Surface Conditioning of NiTi and Ta Stents

H. ZHAO, J. VAN HUMBEECK
Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Heverlee, Belgium

I. DE SCHEERDER
Department of Cardiology, University Hospital Gasthuisberg, Katholieke Universiteit Leuven, Leuven, Belgium

Summary

The present study explores the optimal methods for polishing NiTi and Ta stents. Electrochemical polishing was explored and several parameters were investigated including applied voltage, polishing time, and acid pickling prior to the polishing process. As a comparison, chemical polishing was also conducted. Both mechanical and electrochemical polishing of NiTi sheet materials were investigated to study the influence of electrochemical polishing on the surface composition of NiTi stents. Pickling was necessary prior to electrochemical polishing in order to remove the oxide films covering the stent surface. The surface quality of the NiTi and Ta stents significantly improved when the optimal condition for polishing was achieved.

Key Words

Stents, electrochemical polishing, mechanical polishing, acid pickling

Introduction

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

Surface roughness is an important determinant of thrombogenicity and tissue reaction [5]; 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. A previous experimental investigation with animals [5] has shown that surface treatment can modify the performance of stents. In the 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 decreased thrombogenicity [5,7].

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

Some studies have shown that a smooth surface on the stents could improve the efficiency of healing. Thus, polishing various metallic stents has shown 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 the anode in an appropriate electrolytic solution [13]. 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

Component	Amount (ml)
HF (38 – 49 %)	2
HNO_3 (65 %)	40

Table 1. Composition of pickling solution for NiTi sheets and NiTi stents.

Component	Amount (ml)
HF (48 – 51 %)	5.6
H_2SO_4 (95 – 97 %)	1
HNO_3 (65 %)	8
H_2O	8

Table 2. Composition of pickling solution for Ta stents.

depending on the current distribution or mass-transport conditions. 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]. Previous studies on the surface conditioning of stainless steel stents have shown the effects of electrochemical polishing on the efficiency of physiologic healing. Other studies focused on the electrochemical polishing of other types of stents. The aim of this paper is to investigate and determine the optimal conditions for electrochemically polishing nickel-titanium "nitinol" (NiTi) and tantalum (Ta) stents.

Materials and Methods

Materials

The original materials used in this study were a cold-rolled binary near-equiatomic NiTi rolled sheet (length 100 mm, width 5 mm, and thickness 1.4 mm, AMT, Belgium), binary near-equiatomic NiTi wires with diameters of 1 mm (Krupp, Germany), 0.5 mm, and 0.3 mm (both from AMT, Belgium), non-polished NiTi stents (ϕ 2.5 × 20 mm, ϕ 2.5 × 15 mm, and ϕ 2.5 × 10 mm, research products from Global Therapeutics, USA) and non-polished tantalum stents (ϕ 2.0 × 15 mm, research products from Medtronic, USA). The NiTi sheet was used to study the differences between mechanical and electrochemical polishing. The NiTi wires were used to explore the different conditions for electrochemical polishing of NiTi coil stents. The samples were cleaned for 10 min in an ultrasonic agitation bath using an alkaline solvent with a detergent additive (RW77, Tickopur, Bandelin, Germany). Then they were cleaned for > 10 min using distilled water in an ultrasonic agitation bath and were air-dried.

Acid Pickling

Acid pickling is an effective method for the chemical removal of surface oxides and other contaminants from metallic materials by immersion in an aqueous acid solution [15].

NiTi sheets and NiTi stents: The sheets were immersed in the acid solution [16] (Table 1) for 1, 4, 7, 10, and 14 min at room temperature. Due to the oxides formed

a

Electrolyte	Component	Amount (ml)	
(i)	Perchloric acid (70 %)	6	Electrochemical polishing
	Acetic acid (99.8 %)	94	
(ii)	Perchloric acid (70 %)	5	
	Acetic acid (99.8 %)	100	
(iii)	H_2O_2	50	Chemical polishing
	HF (38 – 40 %)	5	
(iv)	H_2O_2	75	
	HF (38 – 40 %)	5	

b

Electrolyte	Applied voltage (V)	Anodic current (A)	Time (min)
(i)	5	0.023	10
(i)	10	0.045	1
(i)	15	0.1	10
(i)	20	0.16	3, 5, 10
(i)	25	0.22	3, 5, 10
(i)	30	0.2 ~ 0.3	2, 3, 4 ~ 5, 6, 8
(ii)	20	0.15	3, 6
(ii)	25	0.17	3, 6
(ii)	30	0.15 ~ 0.25	2, 3, 4 ~ 5, 6, 8, 10
(iii)			3, 9, 15
(iv)			3, 9, 15

