Int. J. Electrochem. Sci., 16 **(2021)** Article ID: 210364, doi: 10.20964/2021.03.42

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrolytic Polishing Test and Surface Properties of Nitinol Tube

Hua Ji[1], *Yongqi Wang*[2], *Zhiyong Li*[2,*], *Zhaoxia Huang*[2],*Mingxia Chai*[2]

[1] Shandong University of Technology, School of Electrical and Electronic Engineering, 266 xincun west road, 255049, Zibo, China
[2] Shandong University of Technology, School of Mechanical Engineering, 266 xincun west road, 255049, Zibo, China
[*]E-mail: Lzy761012@sdut.edu.cn

Received: 13 October 2020 / *Accepted:* 25 December 2020 / *Published:* 31 January 2021

Nitinol alloy is widely used in biomedicine because of its tensile resistance, fatigue resistance, shape memory effect, and good biocompatibility. This study aims to utilize an electrolytic polishing method to improve the surface condition of nitinol tubes. The electrolyte ratio of a basic electrolytic polishing solution was explored. Orthogonal and single-factor experiments were performed to determine the effects of four electrolytic polishing factors, namely, current density, polishing time, distance between electrodes, and polishing temperature, on the surface morphology of nitinol. The best combination of electrolytic polishing process parameters was then identified. Finally, changes in the surface roughness, surface morphology, and hydrophobicity of nitinol before and after electrolytic polishing were compared.

Keywords: Nitinol tube; Electrolytic polishing; Surface morphology; Surface roughness

1. INTRODUCTION

Nitinol alloys are widely used in aerospace, mechanical electronics, biomedicine, and other fields because of their stable chemical properties, good biocompatibility, and unique shape memory characteristics. With the economic and social development and the aging of the population, vascular diseases have become the main cause of death from diseases worldwide [2-4]. In the last 3 years, vascular diseases accounted for more than half (52.6%) of the death rate from diseases worldwide [5]. Stent medical equipment composed of nitinol tubes is safe to use in the treatment of vascular occlusion and stenosis, and it has good development prospects [6-8].

The acquisition of high-precision contours is important in the manufacturing of nitinol medical equipment. At present, common processing methods for nitinol medical equipment include electrical discharge machining, dry laser processing, and water-guided laser processing [9-13]. However, these methods cannot overcome the large surface roughness and poor surface morphology of nitinol tubes [14]. Tubes without surface treatment release excessive ions that exert inflammatory [15] and carcinogenic effects on the human body [16,17]. Electrolytic polishing can effectively reduce the surface roughness and improve the surface morphology of tubes [18].

Neelakantan et al. studied the electrolytic polishing and mechanism of nitinol in methanol sulfuric acid electrolyte. After electrolytic polishing, a salt film forms on the alloy surface, but the surface roughness value increases by two times [19]. Rokicki et al. studied the effect of electrolytic polishing with 6% sodium hypochlorite on the morphology, roughness, and surface energy of Nitinol. Sodium hypochlorite treatment does not considerably affect the surface properties of Nitinol but can increase its oxygen content, especially on its surface oxide layer [20]. Hassel et al. clarified the electrolytic polishing mechanism of nitinol in methanol sulfuric acid solution. They also analyzed the effects of speed, temperature, and ion concentration on dissolution kinetics [21]. Fushimi et al. determined the electro-dissolution behavior of nitinol in 3 M H_2SO_4 methanol solution by using electrochemical impedance spectroscopy under limited current conditions. They also explored the effects of speed, applied potential, and temperature changes on electrolytic polishing [22]. Azevedo et al. determined the appropriate parameters of electrolytic polishing in the superelastic and shape memory state of nickel–titanium wire. They found that electrolytic polishing in 3.5 mol/L methanol-based H_2SO_4 electrolyte at 20 ℃ can effectively reduce the surface roughness and improve the corrosion resistance of nitinol [23]. Simka et al. evaluated the influence of polishing liquid composition on the surface quality of nitinol by using AFM and SEM. A uniform surface was obtained in a solution of hydrofluoric acid and sulfuric acid, and results showed that electrolytic polishing induces the formation of a titanium dioxide layer on the surface, making nitinol resistant to corrosion [24].

The present study aims to explore the influence of different electrolytic polishing factors on nitinol tubes, improve the surface roughness and surface properties of the tubes, and provide support for biomedical research. The effect of electrolytic polishing nitinol tubes with perchloric acid–methanol electrolyte was studied, and the best ratio of electrolyte composition was determined. Electrolytic polishing parameters such as current density, polishing time, distance between electrodes, and polishing temperature were optimized. The surface properties (surface roughness, surface morphology, and hydrophobicity) of nitinol tubes before and after electrolytic polishing were compared. Results show that electrolytic polishing improves the surface properties of the tubes.

2. EXPERIMENTAL

2.1 Experimental materials

Nitinol tube (Ti 50.9at%, Huamao Group) with an outer diameter of 2.6 mm and an inner diameter of 0.2 mm was used as the workpiece. Laser was used to cut the nitinol into pipes each with a length of 10 mm.

The cut Nitinol sample was ultrasonically cleaned in distilled water for 2 min and then blown dry after taking it out. Surface oxide scale was removed from the sample by using sand paper of different thicknesses (600#, 800#, 1000#, 1500#). Finally, the polished sample was washed with acetone and distilled water for 2 min each, dried, sealed, and stored.

2.2. Experimental work and equipment

A polishing device was designed because the nitinol sample has a curved tubular structure, which is different from the ordinary planar structure. The main structure diagram, including the power supply part, polishing tank part, and anode and cathode clamping parts, is shown in Figure 1. The clamping device of the nitinol tube adopted a three-jaw chuck structure, and the bracket was fixed by the clamping force of the bolt. The upper part of the support shaft was connected to the motor, thereby driving the nitinol tube to rotate. The bracket was supported by a spring at the bottom, and the cathode was fixed in the groove of the base. The polishing liquid is corrosive and easy to observe. Hence, a plastic polishing tank was selected, and the cathode was 304-grade stainless steel. A constant-temperature water tank was adopted in the electrolytic polishing pool to control the temperature, and the temperature was measured with a thermometer. The specific electrolytic polishing parameter range is shown in Table 1. On the basis of the literature and the results of the preliminary experiment, the interval of the perchloric acid–methanol concentration and volume ratio of the nitinol tube was set at 1:13–1:20 to determine the ratio of the electrolyte solution.

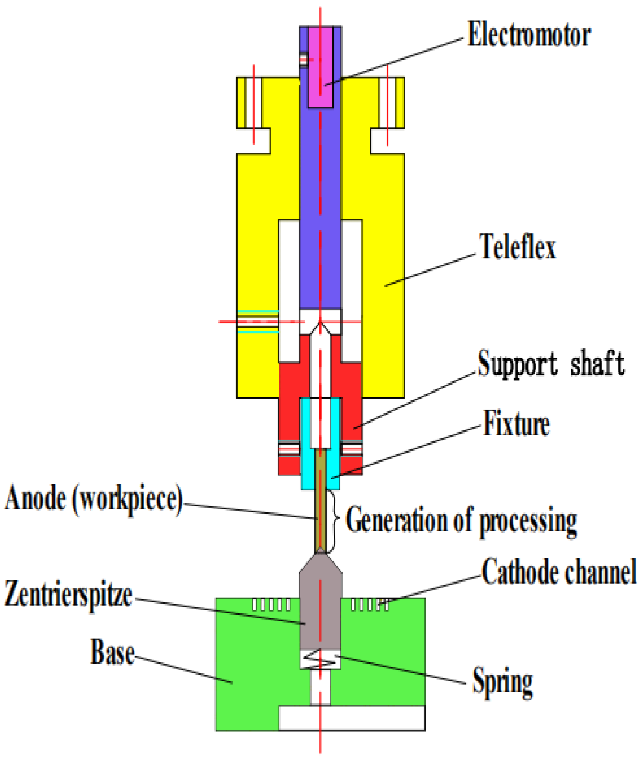

Figure 1. Schematic diagram of electrolytic polishing device

Table 1. Electrolytic polishing parameters

Electrolyte	Current density (A/cm^2)	Temperature (°C)	Distance between electrodes (mm)	Time (s)	Additives (ml/L)	
					Triethanolamine	Absolute ethanol
Perchloric acid-methanol 1:13-1:20	0.8-1.2	10-30	15-25	30-90	1-11	0-100

3. RESULTS AND DISCUSSION

3.1 Optimization of basic electrolytic polishing solution

The other experimental parameters were room temperature of 25 °C, current density of 1.0 A/cm^2, distance between electrodes of 20 mm, and polishing time of 90 s. Surface roughness was used as an index to judge the quality of the electrolyte. A white light interferometer (MicroXAM-100) was used to detect the surface roughness value of the sample, and the arithmetic average of the detection results was taken. As shown in Figure 2, the surface roughness value of the nitinol tube initially decreased and then increased with increasing volume ratio of perchloric acid–methanol. When the volume ratio was increased from 1:13 to 1:17, the surface roughness decreased by 56.8% from 974 nm to 421 nm. When the volume ratio was increased to 1:20, the surface roughness increased to 745 nm (an increase of 76%). The surface morphology of Nitinol tubes with different volume ratios is shown in Figure 3.

