Electrochemical polishing of 316L stainless steel stent***★◆

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Abstract

Using direct current-electropolishing technique, the present study investigated the function of components and effects of operating conditions on polishing quality direct current-electropolishing of 316L stainless steel stent materials. Smooth surface was obtained quickly using this technique.

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INTRODUCTION

Coronary artery disease remains the major cause of illness, disability and one of the primary causes of fatality in worldwide[1]. With the development of the intervention treatment technology, the metal stent for blood vessels becomes an academic focus. As a stent material, the application of stainless steel 316L has had a long history.

Metal stent implanted in the human body can cause thrombotic disease, which is an important factor that affects the recovery of patients. Research analysis showed that a variety of factors affect compatibility of blood and stent. Surface roughness is one main factor. The more rough of the surface, the more area of stent exposed into the blood, leading to a greater probability of clotting[2]. However, because of the complex structure and the small size, after the stent is cut by laser, mechanical polishing cannot support finishing of the surface[3]. Due to its own property, electrochemical polishing has superior advantages in the finishing of the surface[4]. In this study, chemical polishing method with direct current (DC) is used for exploring the surface finishing process of 316L stainless steel stent as an implant, and investigating whether it is practical, and cost-effective.

METHODS

Experimental device (Figure 1).

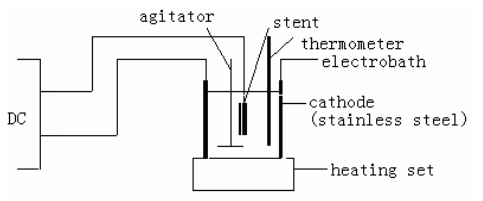

Figure 1 View of experimental equipment

As shown in Figure 1, the experimental device includes cell, heating device, thermometer, cathode material (stainless steel), blender, DC power and a number of wires. Positive electrode connects the polishing sample (anode). Stirrer is placed under the plate surface. Electrolyte solution can be only submerged samples, which contributes to the bubble escaping easily. The distance between the two poles is ranged 3 and 5 cm.

Process

At room temperature, the experiment process is as follows: oil removing by chemical method→cleaning→ removing oxides of surface→cleaning→ electrochemical polishing→cleaning →preparation of neutral solution→cleaning →passivation of the metal →cleaning→drying and then preservation.

Sample preparation

The 316 L stainless steel was cut, with a diameter of 12 mm by line of electric spark, and burnished by 100 coarse sandpaper, followed by water sandpaper of 280, 400, 600, 800 to wear it into the range of the roughness from 0.16 to 0.08 μm.

Experimental stent was obtained in the following process: First of all, 316L stainless steel pipe was etched by laser, and soaked into acid solution. It cannot been used until it was washed with ultrasound.

Oil removal from surface

In order to remove surface oil of the stent, some chemicals were used. The concentration and the conditions are shown as follows:

Chemical and condition	Concentration
$NaCO_3$	20 g/L
NaOH	15 g/L
Na_3PO_4	20 g/L
Emulsifier (OP210)	10 mL/L
Temperature	Normal temperature
Time	10 minutes

Preparation of neutral solution

Sodium bicarbonate solution (5%) was added into the test solution to obtain the neutral solution.

Preparation of passivation solution

The chemicals and conditions employed in the preparation of passivation solution were listed in the following table.

Chemical and condition	Concentration
K_2CrO_3	18 g/L
NaOH	3 g/L
pH	6.5-7
Time	10 minutes

Detection

Microscopic observation

After polishing, stent was observed under the microscope without scratches, distortion or direction.

Corrosion resistance

The experiments of corrosion resistance were performed in Germany Zahner Company with IM6 electrochemical station. After electrochemical polishing, polarization curve of the stent surface (E) in Hanks solution was determined by potentiodynamic method. In addition, the polarization curve determined with mechanical polishing of stainless steel (M) was compared with the polarization curve of the stent surface (E).

Composition of the solution used for polishing and operating conditions

Chemical and condition	Concentration
H_3PO_4（85%）	650 mL/L
H_2SO_4（98%）	250 mL/L
CrO_3	80 g/L
Additive	10 g/L
Temperature	70-80 ℃
Voltage	18 V
Time	2 minutes
Area of cathode and anode	4: 1
Cathode material	Stainless steel

First, chromium oxide solution was added into phosphoric acid. Sulfuric acid was injected until the compound was well mixed and the mixture was cooled to the room temperature. Solution used for polishing was prepared freshly before the experiments.

