Electrochemical polishing of 316L stainless steel slotted tube coronary stents

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Surface smoothness is one of the properties determining the performance of stents. Therefore, surface polishing shows its importance in the exploitation and production of stents. The present study explores electrochemical polishing of 316L stainless steel slotted tube coronary stents produced by laser cutting. Acid pickling was also studied as a pre-treatment of electrochemical polishing of the stents to remove the slag (oxides) formed in the production of the stents. Meanwhile, removal of the material was measured as well, caused by both acid pickling and electrochemical polishing processes. It is found that the slag formed on the surface of stents due to the laser cutting production process could be removed by means of acid pickling. Electrochemical polishing results in a smooth stent surface. Meanwhile, both acid pickling and electrochemical polishing applied in the present study have a proper removal of the stent material.

1. Introduction

Metallic coronary stents are medical devices that can provide endovascular scaffolding to relieve the vascular obstruction. They exert a continuous radial pressure on diseased coronary artery, resulting in a compression of atherosclerotic plaques, sealing of dissections, and expansion of the coronary vessel [1, 2]. When used as adjunct to conventional balloon angioplasty, they improve vessel patency [3, 4].

Surface roughness is an important determinant of thrombogenicity and tissue reaction [5], i.e. the nature of the metal surface is crucial to blood compatibility [6]. A smooth surface can help to prevent the activation and aggregation of platelets, which is recognized to be one component of the process of thrombosis. Previous animal experimental investigation [5] has shown that surface treatment can improve the performance of stents. In animal experiments, the results of implantation of both polished stainless steel and nitinol stents were compared with those of unpolished stents. The conclusions are that metallic surface treatment with polishing effectively results in a decreased thrombogenicity [5, 7].

The most important clinical problem after stent implantation remains neointimal hyperplasia within the stent resulting in a significant stent narrowing in 16–30% [2, 3, 8–10]. Further efforts to improve the clinical results of coronary stents should focus on the decrease of this neointimal hyperplasia. Not only did the previous studies with the animal models show that metallic surface treatment using electrochemical polishing decreased the thrombogenicity but also showed a decrease of neointimal hyperplasia of coronary stents [11, 12].

Those studies in the medical aspects of stents have shown that a smooth surface of the stents could improve the healing efficiency. Thus, polishing of various metallic stents shows its importance in the material aspects of the study of the stents. Electrochemical polishing is a process in which a metallic surface is smoothed by polarizing it anodically in an adequate electrolyte [13]. The electrochemical polishing is classified into two processes: anodic leveling and anodic brightening [14]. Anodic leveling results from a difference in the dissolution rate between peaks and valleys on a rough metal surface depending on the current distribution or mass-transport conditions. On the other hand, anodic brightening is associated with the suppression of the influence of the metal microstructure on the dissolution rate. A smooth electrochemically polished surface, which appears bright to the naked eye, results from a combination of these two factors [14].

Some previous studies of surface conditioning of

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TABLE I Composition of pickling solution

Component	Amount (ml)
HF (48%)	3
HNO_3 (65%)	9
H_2O	to 100

stainless steel stents, which are self-designed 16-mm balloon-expandable stainless steel stents made of a 0.18-mm 316L stainless steel wire, show the effect of electrochemical polishing on the medical healing efficiency [11, 12]. The aim of this paper is to investigate electrochemical polishing of 316L stainless steel slotted tube coronary stents produced by laser cutting.

2. Materials and methods

2.1. Materials

The original material used in this study was 316L stainless steel slotted tube coronary stents produced from a stainless steel tube by laser cutting (Precision Cutting Systems nv, Belgium). The stents were 16 mm long approximately. Their diameter was about 1.6 mm. The wall thickness of the stents was 95 μm. The as-received samples were initially cleaned using distilled water in an ultrasonic agitation bath for 15 min and were dried in air.

