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Surface Processing Technology for 316LVM Stainless Steel Stents

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Abstract

The process of surface finishing is crucial to the performance of stents. This study explored the surface finishing of 316LVM stainless steel stents produced by laser cutting. Our results from measuring the quantity of material removed through these cleaning processes demonstrate that the slag formed on the surface of stents can be removed by means of acid pickling and electrolytic polishing. The stent surface process of stent after achieved a 78% improvement in surface roughness with an acceptable weight loss of 16.7% and a width reduction of 5.95%. In addition, the cleaning processes, as applied in the present study, resulted in the removal of appropriate quantities of stent material, resulting in devices with a superior finish as well as mechanical integrity. It is hoped that these results can contribute to the integrity and accuracy of associated studies in the future, including research preceding clinical animal testing and human trials and protection of patients during implantation procedures.

Key Words: Stent, Surface Finishing, Acid Pickling, Electrolytic Polishing

1. Introduction

Metallic coronary stents provide endovascular scaffolding to relieve vascular obstructions. These devices exert continuous radial pressure on blocked coronary arteries, resulting in the compression of atherosclerotic plaques, the sealing of dissections, and the expansion of the coronary vessel. When used as an adjunct to conventional balloon angioplasty, they can improve vessel patency.

Surface roughness is an important determinant of thrombogenicity and tissue reaction [1], i.e., the nature of the metal surface is crucial to blood compatibility [2]. A smooth surface can help to prevent the activation and aggregation of platelets, which are major components associated with the process of thrombosis. One previous animal experiment [3] compared the results of implanting polished stainless steel and nitinol stents with those of unpolished stents. The results demonstrated that surface treatment can improve the performance of stents by reducing the effects of thrombogenicity [1,3].

The most important clinical problem with stents (after the difficulties associated with implantation), is neointimal hyperplasia within the stent, resulting in a significant narrowing of the stent channel in 16–30% of cases [4–6]. Efforts to improve the clinical results of implanting coronary stents should focus on decreasing neointimal hyperplasia. One previous study tested the effects of 16-mm balloon expandable stainless steel stents produced with 0.18-mm 316L stainless steel wire in an animal model. The results demonstrated that, in addition to reducing thrombogenicity, electrolytic polishing can also reduce neointimal hyperplasia within the coronary stents. [7,8]. Clearly, surface treatment is a crucial step in the

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fabrication of effective coronary stents.

In this study, electrolytic polishing involved the smoothing of metallic surfaces through anodic polarization in an electrolyte [9]. Electrolytic polishing is classified into two processes: anodic leveling and anodic brightening [10]. Anodic leveling is the result of a difference in dissolution rates between the peaks and valleys of a rough metal surface caused by current distribution conditions. In contrast, anodic brightening involves suppressing the influence of metallic microstructure on the dissolution rate. A smooth electrolytic-polished surface, which appears bright to the naked eye is the result of combining these two factors [10]. This study provides a comprehensive investigation of the processes involved in electrolytic polishing 316LVM stainless steel tube stents produced by laser cutting.

2. Materials and Methods

2.1 Materials

The properties of the stent material, including biocompatibility, X-ray and MRI visibility, radial strength, flexibility, transmissibility, formability, and durability combine to determine the performance of device. The materials used in balloon-expandable stents require a high elastic modulus to avoid recoil. They also require low yield strength to enable the shrinkage and expansion of the stent under the relatively low pressure provided by the balloon. This study selected 316LVM stainless steel tubing, due to its wide applicability in surface processing of this nature. The composition is consistent with ASTM F138 [11].

This study employed 316LVM stainless steel, tubular coronary stents in a slotted configuration, produced by laser cutting (Star Cut Tube 18, Rofin Laser Co., Germany). The stents were approximately 25 mm long with a diameter of approximately 6.0 mm. The wall thickness of the stents was 0.150 mm, as shown in Figure 1.