RESULTS AN DISCUSSION

Effect of the solution on electrochemical polishing

H_3PO_4

Phosphoric acid is the main ingredient in the solution for polishing. During polishing, phosphoric acid plays a role of dissolution. Moreover, it formed a protective layer with phosphate in the stainless steel surface to protect the stainless steel surface from erosion[5]. If the concentration of phosphoric acid was too low, the proportion of polishing solution would be small, and the viscosity was also low. So the diffluence of the metal was speed up, which would reduce the degree of polishing. However, if the concentration of phosphoric acid was too high, the speed of polishing was slow. As shown in Table 1, when the concentration of phosphoric acid was 650 mL/L, polishing achieved the best results.

Table 1 Effect of phosphoric acid concentration on the quality of polishing

Concentration of H_3PO_4 (mL/L)	Situation of polished surface
560	Poor surface preparation, poor brightness
590	General Surface formation, poor brightness
620	Smooth surface, the general brightness
650	Smooth and bright surface
680	Smooth and bright surface

H_2SO_4

Sulfuric acid is a component in the polishing solution. In the polishing process, sulfuric acid was not used alone, which avoided precipitation of sulfate crystals hindering experiment polishing. Sulfuric acid can improve the electrical conductivity of the polishing solution, decentralization and efficiency of current in anode. Appropriate amount of sulfuric acid added contributes to leveling the surface of stent and improving surface brightness. When concentration of sulfuric acid was too low, it was difficult to level; whereas when concentration of sulfuric acid was too high, it would reduce surface finish of the stent, thus decreasing the service life of the electric polishing solution. Therefore, the sulfuric acid at 250 mL/L was identified as the appropriate concentration. The results are shown in Table 2.

Table 2 Effect of sulfuric acid concentration on the quality of polishing

Concentration of H_2SO_4 (mL/L)	Situation of polished surface
190	Poor surface preparation, poor brightness
210	General Surface formation, poor brightness
230	Smooth surface, the general brightness
250	Smooth and bright surface
270	Smooth and bright surface

CrO_3

Chromium trioxide is often used in combination with other ingredients such as sulfuric acid and phosphoric acid as the electrolytic polishing agents. Electrolyte solution with the addition of chromium trioxide can improve polishing efficiency. For each electrolyte containing chromium trioxide, it is necessary to maintain a certain form of $Cr_2O_7^{2+}$ for a good polishing result, owning to that the passivation membrane of the surface is produced by strong oxidizing material, *i.e.* $Cr_2O_7^{2+}$. Experimental results showed that when the concentration of chromium oxide was greater than 80 g/L, the quality of polished surface was not improved, but when the concentration of chromium oxide was too low, the quality was declined obviously. Therefore, the proper concentration of chromium trioxide was 80 g/L.

Additives

Adding to the solution of additives, such as ethylene glycol, can help increase the viscosity of the solution polishing, and reduce the sensitivity of impurities of the solution polishing. In this experiment, the appropriate concentration of additives was 10 g/L.

Effect of operating conditions

Pressure

When electrolytic polishing was conducting, only to a certain current density, the effect of polishing can be favorably achieved. This experiment used the same sample size and constant distance between the two poles, and satisfying results were only obtained in a certain range of voltage. Experimental results showed that when the voltage was lower than 15 V, the sample surface was not leveling, and the gloss was also very poor. When the voltage was greater than 21 V, the surface of

samples were uneven and the corrosion pits were visible, in addition to some deep pit. However, under a pressure in the range of 18–21 V, the best flatness was obtained.

Temperature of polishing solution

As well as voltage, the temperature of the experiment is also very important. If electrolyte temperature was too low, it would slow down the speed of dissolution of the anode, or completely contain the electrolyte polishing. And electrolyte plays a role of corrosion, which raises the viscosity of the electrolyte and the anode membrane, and prevents the pervasion of the dissolution product in anode.

When the temperature was too high, the speed of dissolution of the metal increased and viscosity of the electrolyte solution and the product in anode were reduced, so diffusion became easy and the resistance of the electrolyte reduced; on the other hand, with increasing temperature, the adjacent anode layer would assemble quantity of heat, which aggravated to generate the gas in the vicinity of the anode and steam, and caused corrosion on the surface. Moreover, the effect of polishing was delayed. In the experiment, when the temperature was less than 50 ℃, the surface was not smooth, and with increasing temperature gradually, the quality of the surface was improved. However, when the temperature was greater than 80 ℃, the results were not satisfied. Thus, the temperature was identified as 80 ℃.