Table 3. Electrolytes (a) for polishing NiTi sheets and NiTi stents and conditions for polishing of NiTi sheets (b).

a

Electrolyte	Applied voltage (V)	Anodic current (A)	Time (min)
(ii)	30	0.21	2, 3, 4 ~ 5, 8
	25	0.2	2, 3, 4 ~ 5, 8
	20	0.18	2, 3, 4 ~ 5, 8

b

Electrolyte	Applied voltage (V)	Anodic current (A)	Time (min)
(ii)	30	0.25	3
	25	0.17	1, 1.5, 3
	20	0.15	1, 1.5 ~ 2

c

Electrolyte	Applied voltage (V)	Anodic current (A)	Time (min)
(ii)	20	0.15	1.5 ~ 2

Table 4. Conditions for electrochemical polishing of NiTi wires (a), NiTi stents (b), and NiTi stents (c) without pickling.

a

Electrolyte	Component	Amount (ml)	
(i)	H_2SO_4 (95 – 97 %)	50	Electrochemical polishing
	Acetic acid (99.8 %)	20	
	HF (38 – 40 %)	10	
(ii)	H_2SO_4 (95 – 97 %)	90	Electrochemical polishing
	HF (38 – 40 %)	10	
(iii)	H_2SO_4 (95 – 97 %)	50	Chemical polishing
	HNO_3 (65 %)	20	
	HF (38 – 40 %)	20	

b

Electrolyte	Applied voltage (V)	Time (min)
(i)	2.5, 5, 7.5, 10	2
	5	0.5, 1, 2, 3
(ii)	15	3, 6, 9, 12
	10, 15, 20	9
(iii)		2, 4, 6

Table 5. Electrolytes (a) and conditions (b) for polishing of Ta stents.

during the manufacturing process, the stents were also immersed in the acid solution for another 1, 2, 4, 6, and 8 min at room temperature.

Ta stents: After being degreased the Ta stents were immersed in an acid solution (Table 2) for 2.5, 5, 7.5, 10, and 20 min at room temperature; this was done to remove the oxides on the stent struts. After being pickled, all the samples were rinsed with distilled water in an ultrasonic agitation bath for > 10 min and were then air-dried. Evaluation of the results was done by observation with a stereomicroscope (Wild Heerburg, Switzerland).

Chemical Polishing

NiTi sheets and NiTi stents: Chemical polishing was done to compare the polishing effect with electrochemical polishing using the acid solutions H_2O_2 and HF, i.e. electrolytes (iii) and (iv) listed in Table 3a. After being pickled for 7 min, the NiTi sheets were immersed in the selected acid solutions for 3, 9, and 15 min at room temperature (Table 3b).

Ta stents: Chemical polishing of the Ta stents was performed in an acid mixture (H_2SO_4, HNO_3, and HF), i.e., electrolyte (iii) listed in Table 3a. After pickling the stents were immersed in the selected acid solution for 2, 4, and 6 min at room temperature. After chemical polishing, all the samples were rinsed in distilled water in an ultrasonic agitation bath for > 10 min and then air-dried.

Electrochemical Polishing

NiTi sheets and NiTi stents: The device used for electrochemical polishing of NiTi sheets and NiTi stents was self-designed. A 150-ml glass beaker was used as a cell. A DC rectifier (Polipower, Struers, Denmark) was used as the power supply, and the cathode was a stainless steel 316L sheet material (length 15 cm, width 2.5 cm, and thickness 0.2 cm).

