 V to 2 V. With the increase in the potential the current density increases gradually up to 1.5 V. After 1.5 V the current density increases very steeply up to 2 V. In the first cycle the reverse anodic current density is higher than the forward anodic current density. However, with subsequent cycles the current density in passivating regions increases, and the maximum anodic current decreases from cycle 1 to cycle 4 however it again increases at cycle 5. This shows stable passivation of Nitinol as the oxide layer is formed on its surface and subsequent breakdown of the oxide layer. Upon successive cycling, the passive layer however doesn't get protective as it gets breakdown at the higher passivating current density and the maximum current density in cycle 5 is obtained. The passive layer formation in the case of NaNO\(_3\) solution has been confirmed through EDS analysis of the surface (Figure 15) after the completion of CV.

Figure 16 shows the cyclic voltammogram of Nitinol in 0.1 M NaBr solution. From figure 16 (a) it can be seen that at a forward scan at 0.84 V there is a sudden decrease in current density and it remains constant up to 0.96 V. This region can be attributed to the passivation region. Beyond this potential, there is a rapid increase and sudden decrease in potential. This can be attributed to the formation of micro pits. From 1.06 V to 1.31 V the repassivation of pits occur and the current density remains constant, beyond 1.31 V the cyclic voltammogram becomes irregular with increasing current density. This region can be attributed to the propagation of pitting and high pitting occurrence. SEM observations (Figure 17 (a)) show the occurrence of irregular, large, and shallow pits with faceted structures, which yield a rough etched surface. However, the reverse anodic scan does not show any pitting and in cycle 2, cycle 3, and cycle 4 the pitting decreases which can be observed from the voltammogram. Finally, in cycle 5 the pit formation becomes saturated as no irregularities are found in the voltammogram.

Linear sweep voltammetry (LSV) of Nitinol is performed in different electrolytes to determine \(E_{\text{diss}}\), the potential at which the dissolution of material starts, and \(J_{\text{max}}\), the maximum current density that is
obtained during the voltammetric process [32]. The experiments were done in a potential range of 0 V to 6 V vs Ag/AgCl at a scanning rate of 10 mV/sec. The resulting current density vs voltage curve for all three aqueous electrolytes at 0.1 M concentration is given in Figure 18(a). The \( E_{\text{diss}} \) has been calculated at the inflection point of the curve that is given in Figure 18(b). Table 4 summarizes the result for \( E_{\text{diss}} \) and \( J_{\text{max}} \). From Figure 18 (a) it can be observed that at the low potential there is very negligible current attained as no dissolution takes place. However, upon reaching \( E_{\text{diss}} \) there is a sudden increase in current density and at this potential, the material starts to dissolve. The determination of \( E_{\text{diss}} \) and \( J_{\text{max}} \) solely depends upon the material and type of electrolyte and its concentration. Referring the Table 4, it can be observed that the \( E_{\text{diss}} \) for NaNO\(_3\) is 1.68 V which is lower in comparison to NaCl and NaBr, thus Nitinol starts to dissolve early in the case of NaNO\(_3\). On the other hand, the maximum current density achieved is in the case of NaBr is high in comparison to other electrolytes. The rate of dissolution becomes higher at higher current density. However high current density also causes a stray current effect in micro-ECM causing inaccuracies.

| Electrolyte | \( E_{\text{diss}} \) (V) | \( J_{\text{max}} \) (mA/cm\(^2\)) |
|-------------|----------------|-----------------|
| NaCl        | 1.7            | 108.025         |
| NaNO\(_3\)  | 1.68           | 106.699         |
| NaBr        | 2.86           | 159.735         |