2.2. Acid pickling

Acid pickling is an effective method for chemical removal of the surface oxides and other contaminants from metallic materials by immersion in an aqueous acid solution [15]. In this study, pickling of the stents was performed by immersing the stents in an acid solution (Table I) containing HF, HNO_3 and H_2O. Pickling was explored initially at room temperature for 20 and 60 min. Then, it was explored at a temperature of 40 °C for 40 min. The temperature was controled with a thermostat. After being pickled, all the samples were cleaned using distilled water in an ultrasonic agitation bath for 15 min and were dried in air.

2.3. Annealing

Annealing was employed to make the stents implantable, i.e. to make the stents sufficiently soft (ductile). A vacuum furnace (Leybold Heraeus PD 400, Germany) was used to conduct annealing of the stents. The stents were initially heated in vacuum at a heating rate of 3 °C/min from room temperature to temperatures of 1000 and 1100 °C and were then kept at the chosen temperatures respectively for 1 h. Finally, they were slowly cooled in vacuum to room temperature at a cooling rate of 4 °C/min. After annealing, the stents were cleaned using distilled water in an ultrasonic agitation bath for 15 min and were dried in air.

TABLE II Electrolytes for electrochemical polishing

Electrolyte	Component	Amount
(i)	H_2SO_4 (95–97%)	40 ml
	H_3PO_4 (85 wt %)	45 ml
	H_2O	14 ml
(ii)	H_3PO_4 (85 wt %)	42 wt %
	Glycerol	47 wt %
	H_2O	11 wt %

2.4. Electrochemical polishing

Electrochemical polishing was conducted to the stents that were pickled and annealed. The device used for electrochemical polishing was self-designed. A 150-ml glass beaker was used as a cell. A DC rectifier (Polipower, Struers, Denmark) was used as power supply. The stents were used as the anode. Cathode was a 316L stainless steel sheet (15 cm long, 4 cm wide and 0.2 cm thick). Polishing temperatures were controled with a thermostat. Two electrolytes (Table II) were explored. One electrolyte contained H_2SO_4, H_3PO_4 and H_2O. Another one included H_3PO_4, Glycerol and H_2O. The conditions for electrochemical polishing of the stents are presented in Table III, which were determined experimentally. After electrochemical polishing, the stents were cleaned using distilled water in an ultrasonic agitation bath for 15 min and were dried in air.

2.5. Inspection of samples and evaluation of surface qualities

During the experiments, the surfaces of the samples, i.e. the results of electrochemical polishing, were visually checked by means of stereomicroscopy (Wild Heerburg, Germany). A scanning electron microscope (SEM) (Philips 515 SEM, The Netherlands) was used to evaluate the effect of the electrochemical polishing process. Pictures of the stents were taken before and after electrochemical polishing with the SEM.

2.6. Measurements of weights and dimensions of stents

Weights of the stents were measured before and after electrochemical polishing with an electronic analytical balance (Mettler AE 100, Switzerland). Measurement of widths of the stent struts was carried out before and after electrochemical polishing using a micrometer (Filar Micrometer Eyepiece, American Optical 426C, USA) in conjunction with a light optical microscope (Leitz Metalloplan, Germany). Both the weight loss and the width reduction of the stents were calculated.

TABLE III Conditions for electrochemical polishing

Electrolyte	Applied voltage (V)	Anodic current (A)	Time (min)	Temperature (°C)
Electrolyte (i)	3.5	0.4	0.5	75
Electrolyte (ii)	10–12	1.2	1	90–95

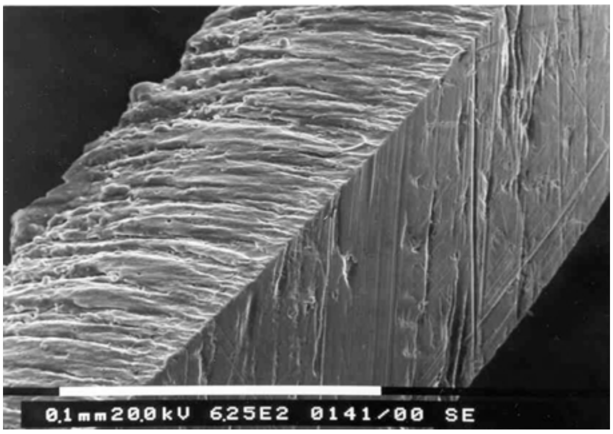

Figure 1 Morphologies of as-received stents: laser-cut zone and outer surface (Precision Cutting Systems nv, Belgium).

