Experimental Investigation of Electropolishing in Ethylene Glycol-NaCl Electrolyte for Surface Integrity of Nitinol Cardiovascular Stents

Xiaoyu SUN,a Xiuting WEI,a Zhiyong LI,a,* Deda LOU,b Yongqi WANG,a and Hangqing LIUa

a School of Mechanical Engineering, Shandong University of Technology, Zibo 255049, China
b Weihai Vissue Medical Device Co., LTD, Weihai 264200, China
* Corresponding author: lzy761012@sdu.edu.cn

ABSTRACT

In order to improve the surface integrity of nitinol cardiovascular stents, this paper presented the method of electropolishing nitinol cardiovascular stents by adding distilled water of different concentration into ethylene glycol - sodium chloride electrolyte to find the optimal electrolyte composition and to investigate the change of surface chemical composition. The I-V curves and surface roughness were measured to determine the optimal polishing voltage range. The optimal polishing voltage and the composition and concentration of electrolyte were obtained by data analysis. Surface integrity of nitinol cardiovascular stents has also improved significantly. In addition, Titanium dioxide film was formed on the surface of the nitinol cardiovascular stents, which played an important role in improving the biocompatibility of the stents.

Keywords : Nitinol Cardiovascular Stents, Electropolishing, Surface Integrity, Process Technology

1. Introduction

Nitinol is a shape memory alloy composed of near equiatomic Ni and Ti, with unique shape memory characteristics and super elasticity. It has been widely used in biological medicine, aerospace and other fields. And nitinol has become the preferred material of stents because of its super performance and good biocompatibility. However, traditional mechanical processing of nitinol is very difficult due to its difficult machining characteristics. Currently, laser cutting is widely used in cardiovascular stents. However, laser processing belongs to thermoforming technology, which will produce thermal damage (such as dross, HAZ, microcrack and recast layer) on the surface as shown in Fig. 1. Therefore, it is essential to improve the surface integrity of cardiovascular stents by post-processing. Electropolishing is a very effective method to improve the microstructure of metal surface and reduce the surface roughness. Peng et al. discussed electropolishing stainless steel, and the results showed that a very thin solid film appeared on the surface of polished parts, which was conducive to the effect of gloss. Mathieu and Piotrowski et al. polished titanium in perchloric acid - acetic acid and methanol - sulfuric acid electrolytic solution respectively, and the results showed that the surface quality of titanium was greatly improved. Pohl et al. studied the influencing mechanism of two different electrolytes (perchloric acid - acetic acid, nitric acid - methanol) on the surface roughness of nitinol after electropolishing. The results showed that smooth and structured surfaces were obtained. However, acid-acid and acid-alcohol electrolytes were not only harmful to the environment but also difficult to control. Speidel et al. studied the effect of various electrolytes stable machining, and the results showed that doping sodium chloride and sodium fluoride could effectively reduce excessive cutting. Fushimi et al. studied the electropolishing of titanium by adding sodium chloride into ethylene glycol electrolyte at room temperature, and the results showed that the electrolyte was harmless to the environment, but it was difficult to apply in practice. Donghyun et al. studied the effect of adding ethanol into ethylene glycol - NaCl electrolyte on electropolishing of titanium plate. The results showed that the mirror surface could be obtained by adding 20% ethanol into the electrolyte, with the surface roughness was 2.341 nm. Figueira and Wever et al. observed the corrosion behavior of nitinol was closer to that of titanium from the polarization curves. And the passive oxidation film (TiO2) formed on nitinol had a higher protective performance, which prevented Ni precipitation, with better biocompatibility. However, these are not directly used in the post-processing of cardiovascular stents.

In order to obtain better post-processing of cardiovascular stents and electrolyte composition, the aims of this paper were: (1) to study the influences of electropolishing nitinol cardiovascular stents by added distilled water (The ingredients needed to make the TiO2 layer) of different concentration into ethylene glycol-NaCl electrolyte at room temperature, (2) to find the best composition and concentration of electrolyte and polishing voltage, and (3) to investigate the change of chemical composition on surface and the changes in the surface integrity.

2. Experimental Details

2.1 Electropolishing system

The electropolishing system includes an electromagnetic stirrer (85-2WS), DC Power supply (MAISHENG) and matching experimental equipment, as shown in Fig. 2. Table 1 list the detailed experimental conditions, and ϕ represents volume fraction. Nitinol cardiovascular stents were used as anode and stainless steel (SUS304) was made into circular cathode (diameter of 42.6 mm), with the polar distance of 20 mm. The sodium chloride (≥99.5 wt%, relative molar weight of 58.44, Tianjin Zhiyuan Reagent Co., Ltd., China) was mixed with ethylene glycol (99.98% pure with 0.1 wt% of H2O, molar weight of 62.07, FANGZHENG REAGENT, China) to form the solution of different concentrations (0, 0.25, 0.5, 0.75, 1, 1.25 mol/L). In the electropolishing experiment, distilled water of different concentrations (0,
0.5, 1, 1.5, 2 vol.%) was added to the electrolyte. In addition, the electromagnetic rotor was kept at 500 r/min and the temperature was maintained at room temperature (28°C ± 1°C).