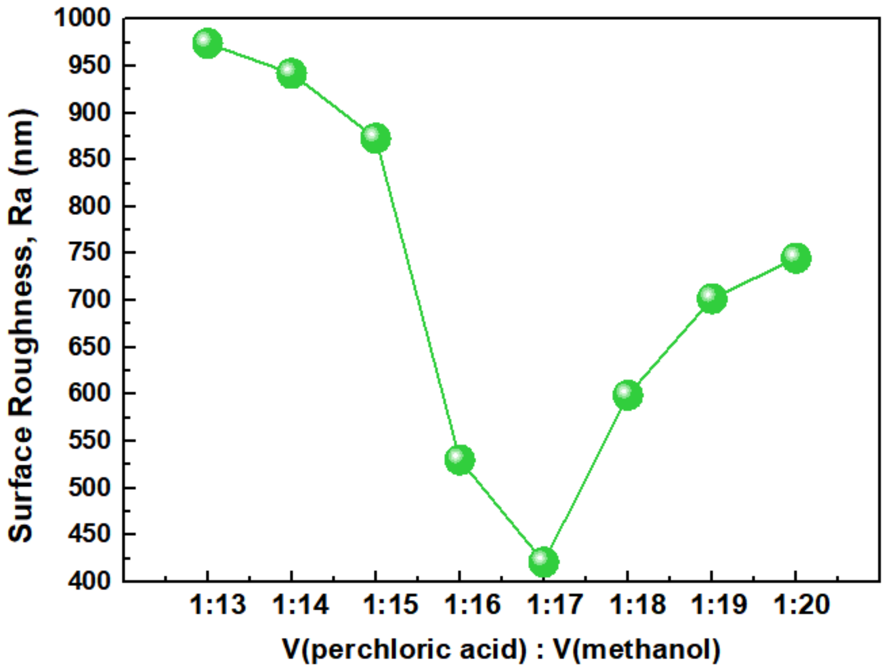

Figure 2. Perchloric acid–methanol volume ratio and surface roughness Ra

As shown in Figure 2, the volume ratio of perchloric acid–methanol significantly influenced the polishing effect. When the volume ratio of perchloric acid to methanol was 1:17, the roughness was the lowest, and the surface was relatively flat without large pits (Figure 3(c)). When the volume ratio was lower than 1:17, pitting corrosion occurred on the surface of the alloy tube, the polishing was uneven, and obvious pits or protrusions appeared. When the volume ratio was 1:13, the roughness value was not improved, and the sample surface was corroded. Although some areas were relatively flat, large bumps and obvious defects were found (Figure 3(a)). As the volume ratio of perchloric acid to methanol was increased, the streaks disappeared and became unevenly distributed pits (Figure 3(b)). When the volume ratio was greater than 1:17, more large-volume pits appeared on the surface of the alloy, the surface quality started to deteriorate, and the surface roughness increased (Figure 3(d)).

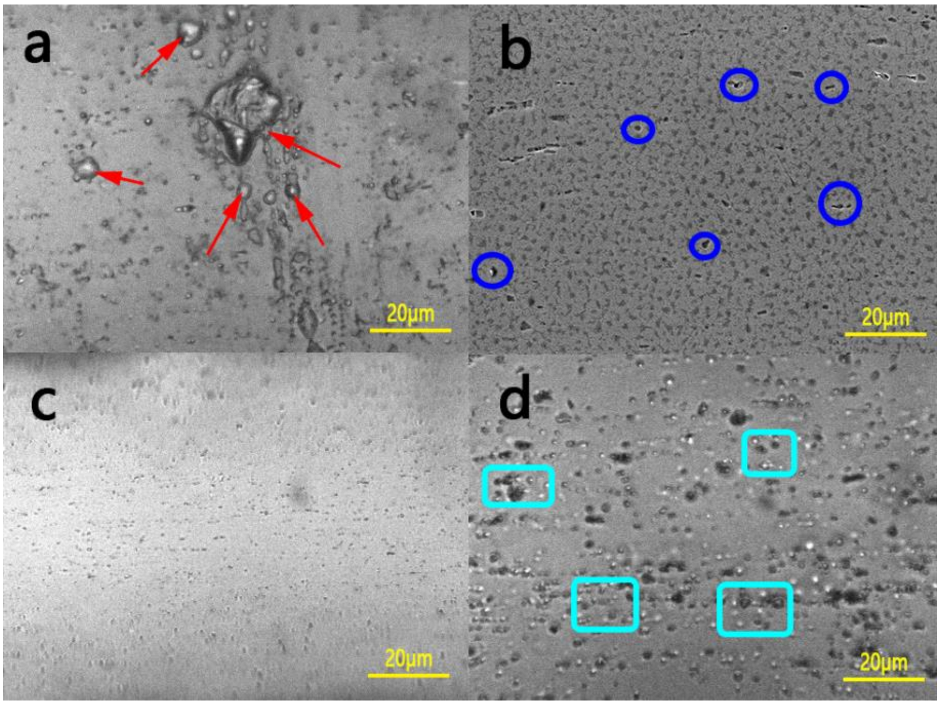

Figure 3. Surface micromorphology of Nitinol specimens under different volume ratios of perchloric acid and methanol: (a) 1:13 (b) 1:15 (c) 1:17 (d) 1:20

The volume ratio of perchloric acid–methanol reflects the strength of the electrolyte's oxidation. Perchloric acid can dissolve nitinol into soluble salts and act as an oxidant [25]. When the volume of perchloric acid–methanol was small, the concentration of perchloric acid in the electrolyte was high (strong oxidizing) and was corrosive to nitinol. Therefore, excessive corrosion appeared on the sample surface. As the volume ratio was decreased, the oxidability of the electrolyte gradually weakened, and the surface defects decreased. However, when the perchloric acid was excessively diluted, the oxidizing property of the solution became weak, which resulted in uneven material removal on the sample surface, and the improvement effect on the surface of the nitinol was minimal.

3.2 Effect of additives

Triethanolamine. In the electrolytic polishing test, incorporation of appropriate additives can effectively improve the performance and polishing effect of the electrolyte [26-28]. According to the different substances contained in additives, they can be divided into organic and inorganic substances. Among them, the use range of organic matter is broad and has good development prospects. Therefore, the influence of the concentration of triethanolamine on the surface roughness Ra value of nitinol was explored using triethanolamine as a variable in the polishing base fluid with the best ratio. The test was carried out in six groups, with each group containing three test pieces. After the test, the surface roughness Ra value was measured with a white light interferometer. The test parameters and results are shown in Table 2.