2.2 Vacuum Annealing

Vacuum annealing is a key technology used to manipulate the final size of crystalline grains within a material. This process is directly related to its ultimate tensile strength, elongation rate, corrosion and fatigue resistance, machining stress, and surface quality. Current methods for the non-destructive testing of material properties include scanning electron microscopy (SEM) and surface hardness measurement. 316LVM is an austenitic stainless steel; however, the solubility of carbon within austenite is limited. When laser cutting produces a large heat-affected zone close to the incision, the super-saturated γ solid solution is re-heated above the $\gamma+M_{23}C_6$ temperature range and water cooling is used to quick-cool it to room temperature. Under such conditions, chromium within the material is unable to proliferate back to the carbide within the austenite; this phenomenon is called "sensitization". As a result, austenite forms a layer containing the chromium element of carbide, referred to as a "bright layer."

The separation of carbides reduces resistance to grain boundary corrosion and point corrosion along the crystal boundaries and on the surface, thereby leading to corrosion and dehiscence. This separation detracts from the mechanical properties of the material as well as the machinability and service life of the stent. Vacuum annealing is an effective means to resolve the material weaknesses caused by laser cutting, and results in ductility sufficient to facilitate implantation.

This study employed a vacuum furnace (Leybold Heraeus PD 400, Germany) for the annealing of stents. The annealing temperature and vacuum status of relations curve of stents, as shown in Figure 2. Following annealing, the stents were cleaned using distilled water in an ultrasonic agitation bath for 15 min and then air-dried.

2.3 Acid Pickling

Acid pickling involves the immersion of metallic materials in an aqueous acid solution to chemically remove surface oxides and other contaminants, as shown

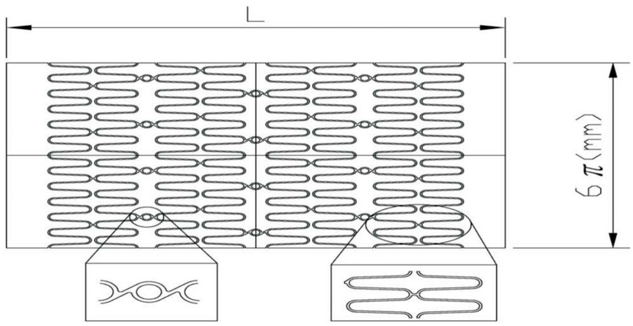

Figure 1. Plane developed view of designed stent.

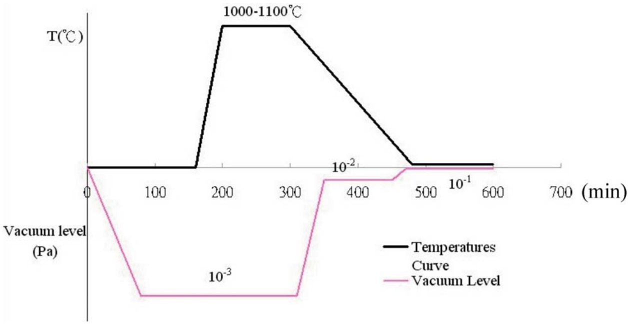

Figure 2. Annealing temperature and vacuum status of relations curve.

in Table 1 is composition of acid solution.

The acid pickling process was divided into two steps. Step 1: The samples were cleaned using distilled water in an ultrasonic bath for 60 min at room temperature and then dried in air. Step 2: After cutting, the stents were pickled for 40 min at a temperature of 40 °C. The temperature was controlled using a thermostat. The samples were then cleaned in an ultrasonic bath of distilled water for 15 min and then dried in air. The pickling process was used to remove slag and burrs from the surface of the laser-cut zone.

2.4 Electrolytic Polishing and Passivation

Removing irregularities through surface treatment is required to produce a defect free surface with consistent leveling, improved fatigue resistance, and low friction coefficient.

Electrolytic polishing involves let the rich chromium on the surface and improve surface smoothness of stents. This process can be divided into two steps: increased flatting of stent surface and brightening. In this process, chromic ions are concentrated in a negatively charged ionic layer, which forms on the surface of the work piece mounted on the surface. The important parameters influencing the process of electrolytic polishing include current density, electrolyte composition, temperature, processing time, the hydrodynamics of the electrolyte, and the area of the substrate undergoing electrolytic polishing.