Electrochemical polishing of NiTi sheets was performed with the selected electrolyte [16] (perchloric acid 70 % and acetic acid 99.8 %) presented in Table 3a. Prior to electrochemical polishing, a pre-treatment using acid pickling was done for 7 min. Several parameters were evaluated to obtain the optimal polishing conditions (Table 3b). They included the electrolyte, the applied voltage, and the polishing time. Initially, the applied voltages (5, 10, 15, 20, and 25 V) were tested with a fixed time of 10 min using electrolyte (i). Then the applied voltages were fixed to 20 and 25 V respective-

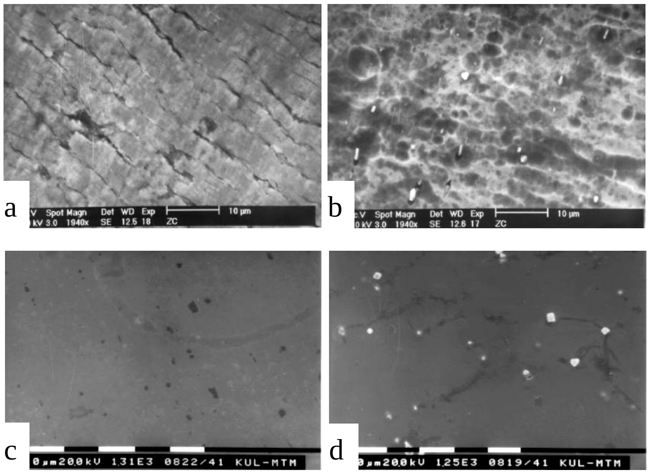

Figure 1. NiTi sheet: Panel a) Surface of the as-received sheet (Philips XL SEM). Panel b) Morphology of the pickled sheet. Panel c) Surface of the mechanically polished sheet. Panel d) Surface of the electrochemically polished sheet.

ly, and the polishing time (3 min, 5 min) was tested. The polishing times of 2, 3, 4, 6, and 8 min were tested at the applied voltage of 30 V. Based on the experiences of electrochemical polishing using electrolyte (i), several applied voltages (20, 25, and 30 V) were selected and tested at 3 and 6 min using electrolyte (ii). Polishing at 30 V was also tested for 2, 4, 6, 8, and 10 min. The polishing processes were conducted at room temperature without stirring.

Electrochemical polishing of NiTi wires was performed with different parameters including the applied voltages and the polishing times to find an optimal setting for electrochemical polishing of NiTi stents. The wires were ground with rough abrasive paper prior to electrochemical polishing. The conditions for electrochemical polishing of NiTi wires are summarized in Table 4a. Selection of these conditions depended on the results of electrochemical polishing of the sheet materials. Several applied voltages (20, 25, and 30 V) were tested for different times (2, 3, 4, and 8 min) using electrolyte (ii) at room temperature without stirring.

Based on the experiences of electrochemically polishing both NiTi sheets and NiTi wires, electrochemical polishing of NiTi stents was conducted. After a 6 min pre-treatment with acid pickling followed by a rinse, electrochemical polishing of NiTi stents was evaluated with different parameters including the applied voltages and the polishing times. The conditions for electrochemical polishing stents are summarized in Table 4b. These conditions were selected based on our experiences with NiTi sheets and NiTi wires, as well as the specific, thin shape of the mesh of the stents. First, the applied voltages of 25 and 30 V were tested for 3 min using electrolyte (ii). Then, the polishing times of 1, 1.5, and 2 min were tested at the applied voltages of 20 and 25 V. The polishing process was done at room temperature without stirring. In addition, electro-