3. Results

3.1. As-received stents

Fig. 1 shows the morphologies of the laser-cut zone of the as-cut stent (''as-received''). The slag is clearly visible in this scanning electron microscope picture. Considerable roughness was observed in the laser-cut zone.

3.2. Pickling of stents

Fig. 2(a) shows a scanning electron microscope picture of a pickled stent. This stent was pickled from the as-cut stent in the acid solution (Table I) at 40 °C for 40 min. The slag in the laser-cut zone was removed effectively by the acid pickling. Fig. 2(b) shows a SEM picture of a stent pickled from the as-cut specimen, in the acid solution (Table I) at room temperature for 60 min. It could be observed that the slag was not removed totally at this condition. Therefore, it can be considered that a raised temperature is more suitable for pickling the 316L stainless steel slotted tube coronary stents.

3.3. Annealing of stents

Fig. 3 shows SEM pictures of the annealed stents, which were obtained by annealing the pickled stents in vacuum. It is clear that annealing at both 1100 °C (Fig. 3(a)) and 1000 °C (Fig. 3(b)) for 1 h results in the grain boundary grooves clearly visible on the surface of the stents. This material is recrystallized at those temperatures. In any case, these two annealed stents could be readily expanded by a balloon. Therefore, it could be considered that the heat treatment applied in this study is acceptable to soften the 316L stainless steel slotted tube coronary stents for the purpose of implantation.

3.4. Electrochemical polishing

Fig. 4(a) shows a SEM picture of a polished stent, which was obtained by electrochemical polishing using electrolyte (ii) (Table II) at the condition presented in Table III. Prior to polishing, pickling was conducted in the acid solution (Table I) at 40 °C for 40 min and annealing was done in vacuum at 1000 °C for 1 h. It could be observed that a smooth surface was obtained after the polishing

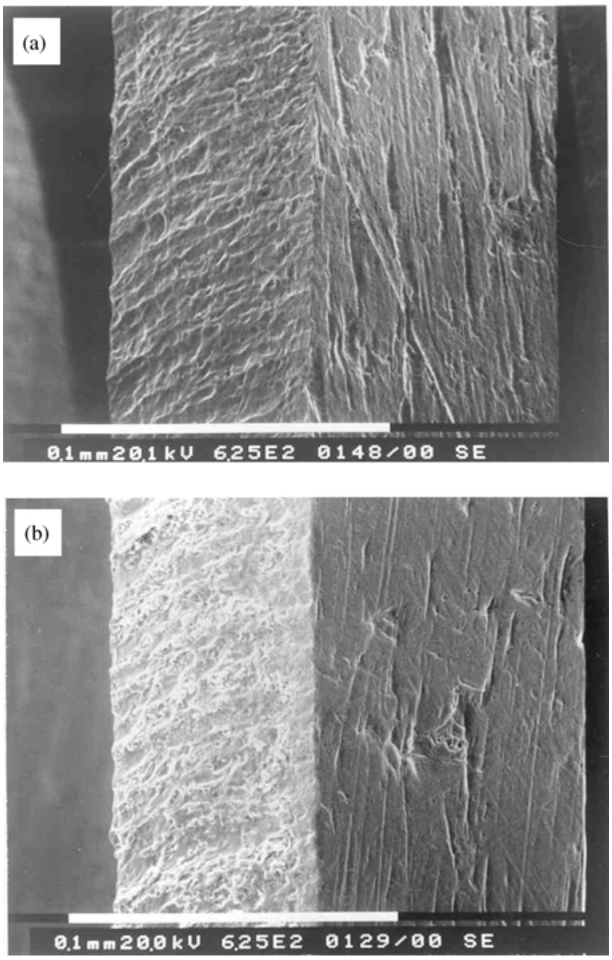

Figure 2 Morphologies of stents pickled (a) at 40 °C for 40 min, (b) at room temperature for 60 min: laser-cut zone and outer surface.