Table 1. Composition of pickling solution

Component	Amount (ml)
HF (48%)	3
HNO_3 (65%)	20–25
H_2O	to 100

A schematic diagram of the electrolytic polishing setup and arrangement of the stent is shown in Figure 3. The experiment is used be about 100-ml plating tank of "Hell cell". A DC rectifier (Gwinstek Co., Taiwan) was employed as the power supply. The stent formed the anode, while the cathode was a 316L stainless steel sheet (10 cm long, 5 cm wide, and 2 cm thick). The temperature of the electrolyte was maintained using a heating coil connected to a thermostat. Following electrolytic polishing, the stent was removed from the bath, repeatedly rinsed with a deionizer water spray, and dried with a hot air drier. This study investigated the electrochemical process involved in electrolytic polishing, as shown in Table 2 is composition of electrolytic polishing solution.

The conditions under which the electrolytic polishing of stents was performed were determined experimentally (Table 3). Following electrolytic polishing, the stents were cleaned using distilled water in an ultrasonic agitation bath for 15 min and then dried in air.

Following electro-polishing, we employed a passivation process to enhance the corrosion resistance of the

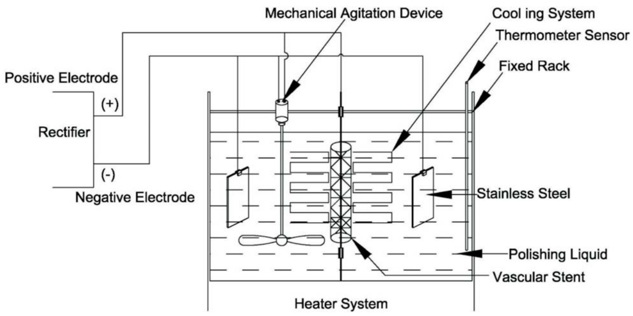

Figure 3. Schematic diagram of electrolytic polishing.

Table 2. Chemical composition of electrolytic polishing solution

Component	Amount
H_2SO_4 (95–97%)	35–40 ml
H_3PO_4 (85%)	45–50 ml
Organic agent	5 ml
H_2O	10 ml

Table 3. Conditions for electrolytic polishing

Power (W)	Applied voltage (V)	Current density (A/dm^2)	Time (sec)	Temperature (°C)
150–200	10–20	1.2	35–55	40–60

stent within a biological environment. This involved promoting the spontaneous formation of a protective Cr_2O_3-enriched passive film on the surface of the stent. Passivation was performed for 25~40 min in an aqueous solution of 20%~30% (v/v) nitric acid in deionized water. The stents were immersed in a beaker containing the passivation solution, maintained at a constant temperature of 75 °C using a water bath. After 25~40 min, the stents were removed and repeatedly washed using deionized water and then a solution of 20%~30% sodium carbonate to neutralize all traces of acid. The stents were then rinsed again with deionized water to completely remove the sodium carbonate. Finally, the stents were stored separately in a closed glass container filled with isopropylalcohol to prevent microbial contamination.

2.5 Surface Roughness

Throughout the experiments, the surface roughness of each sample, was visually checked using a stereomicroscope. A scanning electron microscope (SEM) (LEO 1530 SEM, Germany) was also employed to evaluate the effects electrolytic polishing and passivation of before and after of stent state.

Surface topology was characterized and quantitative roughness measurements were performed using an atomic force microscope (AFM) (SEIKO SPA-300HV AFM, Japan) following the processes of before and after of surface process. The evaluation area for the AFM analysis was 150 × 150 microns. After placing the samples on the platform of the evaluation device, the entire analysis setup was held on an anti-vibration device to ensure accuracy in the measurement of surface roughness.

2.6 Expandability of Stents Using Balloons

A commercial PTCA balloon catheter was used to evaluate the expandability of the stents following surface treatment. The stents (25 mm long) were crimped on the 3.0 × 40 mm balloon using a crimping hand tool (Hellermarnn Tyton, YAC9). The crimped stents were expanded using an inflation device (Boston Scientific, Wanda Standard-5F). Sterile water was used to inflate the balloons for the expansion of stents at a nominal pressure of 1600 kPa as prescribed in the compliance chart provided by the balloon manufacturer. A pressure gauge was attached to the expansion device to record the applied pressure. The balloon was dilated for approximately 60–90 sec before being deflated. The symmetry and fractures of crimped and dilated stents were inspected by SEM.