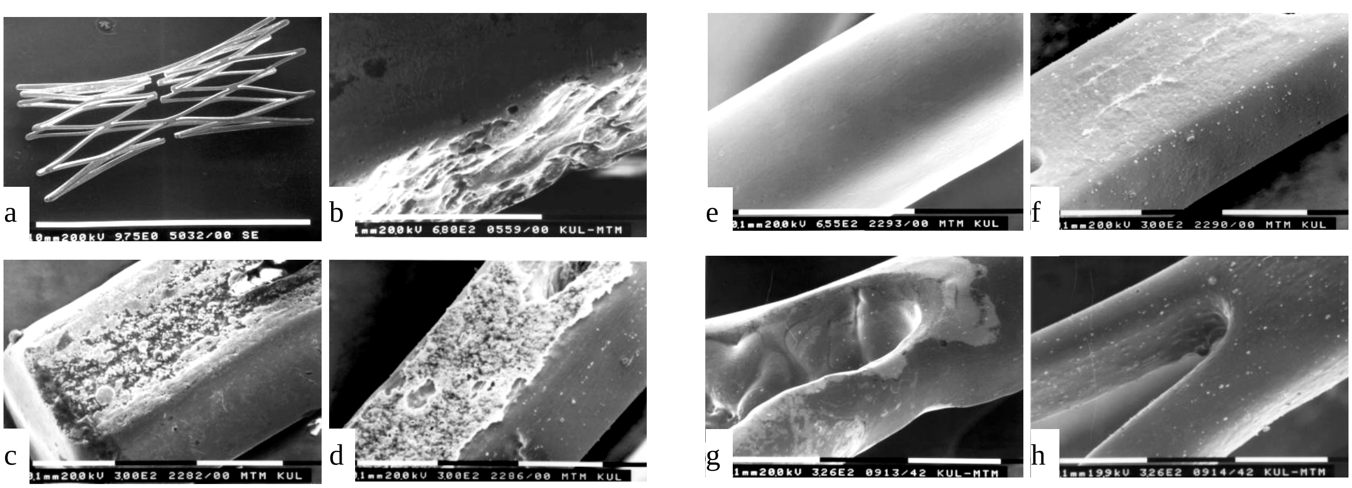

Figure 2. NiTi stent (Global therapeutics, USA): Panel a) An as-received stent. Panel b) Cutting zone morphology of the as-received NiTi stent. Panel c) Inside morphology of the as-received NiTi stent. Panel d) Inside morphology of the electrochemically polished stent without pickling. Panel e) Outside cutting zone morphology of the electrochemically polished stent. Panel f) Inside cutting zone morphology of the electrochemically polished stent. Panel g) The over-polished NiTi stent, which size is not uniform. Panel h) The over-polished NiTi stent with excessive removal of the surface.

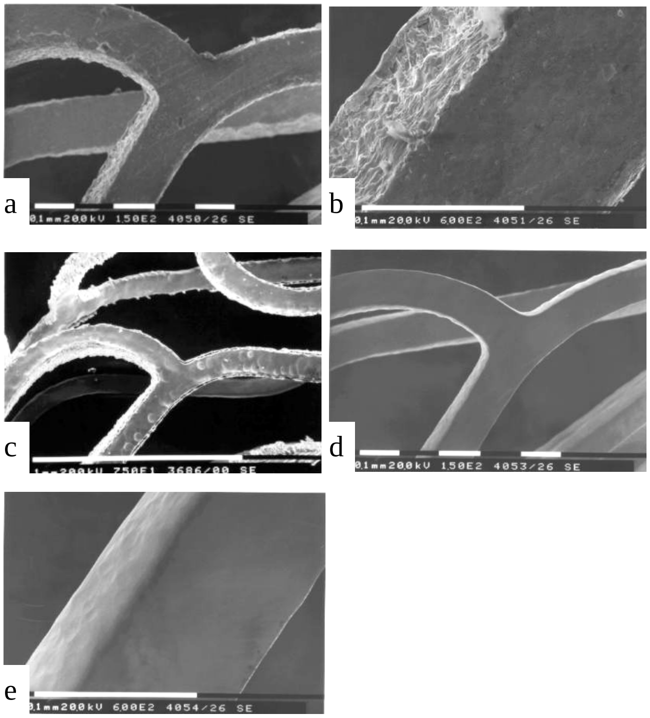

Figure 3. Ta stent (Medtronic, USA). Panel a) Morphology of the as-received stent struts. Panel b) Cutting zone morphology of the as-received stent. Panel c) Morphology of the electrochemically polished stent without pickling. Panel d) Morphology struts of the electrochemically polished stent. Panel e) Cutting zone morphology of the electrochemically polished stent.

chemical polishing of the NiTi stents without pre-treatment by pickling was conducted at an applied voltage of 20 V for 1.5 min at room temperature without stirring (Table 4c).