2.2 Experimental method

The electropolishing experiment was made in six groups, with five samples each group. Before the experiment, these nitinol cardiovascular stents were cleaned in ethanol (≥99.7 wt%, FANG-ZHENG REAGENT, China) for 6 min with a Digital Ultrasonic Cleaner (CDS-200A) to remove all impurities. The detailed electropolishing parameters are shown in Table S1. In the experiment, the concentration of the distilled water was 0 vol.%–2 vol.% with a step of 0.5 vol.%, the range of the voltage was 10 V–20 V with a step of 2.5 V, and the time of the electropolishing was 10 min–30 min with a step of 5 min. In addition, the electropolishing parameters of number 27 is the same as number 14, so the electropolishing parameters carried out once.

2.3 Materials

Nitinol thin-walled (0.2 mm thickness) cardiovascular stents with outer diameter of 2.6 mm and length of 10 mm were used as the material of the electropolishing experiment. The cardiovascular stent was made of nitinol pipe (Ti 43.86 at%, Ni 56.14 at%, OD 2.6 mm, WT 0.2 mm, Tolerance ±0.02 mm) produced by Jiangsu PEIER TECH A LUMINOUS COMPANY with the quality standard of ASTM F2063-12, and through our own laser cutting system cutting forming. The nitinol cardiovascular stent in the electropolishing experiment is shown in Fig. 3.

2.4 Inspection methods

After the electropolishing experiment, all samples were ultrasonic cleaned in ethanol for 90 s and then stored in seal bags respectively. White light interferometer (MicroXAM-100) was used to measure the surface roughness. Environment scanning electron microscope (FEI Quanta 250FEG) was used to observe the surface morphology.
TRUE RMS Multimeter (Pro’sKit® MT-1280) was used to measure the voltage and current for plotting the current density-voltage ($I-V$) and time ($I-t$) curves. X-ray photoelectron spectrometer (Sai mofei 250xi) was used to analyze the surface chemical composition and content.

3. Results and Discussions

3.1 Electropolishing state

3.1.1 Preparation of base electrolyte

Table S2 shows the electrolyte composition and electropolishing parameters in the preparation of base electrolyte experiment. The solubility of NaCl in ethylene glycol is about 1.25 mol/L at room temperature, so the concentration of NaCl was 0–1.25 mol/L with a step of 0.25 mol/L in this experiment. Figure 4 shows the change rule of surface roughness with the concentration of NaCl. It could be seen from the figure that the surface roughness decreased with the increase of NaCl concentration, and the surface roughness was uniform and minimum when the concentration of NaCl was 1 mol/L. So the concentration of base electrolyte in this study was 1 mol/L by considering the surface roughness after polishing and solubility of NaCl comprehensively.

3.1.2 Voltage and current

Figure 5 shows the $I-V$ curves obtained to obtain the optimal electropolishing range of nitinol cardiovascular stents based on the concentration of distilled water in the electrolyte because every system (electrode and electrolyte) was not exactly the same. When the voltage was less than 10 V (region A), pitting reaction occurred and increased rapidly with the increase of voltage and current density. Then the current density increased slowly because pitting reactions and removal of bulk material with the increase of voltage over a narrow voltage range (region B), which was the optimal polishing voltage range (10 V–20 V).

Figure S1 shows the representative $I-t$ curves obtained in the electropolishing nitinol cardiovascular stents with the voltage of 17.5 V and with distilled water of different concentration. At constant voltage, the current increased with the increasing concentration of distilled water, but it did not change basically with time. The current increased at the beginning of the electropolishing because of pitting reactions, and soon remained stable as the bulk material began to be removed.

3.1.3 Material removal

Figure 6 shows the material removal as a function of the time. The material removal amount (obtained by measuring the reduction of wall thickness) increased linearly with the increase of the time. Under the voltage of 17.5 V and distilled water of 1 vol.%, the wall thickness reduced by 60 μm in 30 minutes and the material removal rate was a constant value (2 μm/min), which was consistent well with the $I-t$ curves in Fig. 6(a). Moreover, the thickness of the bridge bar decreased linearly with the increase of the polishing time as shown in Fig. 6(b).

3.2 Surface morphology and image

In order to better see the effect of electropolishing, the surface morphology of the nitinol cardiovascular stents by SEM before and after electropolishing as shown in Fig. S2. From the Fig. S2(a), the surface of the nitinol cardiovascular stent before electropolishing was uneven with grooves and scratches. In addition, the color of the stent before electropolishing was not uniformity, with dark-gray (which was the color of nitinol) and black yellow (color of burn after laser cutting) as shown in Fig. 3. However, Fig. S2(b) and Fig. 7 show a mirror-like surface with uniform color and smooth obtained in this experiment. After electropolishing, the surface of the cardiovascular stent was bright without thermal damage such as heat-affected zone, dross and recasting layer. It also indicated that this electropolishing system could greatly improve the surface integrity of nitinol cardiovascular stents.