3. Results and Discussion

The stent side surface (the surface after fiber laser cutting) showed no visible signs of corrugation and no surface residue was observed by SEM. Figure 4 shows the morphologies of as-cut stents and the laser-cut zone of processed stents. Considerable roughness was observed in the laser-cut zone.

Figure 5 shows the sample used as a research standard for electrolytic pickling (STI Laser Industries Ltd.) [12]. We compared Figures 5 and 6(a) after pickling the stent; the clean surface satisfied the study requirements for electrolytic polishing, in which each section of the stent ribs and connecting rings showed a high degree of uniformity. The size of rib cross sections were the same,

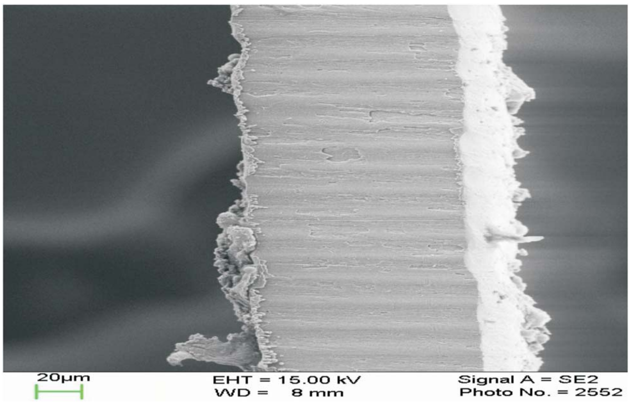

Figure 4. Morphology of laser-cut zone.

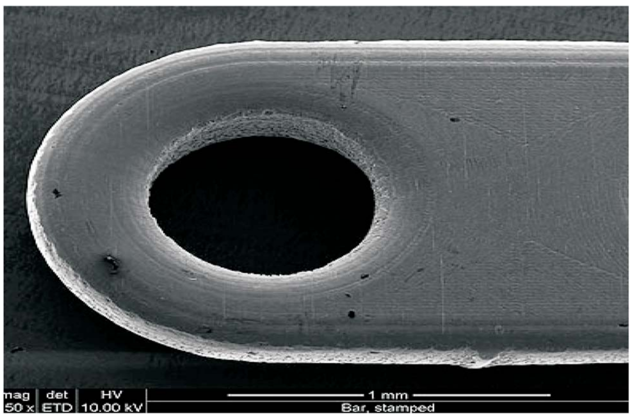

Figure 5. SEM image of stent (STI Co.) after acid pickling [12].

and the incision shape satisfied the basic requirements for stents.

3.1 Acid Pickling of Stent

Figure 6(a) shows an SEM image of a stent after being pickled for 40 min at 40 °C to remove the slag and burrs in the laser-cut zone and on the surface. Clearly, the slag was not completely removed by this process, as Figure 6(b) shows. It can be deduced from this that an increase in temperature is required for the pickling of 316 LVM stainless steel tube stents. Figure 6(b) presents an SEM image of a stent without pickling, in which the stent was held in an ultrasonic agitation bath of distilled water at room temperature for 60 min and then dried in air.

Laser cutting can produce slag (burrs and depositions) on the surface of stents, resulting in a rough surface. The surface quality of stents that undergo electrolytic polishing without acid pickling pretreatment is even worse than that of non-polished stents. The oxides produced by laser cutting process adhere to the surface of the stents after polishing. This study employed acid pickling as a pretreatment to electrolytic polishing of 316LVM stainless steel tube stents. Pickling time and the selection of a suitable acid solution are critical parameters in this process and must be strictly controlled. Oxides cannot be entirely removed without sufficient pickling time; however, the recommended immersion times should not be exceeded 45 min to avoid the excessive removal of stock. The influence of temperature on pickling time is pronounced; an increase in temperature increases the pickling rate. In this study, immersion in distilled water at room temperature for 60 min was less effective than pickling at 40 °C for 40 min (Figure 6). Either weight loss or a change in dimension could be used as a control parameter for the removal of stent material during the pickling process. In the removal of oxides, weight loss and dimension reduction should both be minimized.