Ta stents: The device used for electrochemical polishing of Ta stents was also self-designed. A 100-ml glass beaker was used as the cell. The power supply was a DC rectifier (Polipower Struers, Denmark). A graphite bar (diameter: 10 mm) was used as the cathode. Electrochemical polishing of the Ta stents was conducted using electrolytes (i) and (ii) (Table 5a). Acid pickling was performed for 10 min prior to electrochemical polishing. Several parameters summarized in Table 5b were evaluated to obtain the optimal conditions for electrochemical polishing. They included selection of the electrolytes, the applied voltages, and the polishing times. Electrochemical polishing was conducted at room temperature with stirring. Initially, the applied voltages were tested using electrolyte (i) with a fixed time of 2 min, including 2.5, 5, 7.5, and 10 V. By observing the polishing results with the optical microscope, the voltage was fixed to 5 V and polishing was conducted for 0.5, 1, 2, 3 min. For electrolyte (ii) polishing was initially conducted for 3, 6, 9, 12 min at a fixed voltage (15 V). The time was then fixed at 9 min and the applied voltages were evaluated (10, 15, and 20 V). Finally, electrochemical polishing of the "as-received" samples without pre-treatment by acid pickling was performed at room temperature with stirring. The conditions are presented in Table 6. After being polished, all the samples were rinsed using distilled water in an ultrasonic agitation bath for > 10 min and were air-dried.

Electrolyte	Applied voltage (V)	Time (min)
(i)	5, 7.5	2
(ii)	15	6, 9

Table 6. Conditions for electrochemical polishing of Ta stents without pickling.

Mechanical Polishing of NiTi Sheets

Mechanical polishing of the NiTi sheet was conducted as follows. First the sample was ground with waterproof abrasive paper (type-1200, 4000), using water to keep the sample cool. Then polishing was performed on a high-speed polishing wheel covered with a cloth, gradually using 3-mm and 1-mm diamond paste. Final polishing was performed on a low-speed wheel covered with a cloth, using a slurry of 0.05-mm alumina and water. After mechanical polishing, the sample was rinsed using distilled water in an ultrasonic agitation bath for > 10 min.

Inspection of Samples and Evaluation of Surface Qualities

During the experiments, the surfaces of the samples were visually observed by means of stereomicroscopy (Wild Heerburg). A scanning electron microscope (515 SEM and XL SEM, Philips), was used to evaluate the effect of the electrochemical polishing process. Pictures of the stents were taken before and after electrochemical polishing. Analysis of the composition of the NiTi sheets was done with an energy dispersive spectrometer in conjunction with the SEM.

Results

NiTi Sheets and NiTi Stents

The as-received NiTi sheet samples have black colored surfaces; this is the oxide layer formed during processing. At a magnification of 1940×, considerable roughness was observed on the surface of the "as-received" NiTi sheet (Figure 1). An "as-received" NiTi stent (ϕ 2.5 × 10 mm) is shown in Figure 2a. It was also observed from the SEM pictures that the non-polished NiTi stents have a rough surface (Figures 2b and 2c).

Pickling: Figure 1b shows an SEM picture of a pickled NiTi sheet. This NiTi sheet was pickled in the acid solution (Table 1) for 7 min at room temperature. The grooved surface oxide was removed by acid pickling. Figure 2d shows the morphology of the NiTi stent surface electrochemically polished without pre-treatment by acid pickling prior to the polishing process. It is clear that the rough oxide layer still adheres to the surface inside the stent although other surfaces are polished. It reveals an even worse quality than the as-received non-polished stent. Thus, it can be considered that the oxides cannot be removed by means of electrochemical polishing alone, i.e., the pre-treatment by acid pickling is necessary for electrochemically polishing the NiTi stents. During the experiment, optical microscopy was used to show that there were no apparent changes on the surface of the stents when the samples were immersed in the pickling solution for both 1 and 2 min. Some oxides still adhered to the surface of the stent after pickling for 4 min. When pickling was performed for both 6 and 8 min, we observed that the rough oxides were clearly removed.

Chemical polishing: From evaluation by means of optical microscopy, it is known that the effect of chemical polishing processes in this study is negative, i.e., the selected conditions for chemical polishing did not result in a satisfactory surface quality.

Electrochemical and mechanical polishing: The morphology of the mechanically polished surface of NiTi sheet is shown in Figure 1c (1310 ×). Figure 1d (1250 ×) shows the morphology of the surface of the NiTi sheet, electrochemically polished under the condition presented in Table 7. Prior to electrochemical polishing, the sample was pickled for 7 min. The SEM photographs reveal much smoother surfaces compared with those of both the as-received sample and the pickled sample. There were some white spots on the surface of the electrochemically polished NiTi sheet. Table 8 summarizes the composition of the various polished samples. The elemental composition of the mechanically polished NiTi sheet is 50.13 at. % (atomic percentage) Ti and 49.87 at. % Ni. The composition of the dark part of the electrochemically polished NiTi sheet surface is 50.71 at. % Ti and 49.29 at. % Ni. The white spots on the electrochemically polished NiTi sheet surface have a composition of 90.71 at. % Ti and 9.29 at. % Ni. Thus, it can be assumed that titanium particles might be present as impurities in the NiTi sheet material.