4.3 Effect of ethylene glycol-based NaNO\(_3\) electrolyte on anodic dissolution of NITINOL

All the electrolytes used in the above experiments were aqueous neutral thus contain water that aids in the development of a passive oxide layer on the surface of nitinol. Out of three electrolytes, only aqueous NaNO\(_3\) has been able to successfully machine Nitinol. However, in the machined surface the poor uniformity of the microchannel has been obtained. That’s why instead of the aqueous solution a combination of Ethylene glycol and NaNO\(_3\) has been studied for the anodic dissolution of Nitinol. The experiments were done again in three different levels with three different combinations of concentration and voltage. Figure 19 shows the optical and SEM images of the fabricated microchannel in three different parameters. From the optical images (Figure 19 (a-b)) it is observed that a bright surface has been obtained at the machined region. Figure 20 shows a relationship between average surface roughness (Ra) and the level of process parameters for NaNO\(_3\) and EG + NaNO\(_3\) electrolytes. The surface roughness of the machined surface obtained was 0.891 \( \mu \)m, 0.25 \( \mu \)m, and 0.424 \( \mu \)m for low, mid, and
high-level parameters which is less in comparison to that obtained in the case of aqueous NaNO₃ solution. However, from the SEM images (Figure 19 (d-f)) it can be seen that the surface surrounding the microchannel in all three parameters are affected by bubble marks. These bubble marks on the surface of nitinol decrease the surface integrity of micro features. The bubbles are the hydrogen gas that is being generated at the cathode during the electrochemical reaction. During the dissolution process, these hydrogen gas bubbles don’t affect the machining due to the rapid formation and explosion. However, when the IEG is too low the process of formation and explosion of bubbles stopped and the machining process is continued with the proximity of bubbles to both the surface of the cathode and nitinol. Due to the bubbles, the dissolution is uneven, and partial bubble marks are generated on the nitinol surface [33]. Thus, for efficient machining, a suitable IEG is preferred. Also, proper insulation of the sidewall of the micro tool is required to check the stray current that affects the accuracy of the fabricated microchannel. From the SEM image, we can see that with the increase in level the bubble marks decrease. This is due to the increase in IEG as the concentration of the electrolyte increases.

Figure 21 (a) shows the cyclic voltammograms for EG + NaNO₃ solution. It can be seen that there is no passivation zone as the current increases very steeply from 0 V up to 2 V. From the linear sweep voltammogram (Figure 21 (b)) it can be observed that the $E_{\text{diss}}$ for EG + NaNO₃ solution is 1.7 V which is nearer to 1.68 V that is obtained for aqueous solution. However, the maximum current density ($J_{\text{max}}$) for EG + NaNO₃ obtained is 5.69 mA/cm² which is very much less in comparison to 106.699 mA/cm² which is obtained for aqueous NaNO₃ solution.

### 4.4 Effect of ethylene glycol-based NaNO₃ electrolyte on the accuracy of microchannel

The accuracy of the microchannel is measured in terms of depth overcut (DOC), width overcut (WOC) and length overcut (LOC) which are obtained both in the case of NaNO₃ and EG + NaNO₃ electrolytes. Figure 22 shows the variation of DOC, WOC, and LOC with respect to three levels of parameters for both aqueous NaNO₃ and ethylene glycol-based NaNO₃. From Figure 22 we can observe that in comparison to aqueous solutions ethylene glycol-based NaNO₃ produces very much less DOC, WOC, and LOC. This is attributed to the low conductivity of ethylene glycol which produces low current density reducing the stray current effect thus minimizing the overcut. Also, the EG solution produces sludge that is soluble in ambient conditions and hence can be easily removed from the IEG [28]. These effects form a stable machining condition and the conductivity of the electrolyte remains constant throughout the process, causing a reduction in overcut in depth, width, and length with comparison to aqueous solutions.

### 5. Conclusions

The present study has successfully investigated the dissolution behavior of nitinol in different aqueous and non-aqueous electrolytes for micro-ECM by means of machining blind micro channels in Nitinol. The aqueous electrolytes were used are sodium chloride (NaCl), sodium nitrate (NaNO₃), and sodium bromide...
(NaBr). For in-depth analysis of anodic dissolution behavior and its effect on machining performance, potentiodynamic polarization (PDP) tests of Nitinol were performed in aqueous NaCl, aqueous NaNO$_3$, and aqueous NaBr solutions. The PDP tests that are conducted here are cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The following conclusions were made from the experimental results.