Table 2. Triethanolamine concentration and roughness value

Group	Triethanolamine content（ml/L）	Surface roughness Ra（nm）
1	1	237.6
2	3	265.5
3	5	232.8
4	7	142.6
5	9	387.5
6	11	567.34

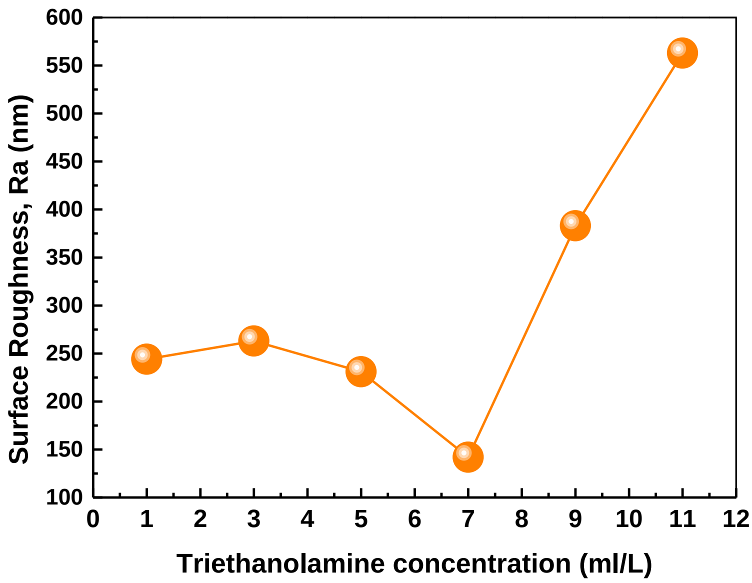

Figure 4. Influence of triethanolamine concentration on surface roughness

As shown in Figure 4, when the concentration of triethanolamine was low, the surface roughness changed more slowly, indicating that the effect of triethanolamine on the tube was not significant. However, when the concentration of triethanolamine exceeded 7 ml/L, the surface roughness of the tube greatly increased. The micro-topography map (Figure 5) shows that triethanolamine can improve the surface micro-topography of the nitinol tube to a certain extent. The low concentration of triethanolamine exerted a certain leveling effect on the nitinol tube, but some pits and pits that were not completely eroded were observed (Figure 5(a)). When the concentration of triethanolamine was 7 ml/L, the pits on the surface were small in volume, relatively smooth, and without large etching pits; the surface integrity was improved, and the polishing effect was the most ideal (Figure 5(b)). As the concentration of triethanolamine was continued to increase, pits started to appear on the surface of the nitinol, the surface unevenness increased, large and small holes emerged, and the polishing effect was very poor (Figure 5(c)). In severe cases, the surface was completely covered with pits, and the surface integrity was poor. These results indicate that the optimal concentration of triethanolamine is 7ml/L.

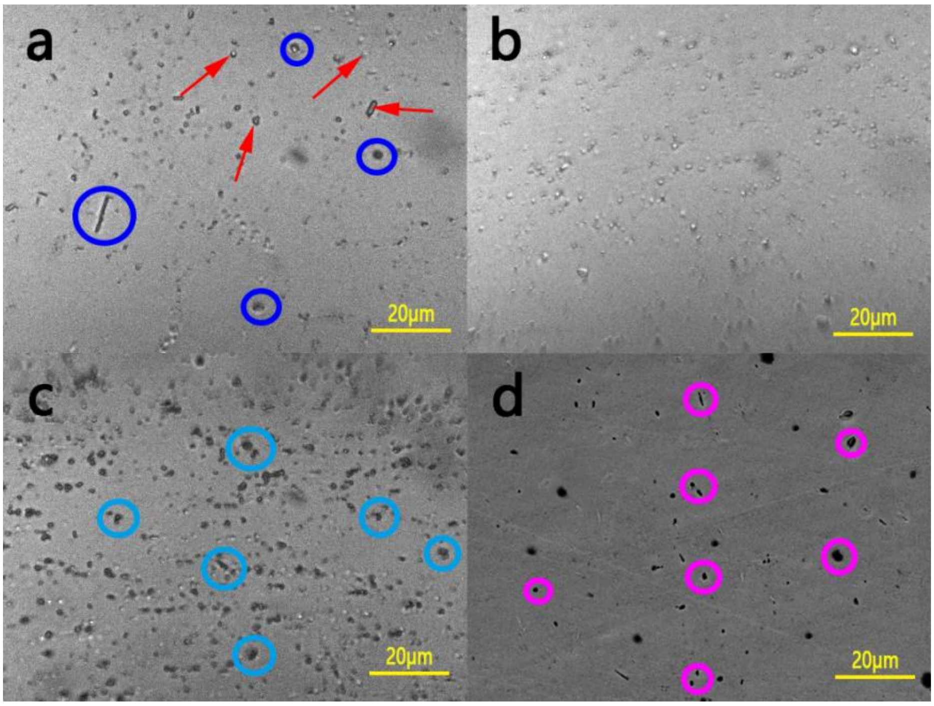

Figure 5. Surface micromorphology of specimens under different triethanolamine concentrations: (a) 5ml/L (b) 7ml/L (c) 9ml/L (d) 11ml/L

Absolute ethanol. A single-factor test was conducted with absolute ethanol as a variable to explore the effect of absolute ethanol on the surface roughness Ra value of nitinol. After the test, the surface roughness Ra value was tested with a white light interferometer. The results are shown in Table 3.

Table 3. Absolute ethanol concentration and roughness value

Group	Absolute ethanol content (ml/L)	Surface roughness Ra (nm)
1	0	498.2
2	20	579.8
3	40	487.6
4	60	502.4
5	80	408.6
6	100	564.5

As shown in Table 3, the surface roughness of the nitinol tube initially decreased and then increased with increasing concentration of absolute ethanol (Figure 6). Without adding absolute ethanol, the surface roughness was 498.2 nm. When 20 ml/L absolute ethanol was added, the surface roughness increased to 579.8 nm, which is not conducive to the reduction of surface roughness. When the absolute ethanol concentration was increased further to 80 ml/L, the surface roughness value decreased to 408.6nm. The corresponding surface morphologies of different concentrations of absolute ethanol are shown in Figure 7.