process. The surface quality is much improved compared to both the pickled stent and the annealed stent. Fig. 4(b) shows a SEM picture of a stent polished using electrolyte (i) (Table II) at the condition presented in Table III. Prior to polishing, pickling was conducted in the solution (Table I) at 40 °C for 40 min. The surface quality is not satisfactory compared to that shown in Fig. 4(a). Anyway, it could be concluded that smoothening of the 316L stainless steel slotted tube coronary stents is effectively achieved by electrochemical polishing conducted at the condition applied in this study.

3.5. Removal of stent material

Table IV presents the weight and weight loss of the ''as-received'', as-pickled and as-polished stents. Table V presents the width and width reduction of the ''as-received'', as-pickled and as-polished stent struts. The ''as-received'' stent has a weight of about 13 mg and a strut width of about 138.47 μm. After pickling in the

TABLE IV Weights and weight losses of stents before and after polishing

Sample	Weight (mg)	Weight loss (%)
Received	~ 13.0	—
Pickled	~ 12.0	~ 7.7
Polished	~ 10.0	~ 16.7

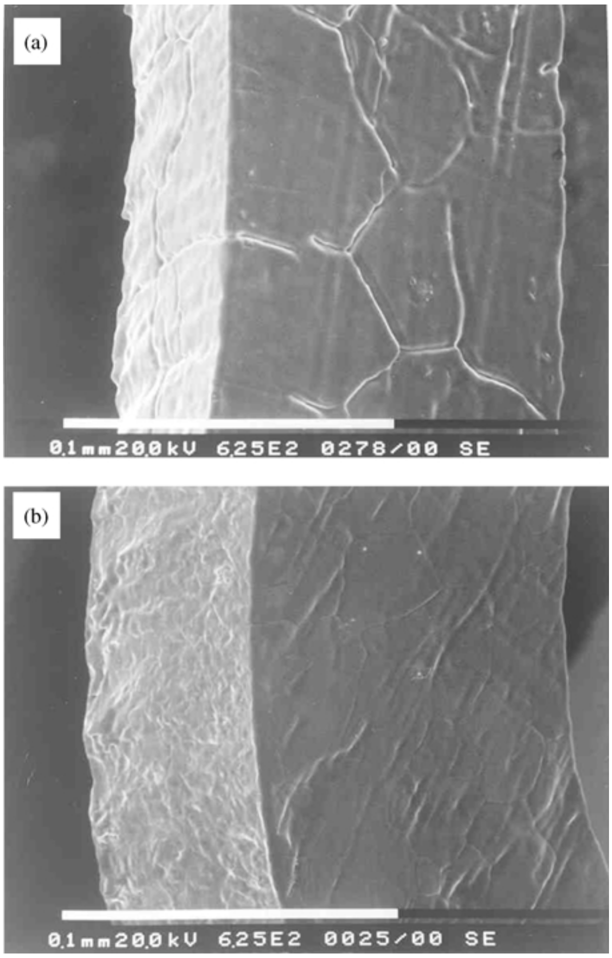

Figure 3 Morphologies of stents annealed in vacuum for 1 h at (a) 1100 °C, (b) 1000 °C from stents pickled at 40 °C for 40 min: laser-cut zone and outer surface.