Electrolyte	Sample	Applied Voltage (V)	Anodic Current (A)	Time (min)
(ii)	NiTi sheet	30	0.15 ~ 0.25	4 ~ 5
(ii)	NiTi stent	20	0.15	1.5 ~ 2
(i)	Ta stent		2	

Table 7. Optimal condition for electrochemical polishing of NiTi sheets NiTi stents, and Ta stents.

Sample	Composition (at. %) Ti	Ni
Sheet mechnically polished	50.13	49.87
Sheet electrochemically polished (white spot)	90.71	9.29
Sheet electrochemically polished (dark part)	50.71	49.29
Stent electrochemically polished	50.06	49.94

Table 8. Composition of the polished NiTi sheets and NiTi stents. at. % = atom percentage.

Electrochemical polishing was studied at various conditions. All of the studies were conducted at room temperature without stirring, after acid pickling. Electrochemical polishing of the NiTi sheet with electrolyte (i) at the applied voltages of 5 V, 10 V, and 15 V did not obtain satisfactory results, when observed by optical microscopy. To achieve electrochemical polishing of titanium in perchloric acid-acetic acid solution, anode potentials in excess of 20 V are required to cause breakdown of the anodic film of TiO2, which protects the metal from dissolution at lower potentials. This has been confirmed by Mathieu and his colleagues [17,18]. In the present study, voltages of 20 V, 25 V, and 30 V were applied for electrochemical polishing of the NiTi sheets. The optimal result was obtained at 30 V for

4 ~ 5 min when the NiTi sheets were polished in electrolyte (i). An elevated temperature (30°C) was also evaluated but improved results were not obtained. It was found that stirring had a negative effect on the polishing. In the experiment with electrolyte (ii), the voltages of 20, 25, and 30 V were applied based on the experience with electrolyte (i). It was also found that the optimal result was obtained at 30 V for 4 ~ 5 min when polishing the sheet material in electrolyte (ii). Based on the effects between electrolyte (i) and electrolyte (ii) on the polished NiTi sheets, we decided to use electrolyte (ii) for polishing the NiTi stents.

In the NiTi wires polishing trials, the voltages of 20, 25, and 30 V were applied for various time periods. The most satisfactory results were obtained by polishing for 3 min at all of the applied voltages; 2-min was not sufficient and 4 min was excessive.

In electrochemical polishing of the NiTi stents, the voltages were also applied at 20, 25, and 30 V for various times. A relatively satisfactory result was obtained by polishing for 1.5 ~ 2 min at 20 V, while a 3-min polishing caused excessive removal of the coating. The polishing time of the stents was shorter than that of the wires and much shorter than that of the sheets. Three minutes of polishing which was satisfactory for the NiTi wires, caused a negative result for the NiTi stents; it was also not sufficient to obtain a smooth surface for the NiTi sheets. The duration of electrochemical polishing depends on a number of factors, including the initial state of the parts to be polished, the nature of the metal and electrolyte, the conditions, and other factors [19]. Electrochemical polishing times in excess of the optimum may markedly impair the quality. The electrochemical polishing time should decrease with increasing current density or by decreasing initial roughness of the surface [19].

The parameters that provided optimal conditions for electrochemical polishing NiTi stents are presented in Table 7. Acid pickling is performed for 6 min prior to electrochemical polishing. Electrochemical polishing at the optimal condition improved the surface quality of the NiTi stents (Figures 2e and 2f). The rough surface of the as-received sample became smooth. In Figures 2g and 2h, two over-polished stents are shown, after excessive polishing. One was apparently attacked; the size was not uniform. Although the other stent had a relatively smooth and uniform surface, the excessive removal of the surface was not acceptable.

Ta Stents

Figure 3a shows part of the stent struts of the as-received non-polished tantalum stents and Figure 3b shows the surface morphology of the stent strut. Considerable roughness on the surface of the non-polished stents was visually observed in the SEM pictures. The dimensions of the non-polished stent struts measured approximately 130.40 mm in width and 108.70 mm in thickness.