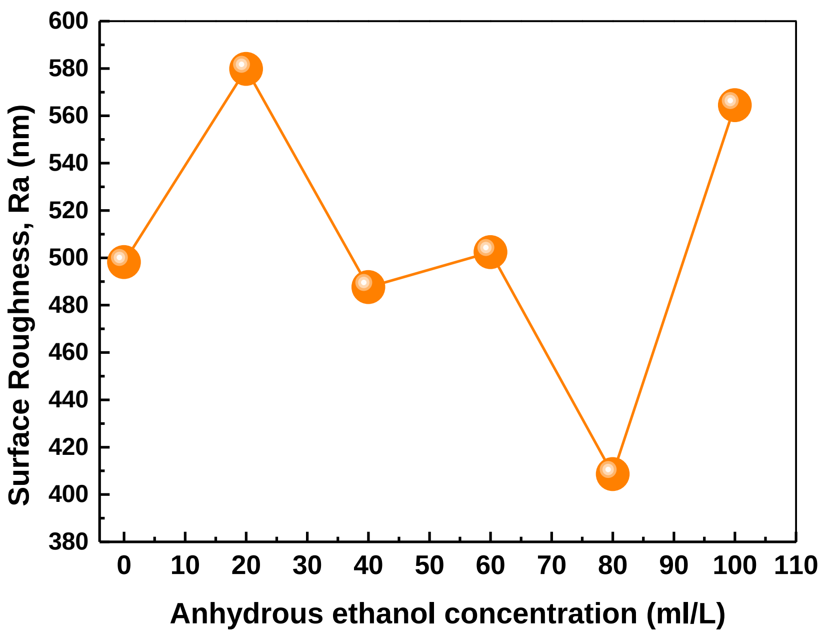

Figure 6. Effect of absolute ethanol concentration on surface roughness

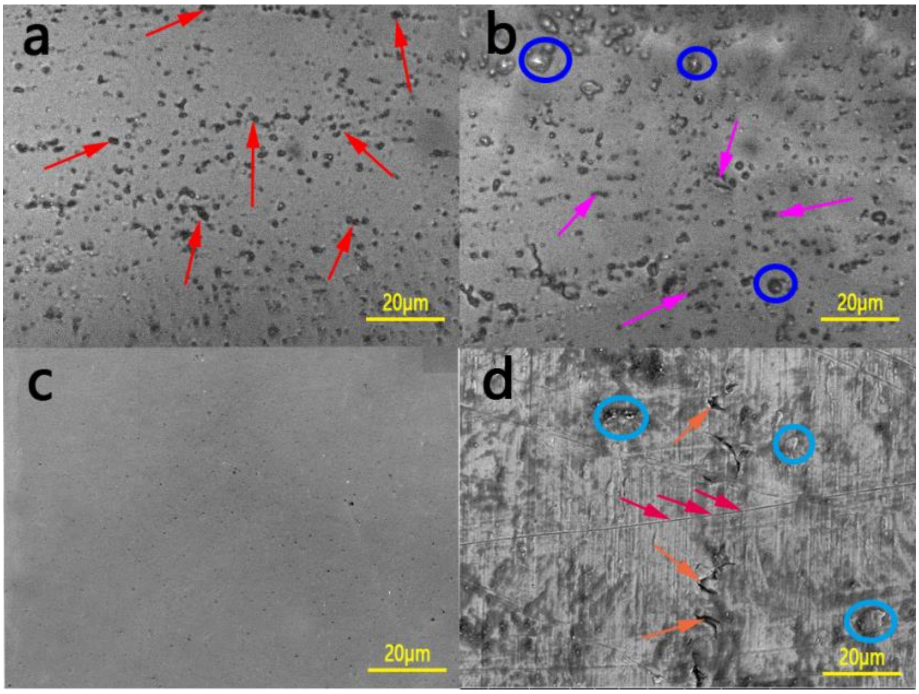

Figure 7. Surface micromorphology of the specimens under different absolute ethanol concentrations: (a) 40ml/L (b) 60ml/L (c) 80ml/L (d) 100ml /L

Figure 7 shows the surface micromorphology of the Nitinol tube under different absolute ethanol concentrations. When the concentration of absolute ethanol was small, several continuous pits appeared on the surface of the Nitinol tube, the surface integrity was low, and the polishing effect was poor (Figure 7a, 7b). When the absolute ethanol concentration was 80 ml/L, the surface became relatively smooth with high gloss and good integrity, indicating that the polishing effect was improved (Figure 7c). As the concentration of absolute ethanol was increased further, uneven pits and stripes appeared on the surface, and the polishing effect became worse (Figure 7d). When the concentration of absolute ethanol was high, the viscosity of the polishing liquid was high, the oxygen evolution reaction was strong, and a large amount of heat was not easily dissipated [29]. As a result, the temperature of the polishing liquid sharply increased, which seriously affected the polishing effect and increased the surface roughness. These results suggest that the optimal concentration of absolute ethanol is 80 ml/L.

3.3 The influence of electrolytic polishing process parameters

The composition of the electrochemical polishing solution for nitinol was determined through the above experiments: perchloric acid–methanol volume ratio of 1:17, additive triethanolamine concentration of 7 ml/L, and absolute ethanol concentration of 80 ml/L. Although the electrolyte reduced the surface roughness of the nitinol tube to a certain extent, it still cannot meet the requirements of use. Therefore, further research and determination of electrolytic polishing process parameters (current density, distance between electrodes, polishing time, and polishing temperature) are needed. A four-factor three-level orthogonal experiment was designed for exploration to find the best parameter combination accurately and efficiently. The L9 (34) orthogonal table is shown in Table 4.

Table 4. Orthogonal test factor level table

Factor	Current density（A/cm2）	Distance between electrodes（mm）	Time（s）	Temperature（℃）
Level 1	0.8	15	30	10
Level 2	1.0	20	60	20
Level 3	1.2	25	90	30

Table 5. Orthogonal test parameters and surface roughness

Test	Current density（A/cm2）	Distance between electrodes（mm）	Time（s）	Temperature（℃）	Surface roughness Ra（nm）
1	0.8	15	30	10	262.04
2	1.0	20	60	10	179.6
3	1.2	25	90	10	170.38
4	0.8	25	60	20	197.6
5	1.0	15	90	20	161.82
6	1.2	20	30	20	159.96
7	0.8	20	90	30	188.54
8	1.0	25	30	30	177.06
9	1.2	15	60	30	219.52
Range	43.233	38.427	26.107	30.88	

Table 5 shows the surface roughness values of Nitinol tube corresponding to different parameters in the orthogonal test. As shown in Table 5, the range of current density, distance between electrodes, polishing temperature, and polishing time decreased in order, indicating that their influence on the surface roughness value decreased in order. The level with the smallest average value among the factors was determined as the best process parameter. Therefore, the best combination of polishing process parameters determined by orthogonal experiment is as follows: current density of 1.0 A/cm^{2,} distance between electrodes of 20 mm, polishing time of 90 s, and polishing temperature of 20 °C.

The specific influence of various factors on electrolytic polishing was explored to improve the electrolytic polishing process. The next step was performed on the basis of the result of the orthogonal experiment, and the single-factor test was conducted according to the degree of influence to optimize further the electrolytic polishing parameters.

Current density. Orthogonal experiment showed that the current density exerted the greatest influence on the result of electrolytic polishing. Thus, the law of current density influence was first investigated. During the test, the current density was a single-factor variable ranging from 0.6–1.6 A/cm^2, the distance among the electrodes was 20 mm, the polishing time was 90 s, and the polishing temperature was 20 °C. The influence of current density on surface roughness is shown in Figure 8. When the current density was increased, the front and back changing trends of the surface roughness were opposites. When the current density was 0.6 A/cm^2, the surface roughness value Ra was 114.2 nm. When the current density was further increased to 1.0 A/cm^2, the surface roughness value Ra was 54.8 nm. This result indicates that the surface roughness significantly improves with increasing current density. However, when the current density was further increased, the surface roughness showed an upward trend. When i=1.6 A/cm^2, the surface roughness value increased to 107.5 nm, indicating that the current density was excessively large, but it caused a negative impact on the surface roughness. Therefore, when the current density was 1.0 A/cm^2, the surface roughness was the smallest, Ra=54.8 nm.

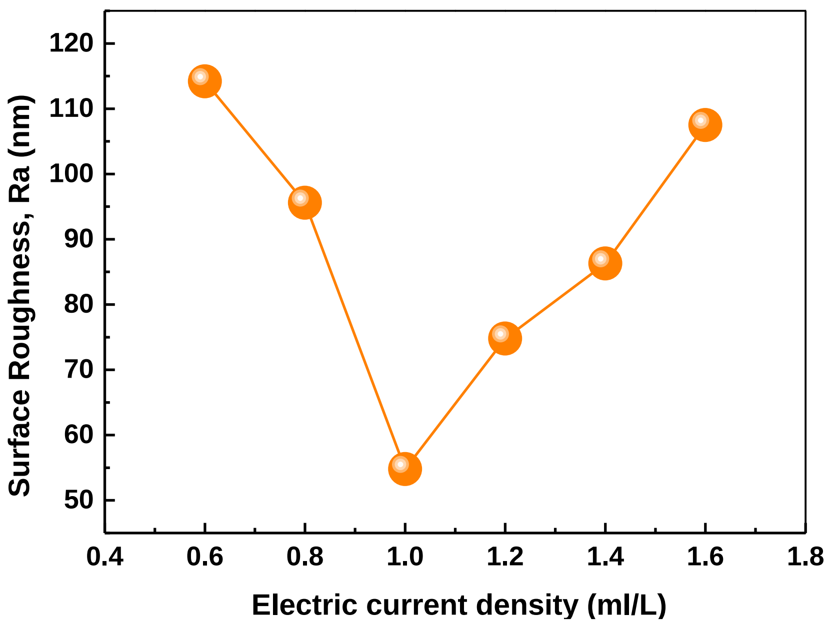

Figure 8. Influence of current density on surface roughness

The difference in surface roughness was also reflected in the surface micro-topography. The micromorphology of the nitinol tube surface obtained under different current densities is shown in Figure 9. When the current density was 0.8 A/cm^2, the surface quality of the polished sample was poor, and the original defects on the surface were not completely removed. In addition, the surface dissolved unevenly and more unevenness was observed, as shown in Figure 9(a). When the current density was increased to 1.0 A/cm^2, the surface roughness value was the smallest, and the surface topography quality improved. As shown in Figure 9(b), the surface became relatively smooth, and defects on it disappeared. As the current density was further increased, over-corrosion occurred and more pits appeared on the surface, as shown in Figures 9(c) and 9(d).