- From the three aqueous electrolytes the aqueous sodium nitrate (NaNO$_3$) was successful in fabricating microchannel with a lowest average surface roughness of 0.848 µm.
- The cyclic voltammetry reveals that there is passivation of Nitinol surface in the case of aqueous solutions. In the case of aqueous NaCl the current density gradually decreases in the repetitive cycle as the oxide layer developed on the surface couldn't dissolve. In the case of aqueous NaBr, a higher current density is achieved with comparison to aqueous NaCl and NaNO$_3$. However small to very large pitting was observed on the surface of Nitinol due to uncontrolled dissolution.
- Linear sweep voltammetry study shows that the dissolution potential ($E_{\text{diss}}$) for aqueous NaCl, NaNO$_3$, and NaBr is 1.7 V, 1.68 V, and 2.86 V respectively. As aqueous NaNO$_3$ was successful for microchannel fabrication, ethylene glycol-based NaNO$_3$ has been utilized for further study.
- The microchannel fabricated through micro ECM at three levels of parameters has a bright surface with surface roughness (Ra) 0.891 µm, 0.25 µm, and 0.424 µm for a low, middle and high level of the parameter.
- From cyclic voltammetry study for ethylene glycol-based NaNO$_3$ reveals that there is no passivation of the Nitinol surface however very low current density has been obtained with respect to aqueous NaNO$_3$ solution. This is due to the low conductivity of EG which minimizes the stray current resulting in low depth overcut (DOC), width overcut (WOC), and length overcut (LOC).

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**Author Contributions**

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Figures

Figure 1

Micro electro-chemical Machine, TTECM-10
Figure 2

(a) Schematic of the Potentiodynamic polarisation test experimental setup
(b) Biologic SP 150 potentiostat

Figure 3

SEM images of in situ fabricated micro tool used for microchannel generation purpose
Figure 4

(a) Sample for microchannel fabrication through micro-ECM with EDS analysis (b) Sample for PDP tests with EDS analysis
Figure 5

Schematic view of microtool movement during generation of microchannel
Figure 6

Schematic showing width, depth, and length of a microchannel.

Figure 7

(a) WC Micro Tool
(b) Aqueous salt Solution
Sludge
Nitinol Workpiece
Optical image of sludge growth during the machining process

Figure 8

Sludge growth on the specimen for different electrolyte condition under three level of parameters
Figure 9

Machined specimen after cleaning for different electrolyte condition under three level of parameters
Figure 10

The 3D surface profile obtained through Taylor Hobson CCI profilometer for the machined surface obtained in NaNO$_3$ electrolyte with 0.2 M and 16 V (a) 3D profile (b) 2D profile (c) Depth measurement

| Parameters         | 0-1  | Unit |
|--------------------|------|------|
| Horizontal distance | 1.956 | mm   |
| Height difference  | -306.031 | µm   |
Figure 11

Relationship between average surface roughness (Ra) and the level of process parameters for NaCl, NaNO₃, and NaBr electrolyte
Figure 12

Cyclic voltammogram of Nitinol in Aqueous NaCl solution (a) Cycle 1 (b) Cycle 2 (c) Cycle 3 (d) Cycle 4 (e) Cycle 5 (f) Comparative study of 5 cycles
Figure 13

(a) SEM image of the Nitinol Surface after CV in NaCl Solution (b) EDS of the respective surface
Figure 14

Cyclic voltammogram of Nitinol in Aqueous NaNO₃ solution (a) Cycle 1 (b) Cycle 2 (c) Cycle 3 (d) Cycle 4 (e) Cycle 5 (f) Comparative study of 5 cycles
Figure 15

(a) SEM image of the Nitinol Surface after CV in NaNO$_3$ Solution (b) EDS of the respective surface
Figure 16
Cyclic voltammogram of Nitinol in Aqueous NaBr solution (a) Cycle 1 (b) Cycle 2 (c) Cycle 3 (d) Cycle 4 (e) Cycle 5 (f) Comparative study of 5 cycles
Figure 17

(a) SEM image of the Nitinol Surface after CV in NaBr Solution (b) EDS of the respective surface

Figure 18

(a) Linear sweep voltammogram of Nitinol for NaCl, NaNO₃, and NaBr (b) Enlarged view of the inflection point
Machined specimen obtained in EG + NaNO₃ solutions through Micro ECM in three different parameters, (a)-(c) Optical images (d)-(f) SEM images.
Figure 20

Relationship between average surface roughness (Ra) and the level of process parameters for NaNO₃ and EG + NaNO₃ electrolytes
Figure 21

(a) Cyclic Voltammogram for EG + NaNO₃ (b) Comparative plot of linear sweep voltammograms for NaNO₃ and EG + NaNO₃
Figure 22

Variation (a) Depth overcut (b) Width overcut and (c) Length overcut of the microchannel with respect to three levels of parameters machined through micro-ECM for electrolytes aqueous NaNO₃ and EG + NaNO₃