Pickling: Figure 3e shows one of the surface morphologies of the tantalum stent that was electrochemically polished without pre-treatment by acid pickling. We observed that the rough oxide layer still adhered to the stent surface. It reveals an even worse surface quality than that of the as-received non-polished sample. Thus, it can be concluded that the oxides on the surface of Ta stents could not be removed by means of electrochemical polishing alone. Pickling is a necessary pre-treatment step for electrochemical polishing for Ta stents that are covered with a rough oxide layer. During the experiment optical microscopy revealed no apparent changes on the surface of the stents when the samples were pickled for both 2.5 min and 5 min. When pickling time reached 7.5 min, some material had peeled off of the stent. Optical microscopy revealed that some oxide layers still adhered to the surface of the stent after pickling for 7.5 min. Additional oxides were peeled away in the solution when pickling lasted for 10 min. Pickling for 20 min was found to cause degeneration of the surface, i.e., the stent became useless because the struts were so weak. Therefore, when pickling of Ta stents is conducted, pickling time should be strictly controlled to remove all the oxides while avoiding surface degeneration.

Chemical polishing: In this study Chemical polishing had no effect on the Ta stents when observed by optical microscopy. The selected conditions for chemical polishing did not result in a satisfactory surface quality.

Electrochemical polishing: Electrochemical polishing of the tantalum stents was studied under various conditions. The applied voltages of 2.5, 5, 7.5, and 10 V were tested with electrolyte (i) for 2 min. Polishing at 2.5 V did not provide a satisfactory result. The surface was still rough. Polishing at 10 V for 2 min was also negative. The stent struts were damaged, due to loss of radial strength. The best result in these explorations was obtained at 5 V; the stent surface became shiny and smooth. Polishing times of 0.5, 1, 2, and

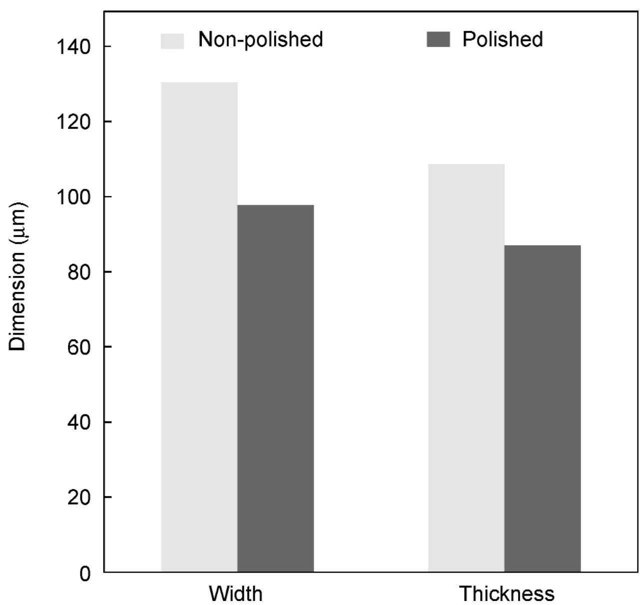

Figure 4. The dimensions of both non-polished and polished Ta stent (Medtronic, USA) struts.

3 min at 5 V were evaluated. Electrochemical polishing for 2 min at 5 V with electrolyte (i) resulted in the most satisfactory surface quality. The surface was still rough after being polished for 0.5 min and polishing for 3 min resulted in damage to the stent struts. Thus, electrochemical polishing with electrolyte (i) at 5 V for 2 min is a relatively suitable condition for polishing this type of Ta stent. In the study of electrolyte (ii), initial polishing was conducted at various times with a fixed voltage of 15 V. It was found that polishing for 9 min resulted in a relatively satisfactory result. The surface was still rough after polishing for 3 min and polishing for 12 min resulted in damage to the stent struts. Then the 9 min time period was fixed and the voltage was changed. Polishing at 10 V still gave a rough surface and polishing at 20 V caused damage to the stent struts. When the results for this group were compared, electrolyte (i) at 5 V for 2 min had the most satisfactory effect (Table 7).

Prior to the electrochemical polishing process, a pre-treatment with acid pickling was performed for 10 min. Figure 3d shows an SEM picture of a portion of the electrochemically polished Ta stent strut. Figure 3e shows the surface morphology of the stent strut. We observed a significant improvement in the smooth surface quality of the Ta stent. Figure 4 shows the dimensions of the stent struts measured from the SEM pictures. After electrochemical polishing at the optimal condition, the dimensions changed from approximately 130.40 × 108.70 mm (as-received stent struts) to 97.80 × 87.00 mm ; the width had decreased more than the thickness. This might result from the different oxide thicknesses on the different surfaces.