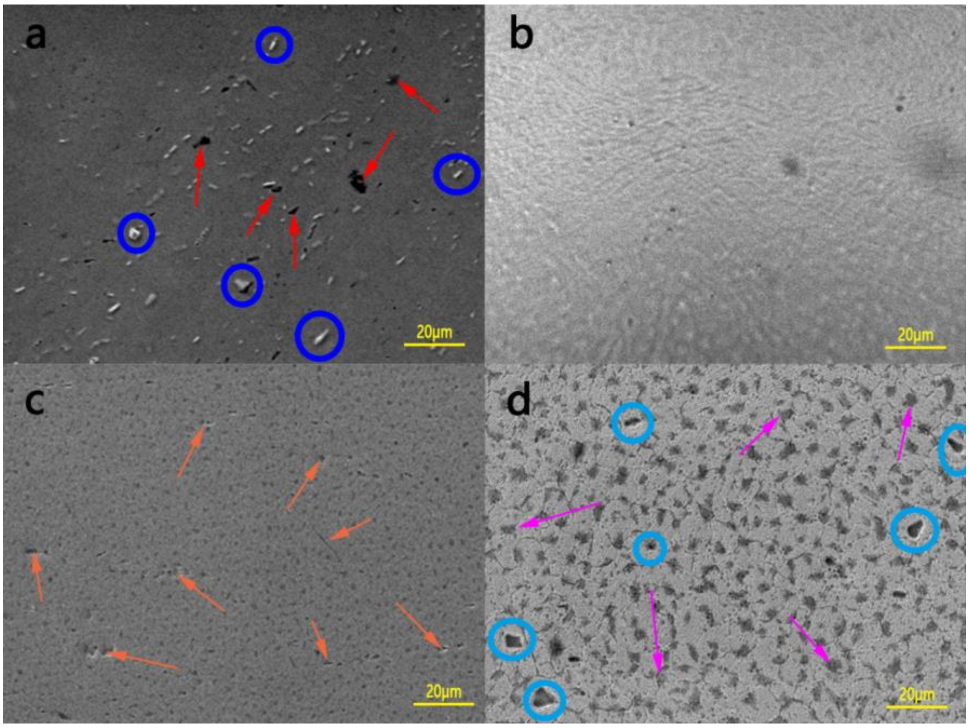

Figure 9. Surface micromorphology under different current densities (a) i=0.8 A/cm^2 (b) i= 1.0 A/cm^2 (c) i=1.2 A/cm^2 (d) i= 1.4A/cm^2

Distance between electrodes. The distance between electrodes is the second significant factor affecting the quality of electrolytic polishing. Therefore, it served as the test variable, and other parameters were current density of 1.0 A/cm^2, polishing time of 90 s, and polishing temperature of 20 °C. The relationship between surface roughness and distance between electrodes is shown in Figure 10.

As shown in Figure 10, the surface roughness initially decreased and then increased with increasing distance between the electrodes. When the distance between electrodes was increased from 10 mm to 20 mm, the corresponding surface roughness decreased from 95.1 nm to 52.6 nm. When the distance between electrodes was further increased to 25 mm, the corresponding surface roughness increased to 79.5 nm. Therefore, when the distance between the electrodes was 20 mm, the surface roughness was the minimum value of 52.6 nm.

The surface micromorphology of the Nitinol alloy obtained at different distances between electrodes is shown in Figure 11. When the distance between the electrodes was 10 mm, the surface micromorphology of the sample obtained after electrolytic polishing was poor, many black spots appeared on the surface, and many bumps were left by uneven fall off (Figure 11(a)).

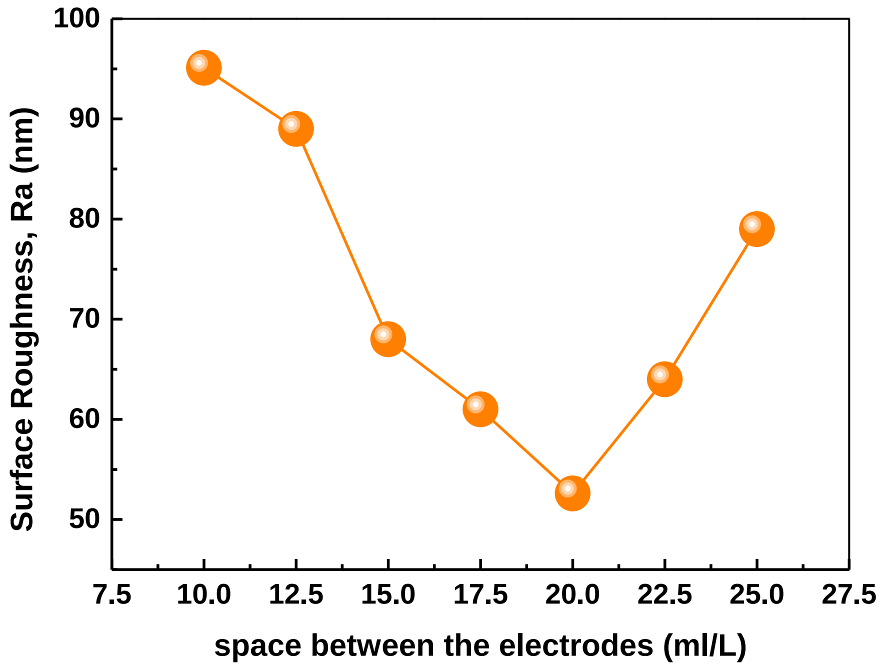

Figure 10. Influence of distance between electrodes on surface roughness

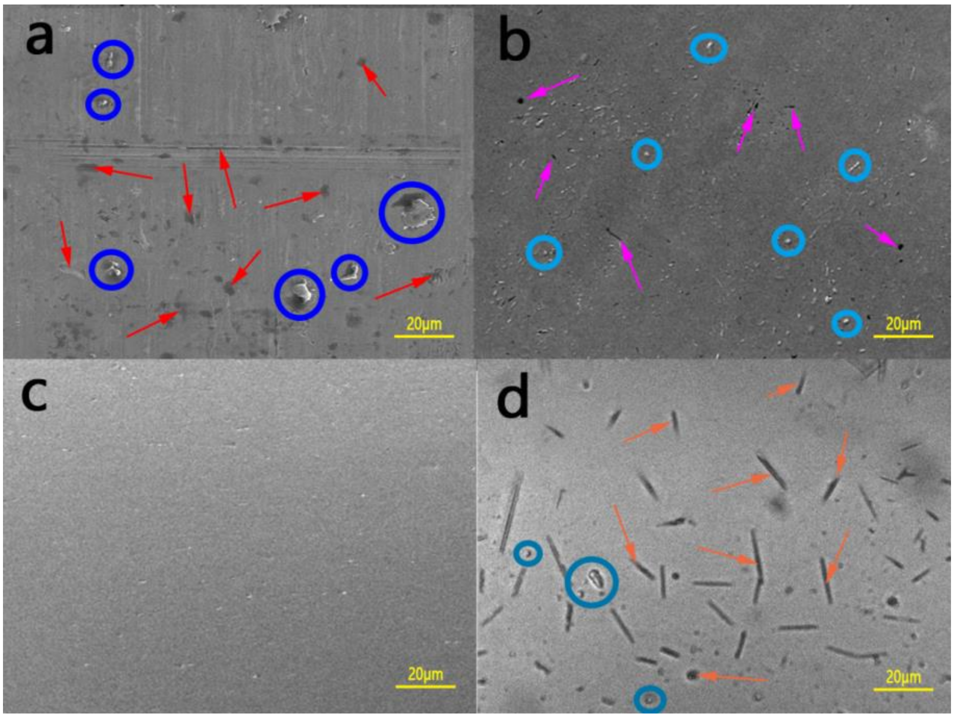

Figure 11. Surface micromorphology of different distances between electrodes: (a) d=10 mm (b) d=15 mm (c) d=20 mm (d) d=25 mm

The small distance at this time possibly hindered the circulation of the electrolyte and prevented the removal of products from the reaction, which affected the subsequent polishing [30]. When the distance between the cathode and anode was increased, the condition and surface quality improved, and the pitting pits obviously decreased in size (Figure 11(b)). When the distance between the two poles was 20 mm, the defects on the surface lessened, the surface became relatively flat, and the gloss and surface quality improved (Figure 11(c)). When the distance between the electrodes was increased to 25 mm, the surface quality of the tube deteriorated, and striped corrosion marks appeared (Figure 11(d)). This phenomenon is because the current density was reduced and the electrolysis capacity was weakened when the spacing was excessively large, which decreased the polishing effect.