3.2 Vacuum Annealing of Stents

Figure 7 presents SEM images of vacuum annealed stents. Samples without annealing (Figure 7(a)) and those annealed at 1030 °C (Figure 7(b)) for 1 h clearly exhibit grain boundary grooves on the surface. The material recrystallized at that temperature. Regardless, these vacuum annealed stents were readily expanded using a balloon. These results demonstrate that the heat treatment applied in this study was adequate to soften the 316LVM stainless steel tube stents for the purpose of implantation.

The hardness data were measured at five different positions on the stent surface before and after heat treatment. Table 4 shows the hardness data before and after vacuum annealing at a temperature of 1030 °C, obtained from four positions on the surface of the stent. Following annealing, the average hardness value (HV) was reduced from HV 218 to HV 173.

Vacuum annealing was then used to soften the material, remove internal stress, and adjust the mechanical properties of the material to facilitate implantation. In this study, the stents were annealed and softened through slow cooling. To minimize the possibility of scaling deformation during the heat treatment process, we employed vacuum annealing at an optimum temperature of 1030 °C. Temperatures exceeding 1030 °C resulted in deformation and dissolution along the edge of the stent; temperatures below 1030 °C were insufficient to eliminate internal stress, such that crimping the stent resulted in rebound.

After annealing, the surface of the stents presented superior smoothness and uniformity than that of the non-annealed (acid pickled) samples (Figure 7(a)). After an-

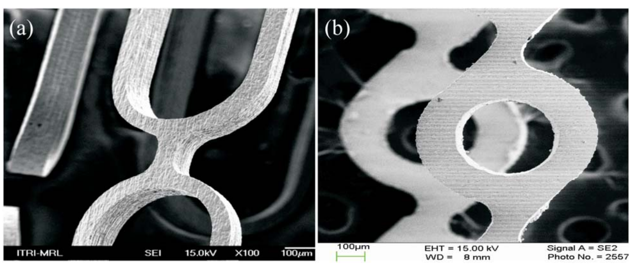

Figure 6. SEM images of stents: (a) with acid pickling and (b) without acid pickling.

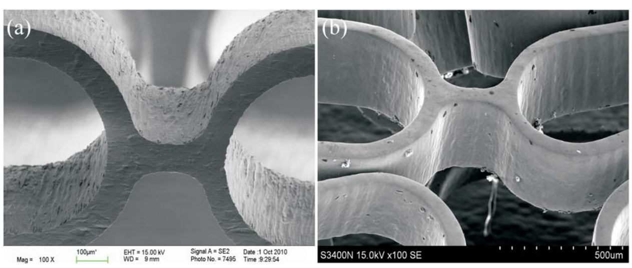

Figure 7. Morphologies of stents: (a) before and (b) after vacuum annealing.

Table 4. Hardness before and after vacuum annealing (HV)

Position	Position 1	Position 2	Position 3	Position 4	Average
Before annealing	223	218	213	217	218
After annealing	174	172	171	174	173
Reduction in hardness	49	46	42	43	

nealing, a very flat grain boundary appeared on the surface (Figure 7(b)). Generally, the quality of the original surface has a considerable influence on the outcome of polishing.

3.3 Electrolytic Polishing of Stents

Figure 8 presents an SEM image of a stent following electrolytic polishing under the conditions presented in Tables 2 and 3. It can be observed that the polishing process improved the surface quality considerably, compared to an annealed stent, as shown in Figure 7(b). Prior to polishing, pickling was performed at 40 °C for 40 min (Table 1). Clearly, the surface quality do meet the standard shown in Figure 6(a). Thus, it can be concluded that the electrolytic polishing conducted under the conditions in this study fulfilled the requisite smoothing of the 316LVM stainless steel tube stents.

Electrolytic polishing involves brightening and smoothing the surface of metals by immersing samples in an electrolyte and applying a positive direct current. The main electrical parameters of the electrolytic polishing process include anodic potential, anodic current density, and applied voltage. The nature and rate of electrochemical reactions are determined by the anodic potential. The electrolytic polishing process must be controlled in accordance with the anodic potential and may, in fact, be controlled according to the anodic current density or (in some cases) applied voltage. In the present study, applied voltage and anodic current were used as control parameters in the electrolytic polishing process. Electrolytic polishing generally occurs at the limiting current density (the current maximum or plateau in the current-voltage curve). The rate of dissolution at the limiting current is controlled by the transport of cationic reaction products from the anode into the electrolyte. Within the region of the limiting-current plateau, applied voltage also plays an important role in the resulting surface finishing. Temperature is another critical parameter in electrolytic polishing. Polishing time is used to determine the removal of material from the stents in cases where the other parameters are fixed. Under the conditions in this study, electrolytic polishing achieved a 78% reduction in surface roughness with an acceptable weight loss of 16.7% and a width reduction of 5.95%.