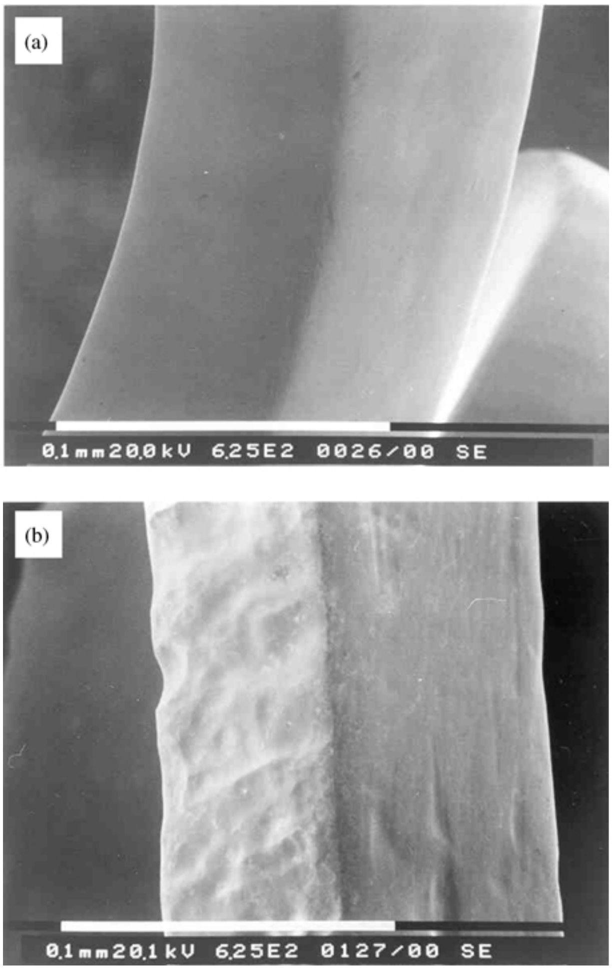

Figure 4 Morphologies of stents polished using (a) electrolyte (ii), (b) electrolyte (i) (Table II) from pickled (40 °C, 40 min) + annealed (vacuum, 1000 °C, 1 h) stents: laser-cut zone and outer surface.

TABLE V Widths and width changes of stent struts before and after polishing

Sample	Width (μm)	Width reduction (%)
Received	138.47 ± 1.47	—
Pickled	130.98 ± 1.28	5.41
Polished	123.19 ± 1.47	5.95

selected acid solution (Table I) at 40 °C for 40 min, the weight of the stent was about 12 mg. The weight loss is thus 7.7%. The strut width decreased to 130.98 μm. The width reduction is thus 5.41%. After polishing using electrolyte (ii) (Table II) at the condition presented in Table III, the weight of stent became 10 mg and the strut width was reduced to 123.19 μm. Prior to polishing, pickling was carried out at 40 °C for 40 min and annealing was done in vacuum at 1000 °C for 1 h. The polishing process results in a weight loss of 16.7% and a width reduction of 5.95%.

3.6. Another pre-treatment of polishing

Fig. 5(a) shows a SEM picture of a stent annealed from the as-cut stent in vacuum at 1100 °C for 1 h. The grain boundary grooves could be observed. Fig. 5(b) shows a SEM picture of the stent pickled (40 °C, 40 min) from the annealed stent (Fig. 5(a)). It could be found that the grain boundary grooves became much deeper, resulting in an extremely bad surface quality. With such a surface quality, the stent was then polished electrochemically using electrolyte (ii) (Table II) at the condition presented in Table III, resulting in the surface quality shown in Fig. 5(c). The surface quality is not satisfactory.

4. Discussion

This study shows that the surface quality of the 316L stainless steel slotted tube coronary stents is improved by means of electrochemical polishing.

4.1. Acid pickling

Laser cutting causes appearance of the slag (burrs and depositions) on the surface of the stents during the manufacturing process, resulting in a rough surface. First of all the slag must be removed before electrochemical polishing as was earlier discussed for electrochemical polishing of NiTi and Ta stents [16]. The surface quality of the stents polished electrochemically without a pre-treatment of pickling is even worse than non-polished stents. The oxides produced by the laser cutting process still adhered to the surface of the stents after polishing,