Polishing temperature. A single-factor test was carried out as a single variable to explore the effect of polishing temperature on the surface roughness of Nitinol tube. When the best current density and distance between electrodes were used, the polishing time was 90 s. The effect of polishing temperature on surface roughness is shown in Figure 12. The figure shows that as the polishing temperature was increased, the surface roughness initially decreased and then increased. In the range of 10 ℃–20 ℃, the surface roughness continuously decreased from 76.8nm to 51.1nm. In the range of 20 ℃–30 ℃, the surface roughness increased sharply from 51.1nm to 94.8 nm. In the two intervals, the roughness changed drastically, and the trend of the broken line was almost straight. Therefore, the best polishing effect was obtained when the polishing temperature T was 20 ℃and the surface roughness Ra was 51.1 nm.

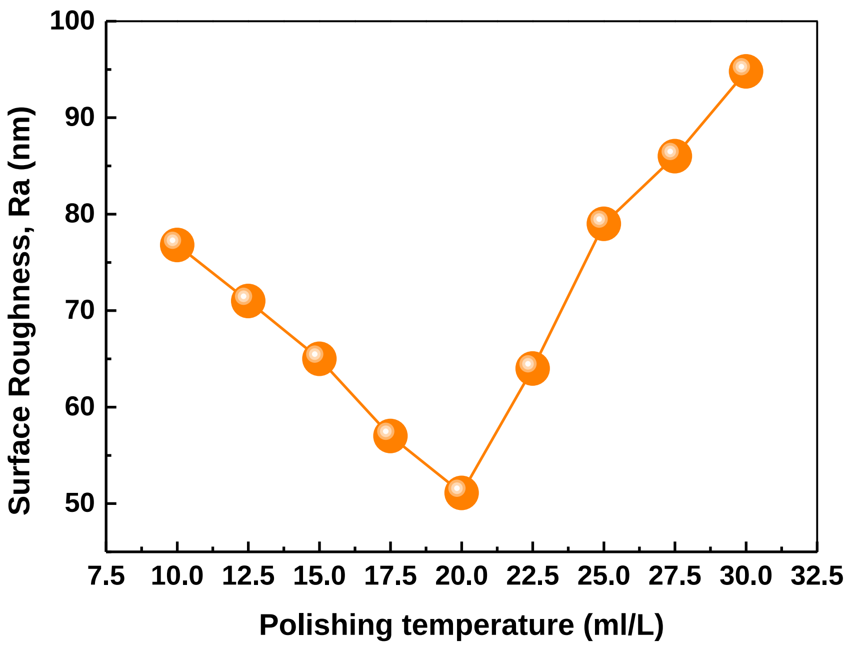

Figure 12. Effect of polishing temperature on surface roughness

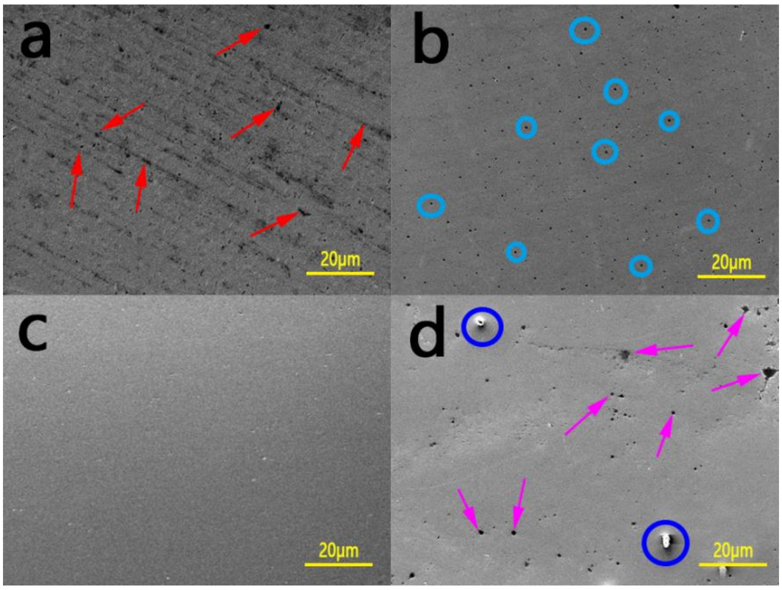

Figure 13. Surface micromorphology at different polishing temperatures: (a) T=10 ℃ (b) T=15 ℃ (c) T=20 ℃ (d) T=30 ℃

The surface morphology observed at different temperatures is shown in Figure 13. When the polishing temperature was 10 °C, black spots started to appear in some areas on the surface of the nitinol tube, and its overall smoothness was destroyed. In addition, defects such as ripples and scratches appeared on the surface, the polishing effect was uneven, and the surface quality was poor (Figure 13(a)). The surface quality improved when the polishing temperature was increased to 15 °C, but many small pits appeared on the surface, and the polishing effect was poor (Figure 13(b)). When the polishing temperature was increased to 20 °C, the surface of the nitinol was smooth, the brightness was high, and a surface with improved polishing quality can be obtained (Figure 13(c)). When the polishing temperature was further increased, the lines on the surface of the sample became more obvious and irregular, more pits appeared, and the surface quality decreased (Figure 13(d)).

Polishing time. The influence of polishing time on electrolytic polishing was explored using polishing time as a variable and optimal parameters (current density of 1.0 A/cm^2, distance between electrodes of 20 mm, and polishing temperature of 20 °C). The single-factor test results of polishing time are shown in Figure 14. The figure shows that the surface roughness initially decreased and then decreased with the extension of polishing time. When the polishing time reached 90 s, the surface roughness of the nitinol tube continued to decrease. When it exceeded 90 s, the surface roughness value of the nitinol gradually increased. When the polishing time was 30 s, the surface roughness Ra was 145.3 nm. At 90 s, the minimum surface roughness was 49.2nm. Subsequently, the surface roughness started to increase to 104.9 nm at 120 s.

The micromorphology of the nitinol tube surface corresponding to different polishing times is shown in Figure 15. When the polishing time was t=30 s, some impurities on the surface cannot be completely removed because the polishing time was too short. Thus, the surface was uneven, as shown in Figure 15(a). When the polishing time was t=60 s, although the defects were reduced, the surface was still uneven, as shown in Figure 15(b). When the polishing time was t=90 s, the surface of the nitinol tube was smooth and flat, the gloss was high, the spots disappeared, and the surface quality was the best, indicating that the best polishing effect was achieved at this time, as shown in Figure 15(c).