3.3 Surface roughness

Figure S3 shows the surface roughness as function of the voltage in the electrolyte with different concentration distilled water. From these curves we could see that the minimum surface roughness values were obtained when the voltage was 17.5 V, except for φ2 electrolyte. Therefore, the optimal electropolishing voltage found in this experiment is 17.5 V.

When the voltage was maintained at 17.5 V, the surface roughness (this is the mean value of a set of measurements) first decreased and then increased with the increasing the concentration of distilled water as shown in Fig. 8(a). When the concentration of distilled water was 1 vol.%, the minimum surface roughness value
(78.4 nm) was obtained. This is because distilled water has a higher polarity (index $= 1.0$), the polarity index is a value calculated according to the dielectric constant by S. Kim and V. V. Yuzhakov, which is used to characterize the polarity$^{18,19}$ than ethylene glycol (index $=0.79$) and a lower viscosity than ethylene glycol, which speeds up the reaction and helps remove the material. However, the excess distilled water leads to a drastic electrochemical reaction, with a large number of bubbles produced on the surface of the cathode, which has a bad effect on the anode. Therefore, the optimum concentration of distilled water obtained in this study was 1 vol.%

Figure 8(b) shows the surface roughness (this is the mean value of a set of measurements) as a function of the time with constant voltage (17.5 V) and concentration of distilled water (1 vol.%). When the time was 15 min, the surface roughness was minimum. When the time exceeded 15 min, the surface roughness increased with the increase of time. This is because the longer the polishing time, the more products in the electrolyte and the more bubbles in the cathode, which has an adverse effect on the polishing of the sample. Therefore, the electropolishing time selected in this study was 15 min.

3.4 Surface chemical composition

Table 2 shows the surface chemical composition and content before and after electropolishing. From the table we could see that the chloride, titanium dioxide (TiO$_2$) and nickel hydroxide (Ni(OH)$_2$) were produced on the polished surface. With the addition of distilled water, the content of titanium dioxide increased slightly. As the polishing time increased, the content of titanium dioxide on the surface changed little, but a small amount of nickel hydroxide was produced.

Figure S4 shows Ti 2p results of the number (a) 04, (b) 14 and (c) 30 samples after electropolished. The titanium dioxide were produced on the surface in all conditions. During the electropolishing, the electrolyte turned pale yellow, which indicated that titanium ions generated by anode dissolution combine with chloride ions in the solution to form titanium chloride, as shown in Eq. (1).

$$\text{Ti}^{4+} + 4\text{Cl}^{-} \rightarrow \text{TiCl}_4(\ell)$$  \hspace{1cm} (1)

$$\text{TiCl}_4(\ell) + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2(s) + 4\text{H}^{+} + 4\text{Cl}^{-}$$  \hspace{1cm} (2)

Because distilled water was added in the electrolyte, the titanium chloride reacted preferentially with water molecules to produce
The main conclusions are as follows: surface chemical composition were studied through experiments. The surface properties is improved very well. The optimal nitinol cardiovascular stents at room temperature. After polishing added into ethylene glycol-NaCl electrolyte to electropolish the surface because the reaction between nickel ions and water polishing time was 30 minutes, nickel hydroxide appeared on the stents when the polishing time was short. However when the polishing time, and the optimal polishing time obtained in this study was about 15 min. 4. When the concentration of distilled water was 1 vol.% with voltage of 17.5 V and time of 15 min, the best surface was obtained with Ra of 78.4 nm. In addition, the material removal rate was 2 µm/min in this condition.

Supporting Information
The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00047.

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Table 2. Surface chemical composition & content before and after electropolishing.

| Number | Ti  | Ni  | Cl 2p | C 1s | O 1s | TiO2 | Ni(OH)2 |
|--------|-----|-----|-------|------|------|------|---------|
| Original stent | 43.86 | 56.14 | 0 | 0 | 0 | 0 | 0 |
| 04 | 0.74 | 40.86 | 0.9 | 14.92 | 8.6 | 33.98 | 0 |
| 14 | 0.7 | 38.70 | 0.97 | 13.36 | 9 | 37.27 | 0 |
| 30 | 0.16 | 40.48 | 0.37 | 12.15 | 8.41 | 37.81 | 0.62 |

4. Conclusions
In this experiment, distilled water of different concentrations was added into ethylene glycol-NaCl electrolyte to electropolish the nitinol cardiovascular stents at room temperature. After polishing the surface properties is improved very well. The optimal composition and concentration of electrolyte and the change of surface chemical composition were studied through experiments. The main conclusions are as follows:

1. The optimum concentration of base electrolyte (ethylene glycol-NaCl) in this study was about 1 mol/L by considering the surface roughness after polishing and solubility of NaCl comprehensively.

2. The $I$–$V$ curves were measured to determine the polishing voltage range of 10 V–20 V, and the optimal polishing voltage obtained in this study was about 17.5 V.

3. TiO$_2$ film was produced on the surface in all experimental conditions, which played an important role in improving the biocompatibility of the cardiovascular stents. In addition, the Ni(OH)$_2$ would be produced on the surface under the long polishing time, and the optimal polishing time obtained in this study was about 15 min.

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