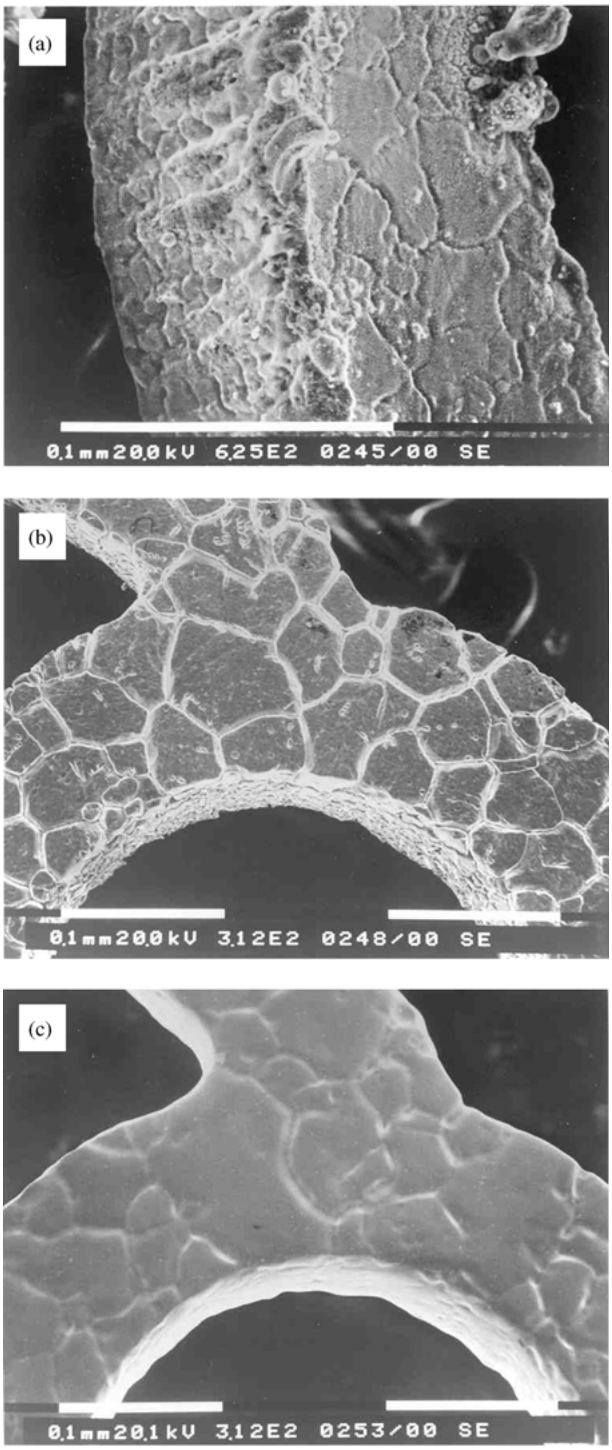

Figure 5 (a) A stent annealed (vacuum, 1100 °C, 1 h) from as-received stent, (b) A stent annealed (vacuum, 1100 °C, 1 h) from a pickled stent (40 °C, 40 min), (c) A stent polished using electrolyte (ii) (Table II) from annealed (vacuum, 1100 °C, 1 h) + pickled (40 °C, 40 min) stent: outer surface and laser-cut zone.

resulting in the worse surface quality. In the literature [17], it is also mentioned that the burr and the depositions must be removed after laser cutting in further production steps. In this study, acid pickling was employed as a pre-treatment of electrochemical polishing of the 316L stainless steel slotted tube coronary stents. Pickling time is a critical parameter with a selection of a suitable acid solution. In particular, the small sized coronary stents should be strictly controlled for pickling. As mentioned in the literature [18], the recommended immersion times for pickling solutions should not be exceeded to avoid excessive stock removal. On one hand, oxides could not be removed entirely with insufficient pickling time. Also, if a suitable pickling time was exceeded, excessive removal would be resulted in. Moreover, the influence of temperature on pickling time is pronounced [15]. Increase in temperature causes an increase in pickling rate. In this study, pickling at room temperature for 60 min is less effective than pickling at a raised temperature of 40 °C for 40 min (Fig. 2). Excessive removal should be avoided during the pickling process of stents. Either weight loss or dimension change is the parameter that controls removal of the stent material in the process of pickling. While removing the oxide from the stents, weight loss and dimension reduction of the stents should be as small as possible.