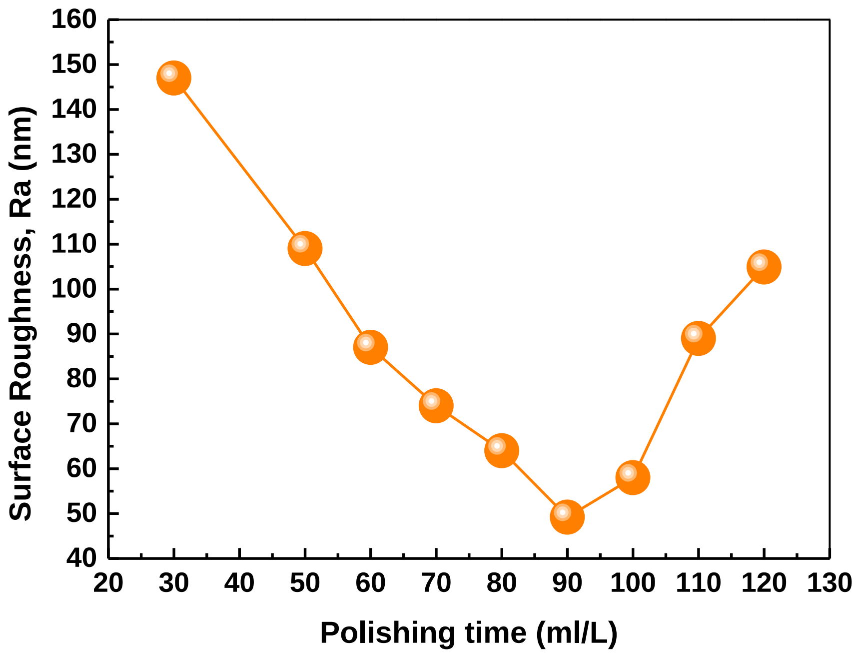

Figure 14. Effect of polishing time on surface roughness

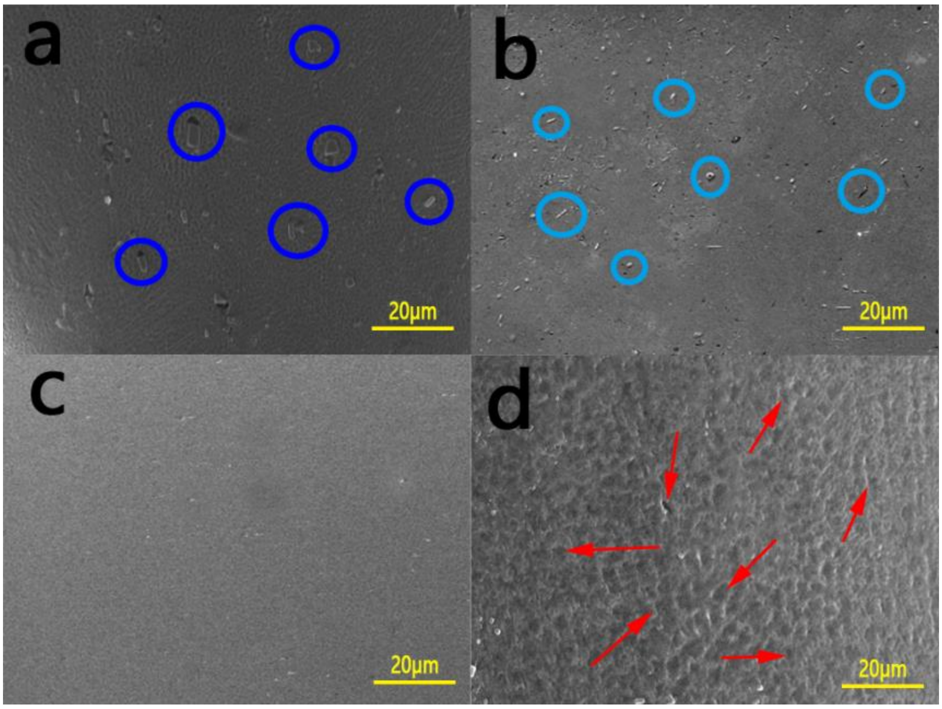

Figure 15. Surface morphology corresponding to different polishing times: (a) t=30 s (b) t=60 s (c) t=90 s (d) t=120 s

When the polishing time exceeded 90 s, the surface quality decreased, large pits appeared on the surface, and the surface became dull, as shown in Figure 15(d). This result can be ascribed to the fact that the long polishing time and excessive reaction destroyed the smooth surface and triggered excessive corrosion [31].

3.4 Surface topography

Figure 16 shows the comparison of the surface morphology of Nitinol tube before and after electrolytic polishing. Figures 16(a) and 16(b) are low and medium magnification images before polishing. Alternating vertical and horizontal scratches appeared on the tube surface, many spots of different depths were present, and the surface was rough and uneven. In the high-magnification image (16(c)), this phenomenon became clear. By contrast, the electrolytic polished image (Figures 16(b)(d)(f)) shows that the surface of the electrolytically polished nitinol was flat and smooth, with high brightness and no scratches.

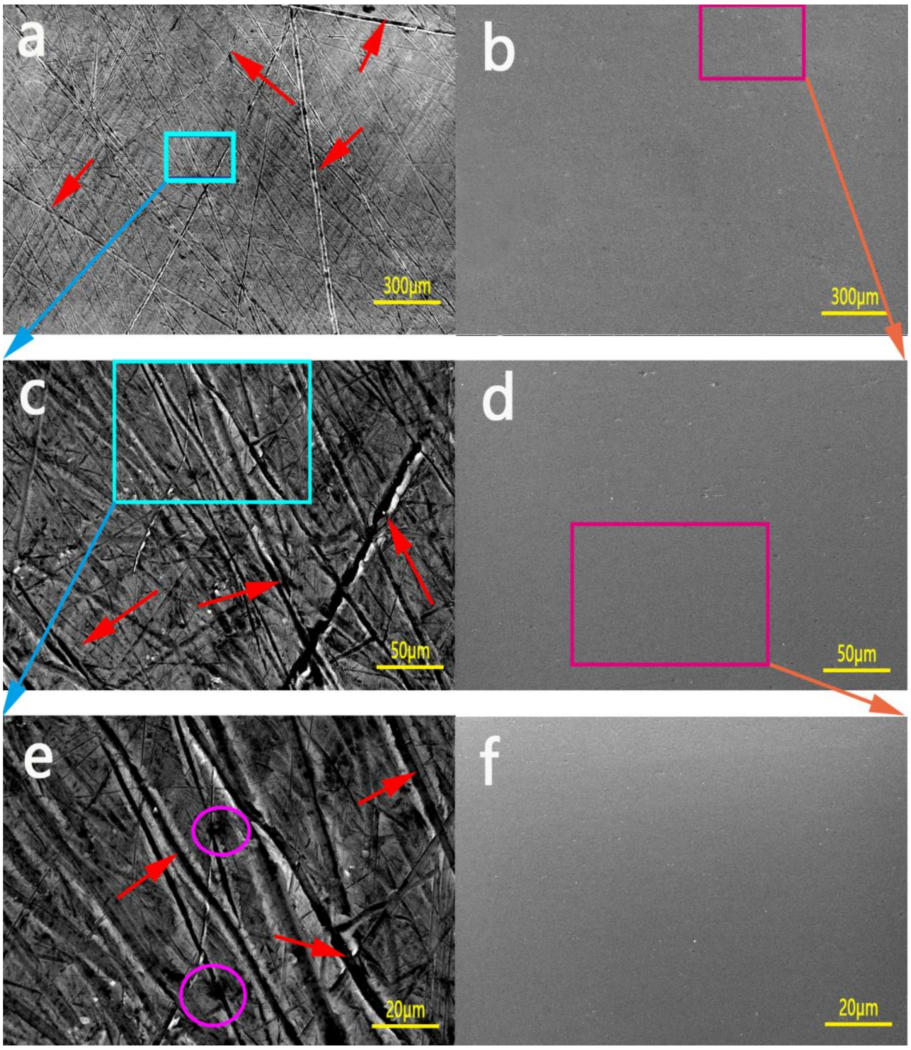

Figure 16. Comparison of surface morphology of Nitinol tube before and after polishing

As a biomedical metal material, the surface state of the material and the binding state of the human cell tissue were severely affected by the hydrophilic and hydrophobic properties of the surface of the material. Therefore, the hydrophilic and hydrophobic properties before and after electrolytic polishing must be explored.

After ultrasonic cleaning and drying, the nitinol tube was placed on the workbench of the OCA15EC contact angle measuring instrument, and 1 μl of deionized water was dropped on the surface to measure the contact angle. Three different points on the surface of each tube were tested, and the average value was taken as the test result to ensure its accuracy.

The contact angle on the surface of the nitinol tube before and after electrolytic polishing is shown in Table 6. The left and right contact angles of the tube before polishing were 47.5° and 50.2°, respectively, which belong to the hydrophilic range. The contact angles after electrolytic polishing were 83.4° and 83.9°, which are still in the hydrophilic range. The contact angle increased after polishing, indicating that the hydrophilicity was reduced and the tube surface was closer to hydrophobicity. This phenomenon may be ascribed to the fact that the surface roughness after electrolytic polishing reduced, the surface morphology improved, and the contact angle increased. The increase in contact angle and the increased hydrophobicity of the nitinol were not conducive to the adhesion of proteins in blood and tissue fluid, inflammation and re-blocking were not easy to occur, and improving blood compatibility was beneficial. Therefore, the surface biocompatibility of the nitinol after electrolytic polishing improved.