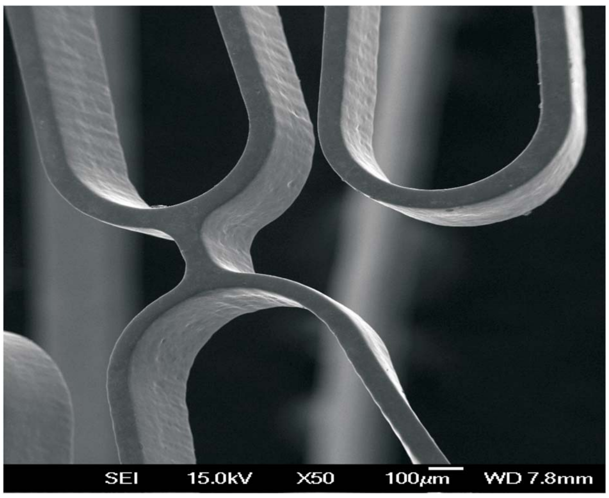

Figure 8. SEM image of stent after electrolytic polishing.

3.4 Removal of Surface Material

Table 5 presents the weights of the stents before and after electrolytic polishing as well as the weight loss. Table 6 presents the width and reduction in width of the strut ribs.

Table 5. Weights and weight losses of stents before and after polishing

Sample	Weight (mg)	Weight loss (%)
After laser cutting	~12.0	–
Acid pickled	~11.0	~8.3
Electrolytic polished	~9.0	~9.1

Table 6. Widths and width changes of stent struts before and after polishing

Sample	Width (μm)	Width reduction (%)
After laser cutting	88.5	–
Acid pickled	83.63	5.5
Electrolytic polished	78.18	6.5

3.5 Surface Roughness

Figures 9(a) and 9(b) present AFM images of the pickled and electrolytic polished stent surfaces, respectively, covering an evaluation area of 150 × 150 microns. A comparison of these images shows a significant reduction in the surface roughness of the electrolytic polished stent, compared to the acid pickled stent (after pickling, the surface roughness was Ra = 78 nm; after electrolytic polishing it was Ra = 14.3 nm). This represents a 78% reduction in surface roughness and demonstrates the efficacy of the electrolytic polishing process in improving surface smoothness.

3.6 Balloon Expandability of Electrolytic Polished Stent

Figure 10 presents a microscopic image of a stent crimped on a balloon catheter without strut overlap. The crimping profile of the stent was measured to have a diameter of 3.05 mm using a contact micrometer. A low crimping profile can help to ensure that the stent can easily navigate through small vessels and tortuous blockages, as shown in Figure 11.

Optical image investigation of the expanded stent in Figure 12 revealed that the pressure applied by the balloon was sufficient to provide uniform expansion of the stent to a diameter of approximately 8 mm. None of the struts had expanded disproportionately and appropriate straightening of struts was observed between alternate links. Surface finishing has a considerable influence on stent expansion, which is crucial in stent implantation during angioplasty. Uneven removal of material can result in insufficient expansion of the stent, which can detract from the effectiveness of scaffolding within the artery.

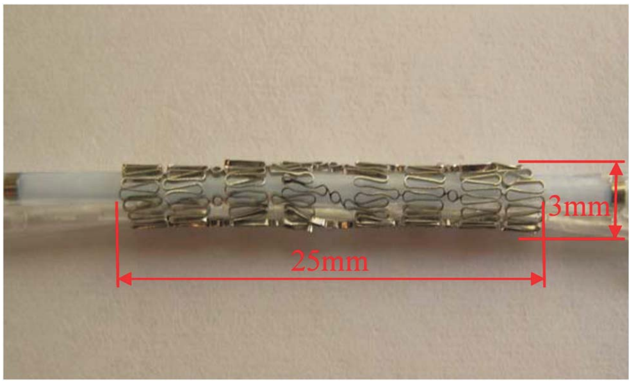

Figure 10. Microscopic image of stent crimped on balloon catheter.