4.2. Annealing

The ''as-received'' stents are made from tubes by laser cutting. Firstly, it is required to soften the stents for implantation. The carbon content (0.03% max) of low-carbon austenitic stainless steels including 316L is low enough to reduce precipitation of chromium carbides which markedly decrease the resistance to intergranular corrosion. They do not require a quenching treatment [19]. Therefore, in this study, annealing was performed and slow cooling was applied in vacuum to soften the stents. The vacuum furnace was used to anneal the stents, completely free from scale during heat treatment. Two temperatures, 1000 °C and 1100 °C, were explored. In the trial of expanding the annealed stents, it was found that the samples annealed at the above-applied temperatures were implantable. Annealing results in an even worse surface quality of stents compared with the non-annealed (as-pickled) samples (Fig. 2(a)). The grain boundary grooves appear on the surface (Fig. 3) after annealing. The sample annealed at 1100 °C has deeper grooves than that annealed at 1000 °C i.e. the depth of the grain boundary grooves increases with increase of the annealing temperature. In general, the original surface quality influences the final effect of polishing. In case of softening the stents to be implantable, therefore, the annealing temperature should be controlled as low as possible.

4.3. Electrochemical polishing

Electrochemical polishing is a method of brightening and smoothing the surface of metals [14, 20] by immersing the parts in an electrolyte and applying positive direct current to the sample. The main electrical parameters of electrochemical polishing process are the anodic potential, the anodic current density and the applied voltage. The nature and rate of any electrochemical reaction are both determined by the electrode potential. The electrochemical polishing process should also be controlled on the basis of the anodic potential. In practise, the electrochemical polishing process is controlled on the basis of the anodic current density and, in some cases, on the basis of the applied voltage [21]. In the present study, the applied voltage and the anodic current were used as the controlling parameters during the electrochemical polishing process. Electrochemical polishing generally occurs at the limiting current density (a current maximum or plateau in the current–voltage curve) [21–24]. The rate of dissolution at the limiting current is controlled by the transport of cationic reaction products from the anode into the electrolyte [24]. Within the limiting-current plateau region, the applied voltage also plays an important role for the resulting surface finishing [23]. The temperature is a critical parameter for electrochemical polishing as well. Polishing time is a parameter that influences the removal of material from the stents in case other parameters are fixed. Either weight loss or dimension change is the parameter that controls removal of the stent material in the process of electrochemical polishing. In this study, under the applied condition, electrochemical polishing results in an acceptable weight loss (16.7%).

4.4. Comparison of the two different pre-treatment procedures of polishing

In this study, it is found that the sequence of pickling and annealing prior to the electrochemical polishing is crucial for achieving a satisfactory polishing result. After annealing, the as-cut stents could be homogeneous, resulting in some grain boundary grooves on the surface of the stent (Fig. 5(a)). Pickling of these annealed stents causes that the grain boundary grooves become much deeper, resulting in a much worse surface quality (Fig. 5(b)). With such a surface quality, no satisfactory polishing could be achieved (Fig. 5(c)). When annealing was done after pickling the as-cut stents, the surface quality of stents is much better than for the stents pickled after being annealed. With such a surface quality (Fig. 3), the stents are polished resulting in a smooth surface (Fig. 4). It could be assumed that removal of the stent material by pickling at the grain boundary is faster, therefore, more material is removed at the grain boundary, resulting in deeper grain boundary grooves.

5. Conclusions

The slag formed on the surface of stents due to laser cutting during production of the 316L stainless steel slotted tube coronary stents could be removed by means of acid pickling applied in the present study. Heat treatment results in a suitable softness (ductility) of stents for implantation. A smooth surface of the 316L stainless steel slotted tube coronary stents is achieved after electrochemical polishing. Both the acid pickling and the electrochemical polishing processes have an acceptable removal of the stent material.

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