Table 6. Comparison of contact angles of nitinol tubes before and after polishing

	Left contact angle	Right contact angle	Average contact angle
Before electrolytic polishing	**47.5**	**50.2**	**48.85**
After electrolytic polishing	**83.4**	**83.9**	**83.65**

3.5 Comparison with similar results

Reports on the use of electrolytic polishing in investigating nitinol tubes and exploration of polishing factors are rare. Only one study [32] explored two electrolytic polishing factors, and it still used nitinol-braided stents as research objects. By contrast, a large amount of data on the electropolishing of nickel-titanium alloy plates have been published [32], [33], [34], [35]. Although the surface roughness of these plates is smaller than that reported in the present study, the gap is not large. The possible reason is that the research objects of the previous studies are flat plates, and the research object of the present study is a tube. The electropolished surface of a tube is curved, and thus polishing is difficult. In addition, some of these studies [32-35] did not verify the degree of influence of electrolytic polishing factors or additives and did not perform hydrophobicity experiments. See Table 7 for specific comparison.

Table 7. Compared with similar discussion and results

No.	Research object	Additive experiment	Electrolyte	Factor influence (decreasing)	Ra (nm)	Hydrophobicity optimization	Ref.
1	Nitinol-braided stents	N.A.	Acetic acid and perchloric acid	Time, temperature	N.A.	N.A.	[32]
2	Nitinol plate	N.A.	Sulfuric acid, hydrofluoric acid and ethylene glycol	N.A.	9.5	N.A.	[33]
3	Nitinol plate	N.A.	Phosphoric acid, sulfuric acid and distilled water	N.A.	41.3	N.A.	[34]
4	Nitinol plate	N.A.	Sulfuric acid and methanol	N.A.	Over 20	N.A.	[35]
5	Nitinol plate	N.A.	Sulfuric acid and methanol	N.A.	32	N.A.	[36]
6	Nitinol tube	Triethanolamine and absolute ethanol	Perchloric acid and methanol	Current density, distance between electrodes, polishing time, polishing temperature	48.6	Exist	This work

4. CONCLUSIONS

Using Nitinol tube as the research object, this study optimized the composition of the electrolytic polishing solution. The specific effects of current density, distance between electrodes, polishing temperature, and polishing time on electrolytic polishing were explored through orthogonal experiments. Then, a single-factor experiment was performed to optimize and analyze the influence of each factor on the surface roughness and surface morphology. Finally, the best combination of process parameters was determined, and a nitinol tube with better surface quality was obtained. The main conclusions are as follows:

(1) When the volume ratio of perchloric acid to methanol is 1:17, the surface roughness obtained by electrolytic polishing is the smallest and the surface morphology is improved. On this basis,

triethanolamine and absolute ethanol are selected as additives, and the optimal concentration is 7 ml/L triethanolamine and 80 ml/L absolute ethanol.

(2) The importance of current density, distance between electrodes, polishing time, and polishing temperature gradually decreases. The best combination of process parameters is as follows: current density of 1.40 A/cm^2, pole spacing of 20 mm, polishing time of 90 s, and polishing temperature of 20 ℃. The minimum surface roughness average obtained by electrolytic polishing with this parameter is 48.6 nm.

(3) After electrolytic polishing, the surface roughness value of the nitinol tube is greatly reduced, and the surface morphology becomes smooth. The surface contact angle increases by about 40°, the hydrophilicity decreases, the surface becomes difficult to adhere to other substances, and the biocompatibility improves.

ACKNOWLEDGEMENTS
This study was supported by the NSFC (Grant No.51775321) and Natural Science Foundation of Shandong Province of China (Grant No. ZR2020ME161). The authors declare that they have no conflict of interest.

References

1. T. Duerig and A. Pelton, *Mater. Sci. Eng.*, 273 (1999) 149.
2. J.A. Leopold and X. Huang, *Adv. Manuf. Technol*, 11 (2020) 1493.
3. I.Y. Millwood, R.G. Walters and X.W. Mei, *Adv. Manuf. Technol.*, 211 (2019) 14.
4. Foulquier, Sébastien, E.P. Daskalopoulos and G. Lluri, *Pharmacol. Rev*, 70 (2018) 68.
5. Y.X. Liao and Y.H. Chen, *Chinese. Med. J-Peking*, 2 (2020) 133.
6. S. Shabalovskaya, J. Anderegg and J.V. Humbeeck, *Acta Biomater.*, 4 (2008) 447.
7. A. Becker, F. Bamberg, M. Greif and F.Von Ziegler, *J. Am. Coll. Cardiol.*, 59 (2012) 1073.
8. S. Sinha, H. Begam and V. Kumar, *J. Mater. Res.*, 33 (2018) 2554.
9. S.H. Duda, M. Bosiers and J. Lammer, *J. Endovasc. Ther.*, 13 (2006) 701.
10. S. Cai, J.E. Schaffer and M.R. Daymond, *Appl. Phys. Lett.*, 105 (2014) 103.
11. T.D.B. Kannan, R. Pegada, P. Sathiya, *J. Braz. Soc. Mech. Sci. Eng.*, 40 (2018) 207.
12. S. Datta, M.S. Raza and P. Saha, *Mater. Manuf. Processes*, 21 (2019) 1.
13. M.R. Hassan, M. Mehrpouya and S. Dawood, *Appl. Mech. Rev.*, 564 (2014) 533.
14. E. Abedi, S. Daneshmand and R. Hessami, *Life Sci. J*, 10 (2013) 944.
15. J. Belohlavek, S. Belohlavkova and J. Hlubocky, *Ann. Thorac. Surg.*, 96 (2013) 57.
16. S.A. Shabalovskaya and S.Y. Ti, *Bio-Med. Mater. Eng.*, 12 (2002) 69.
17. Ákos Lengyel, Péter Nagy and Eszter Bognár, *Corros, Sci.*, 729 (2013) 436.
18. Yongqi Wang, Xiuting Wei and Zhiyong Li, *Int. J. Electrochem. Sci.*, 15 (2020) 8823.
19. L. Neelakantan, M. Valtiner and G. Eggeler, *Phys. Status. Solidi. B*, 207 (2010) 807.
20. R. Rokicki, W. Haider and T. Hryniewicz, *Appl. Surf. Sci*., 23 (2012) 2127.
21. A.W. Hassel, *Electrochim. Acta*, 53 (2008) 915.
22. K. Fushimi, L. Neelakantan and G.Eggeler, *Phys. Status Solidi A*, 215 (2018) 180.
23. L.N. Azevedo, S.L. Oliveira and S.L.D. Arruda, *Mater. Res.*, 20 (2017) 572.
24. W. Simka, M. Kaczmarek and A. Baron-Wieche, *Electrochim. Acta*, 55 (2010) 2437.
25. S.H. Chang and S.K. Wu, *J. Mater. Eng. Perform.*, 21 (2012) 2670.
26. Omid Kalantari, Jerzy and Masao, *Bun. Kaga*,. 14 (1972) 351.
27. Y.Q. Wang, X.T. Wei, Z.Y. Li and X.Y. Sun, *Int. J. Electrochem. Sci.*, 15 (2020) 8823.
28. Spivey, Meghdad Fallah and T. Shedlovsky, *J. Phys. Chem.*, 7 (1967) 71.

29. Jones and C. Harry, *Z. Phys. Chem.*, 1 (2017) 114.
30. C.C. Chen, J.H. Chen, C.G. Chao and W.C. Say, *J. Mater. Sci.*, 40 (2005) 4053.
31. A. Baron, W. Simka, G. Nawrat, D. Szewek and A. Krzyżak, *Adv. Ind. Manuf. Eng.*, 18 (2006) 1.
32. J. Kim, Jerzy, A.R. Unan and C.S. Kim, *J. Biomed. Mater. Res.*, 17 (2017) 2333.
33. A. Marquardt, M. Fronscher, E. Kasoab and T. Gries, *G, J. Ind. Eng. Chem.*, 34 (2016) 710.
34. L. Neelakantan, J. Marciniak, G. Nawrat and J. Żak, *Electrochim. Acta*, 51 (2012) 1371.
35. Y. Marquardt, W. Tsao and J.C. Pound, *J. Biomed. Mater. Res. Part B.*, 3 (2019) 216.
36. S. Virani, M. Stratmann and A.W. Hassel, *Electrochim. Acta*, 41 (2017) 33.