Polishing time

It is a necessary condition to precisely adjust the time of electrolytic polishing for good results. Experiments showed that the rate of polishing in the first several minutes was rapid, and gradually slowed down even stopped. The original material on the surface smoothness was poor, and the effect was more obvious. Similarly, changes of the capacitance of the interface between metal and solution, resistance and reflectivity of the samples also completed in the first few minutes, and then stabilized. In the experiment, when the sample was polished for one minute, its surface was smooth, but its metallic luster of surface was poor; when it was polished for two minutes, the ideal results were obtained. However, when the time increased to 4 minutes, the flatness did not decline fast, and yet the gloss of the sample surface became bad, even to be erosive. Therefore, two minutes is sufficient for polishing.

Corrosion resistance

As shown in Figure 2, for the stainless steel, corrosion potential of electrochemical polishing was higher than that of mechanical polishing, and electrochemical polishing from the thermodynamics maintained a more stable state. It is mainly attributed to the protection layer on the surface of stainless steel with the thick and dense oxide membrane which was formed during the polishing and post-processing. Thus, the state energy of the metal with electrochemical polishing was obviously much lower than the metal directly exposed to or polished mechanically. Thus there is a natural high corrosion potential. Corrosion current density of electrochemical polishing stainless steel, *i.e*. natural corrosion rate, was slightly smaller than that of the mechanical polishing. That is, corrosion resistance of the electrochemical polishing stainless steel was better than the mechanical polishing.

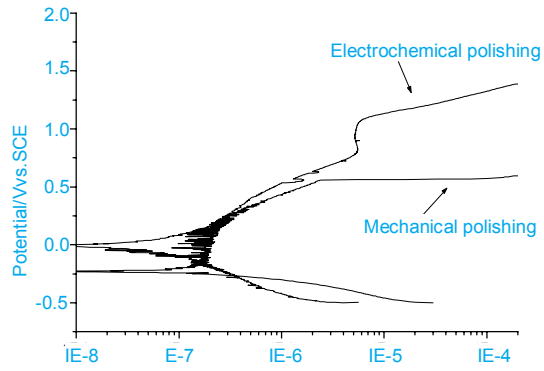

Figure 2 Anode polarization of electrochemical polishing and mechanical polishing

In addition, the surface pitting potential following electrochemical polishing was higher than that following mechanical polishing. That is, the stability of the passivation membrane in the corrosion solution was enhanced. It is of great significance for the scaffold.

There was a hardening deformation layer on the surface of mechanical polishing, so in the mechanical grinding process, abrasive inevitably was embedded into the layer, which accelerated the corrosion rate of deformation layer.

After electrochemical polishing, the deformation layer of the metal was dissolved, and the activity of its surface reduced. Moreover, the surface formed a continuous passivation membrane, which effectively prevented solution, so as to enhance the corrosion resistance.

In this study, the optimal conditions of the 316L polished stent were studied. At the same time, a qualified and well-proportioned vascular stent was obtained, with bright and smooth surface (Figures 3 and 4).

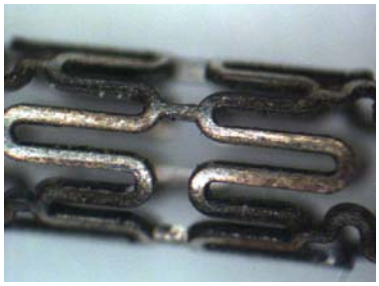

Figure 3 Unpolished stent (× 40)

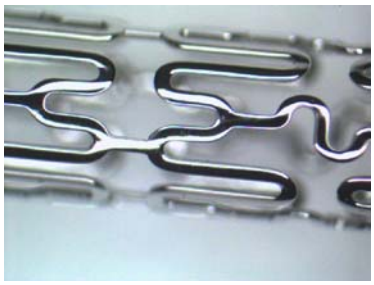

Figure 4 Polished stent (× 40)

Conclusion

The polishing solution in the experiment is effective and cost-effective. After 316L stainless steel samples were polished, its surface was smooth and bright, with increased corrosion resistance. After polishing the stent, a bright stent with uniform size and smooth surface was obtained.

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316L 不锈钢血管支架材料的电化学抛光工艺***♦

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摘要

用直流电化学抛光技术，研究了 316L 不锈钢血管支架材料电化学抛光液中各成分的作用及操作条件对抛光质量的影响。通过优化，用实验得到的工艺能很快获得光亮平整的抛光表面。

关键词：血管支架材料；316L 不锈钢；抛光工艺；电化学；生物材料
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