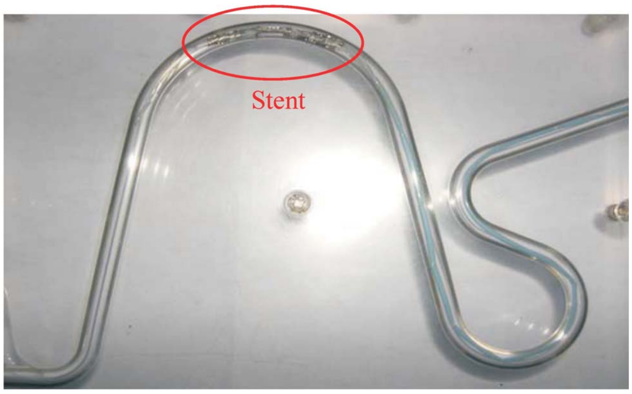

Figure 11. Model used to simulate vessels with tortuous blockages.

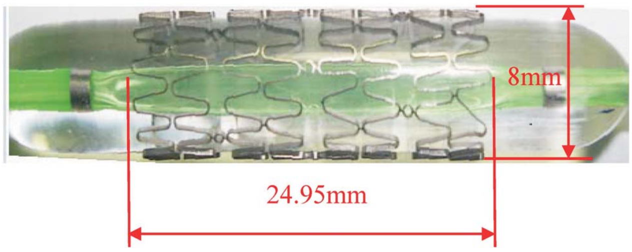

Figure 12. SEM images of expanded stent (max. outer diameter 8 mm).

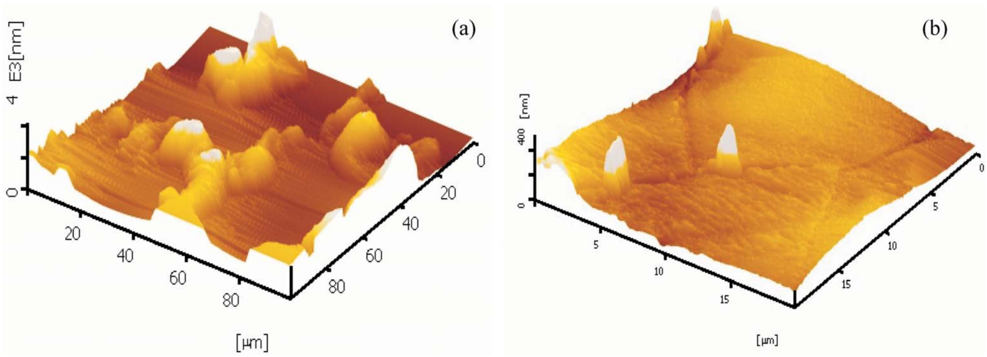

Figure 9. Morphologies of stents: (a) vacuum annealed and (b) electrolytically polished to reduce surface roughness.

4. Conclusions

This study demonstrated that the surface quality of 316LVM stainless steel tube stents can be significantly improved through acid pickling, vacuum annealing, electrolytic polishing and paassivation. The surface process conditions used in this study significantly improved surface smoothness, as confirmed by the SEM and AFM analyses. Compositional analysis of electrolytic polished and passivated stent surfaces showed a higher Cr metal amount, indicating enhanced corrosion resistance in a biological environment. The stent surface process of stent after achieved a 78% improvement in surface roughness with an acceptable weight loss of 16.7% and a width reduction of 5.95%.

To ensure the mechanical strength of the stent following the removal of material during surface treatment, we examined the profiles of stents in crimped and balloon expanded states. The original laser-cut stents were too rigid for balloon expansion; passivated coronary stents were easily crimped on the balloon and subsequently dilated. A uniform expansion profile was observed in scanning electron micrographs and optical images depicted nearly no foreshortening in the dilated stents.

This study outlines the processes involved in the development of a new type of stent. It is hoped that these results can contribute to the integrity and accuracy of associated studies in the future, including research preceding clinical animal testing and human trials, protection of patients during implantation procedures, and safe operation by medical personnel.

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