Discussion

Acid Pickling

Due to the formation of oxides on the surface of the as-received NiTi and Ta stents by laser cutting during the manufacturing process, a pre-treatment with pickling is necessary to remove these oxide films prior to electrochemical polishing. Acid pickling is defined as chemical removal of the surface oxides (scale) and other contaminants from metallic materials by immersion in an aqueous acid solution [15]. The general mechanism of removal of the oxide is penetration of acid through cracks in the scale and the reaction of the acid with the metal, which generates hydrogen gas. As the hydrogen gas pressure increases, a point is reached where the scale is blown off the metal surface [15]. Oxide films formed on the surface of Ti and Ti alloys can be satisfactorily removed by acid pickling in a mixture of HF and HNO_3. The ratio of HNO_3 to HF should be at least 15:1 [16]. In this study, acid pickling with HNO_3 and HF was used to treat NiTi stents (Table 1). Tantalum stents were also pickled in an acid solution prior to polishing (Table 2). The results show the significance of pre-treatment with the pickling process. Both NiTi stents (Figure 2d) and Ta stents (Figure 3c) that were electrochemically polished without pre-treatment by acid pickling prior to polishing revealed even worse surface qualities than those of the as-received samples (Figures 2c and 3a). The rough oxide layers still adhered to the surfaces of the stent struts. Pre-treatment prior to electrochemical revealed stents with smooth surfaces (Figures 2e and 3e). The oxides could not be removed by means of electrochemical polishing alone; pickling was a necessary pre-treatment step prior to electrochemical polishing for both NiTi stents and Ta stents that were covered with rough oxide layers. As mentioned in the literature [16], the recommended immersion times for pickling solutions should not be exceeded to avoid excessive stock removal. Pickling time is a critical parameter and it must be strictly controlled. Pickling for an insufficient time results in inadequate oxide removal, which in turn can influence the final polishing effect. However, if a suitable pickling time was exceeded, the surface could be attacked by the acid, resulting in excessive removal of the oxide layers. In this study, we tested various pickling times to find the optimal polishing condition. In order to control the effect of acid pickling, future trials should be conducted to determine the relation of the weight loss of the stents, their dimension and surface morphology with the pickling time.

Electrochemical Polishing

Electrochemical polishing is a method for brightening and smoothing the surface of metals [14,20] by immersing them in an electrolyte solution and then applying positive direct current to the sample. The main electrical parameters of the electrochemical polishing process are the anodic potential, the anodic current density and the applied voltage. The nature and rate of any electrochemical reaction are determined by the electrode potential. In practice, 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 [19]. In the present study, the applied voltage was selected as the controlling parameter during the electrochemical polishing process. The anodic current density was difficult to determine due to the specific shape of the stents. Electrochemical polishing generally occurs at the limiting current density (a current maximum or plateau in the current voltage curve) [18-21]. The rate of dissolution at the limiting current is controlled by the transport of cationic reaction products from the anode into the electrolyte [22]. Within the limiting-current plateau region, the applied voltage also plays an important role in the surface finishing [21]. In this study variations in the applied voltage were evaluated at a fixed time for a selected electrolyte. In order to observe the polishing results, an optimal applied voltage was fixed and electrochemical polishing was performed at various times. The process was applied to the different electrolytes. By evaluating the polishing results, optimal conditions for polishing either NiTi stents or Ta stents were obtained. Microscopic study of the resulting surface topography of the stents was qualitatively conducted by means of light optical microscopy or SEM. The present work only focused on finding an optimal condition for polishing either NiTi stents or Ta stents. Further work should be done to develop a practical process for polishing the stents. Parameters should include roughness and weight loss measurements, as well as mechanical tests to strictly control the electrochemical polishing process of both NiTi stents and Ta stents.

Electrochemical polishing of stainless steel, Ti alloy and Ta stents has already been studied by electrochemical methods [14,17,18,21-25]. Electrochemical polishing of stainless steel stents associated with animal models has shown positive results [11,12]. Electrochemical polishing was one of the methods used to study the influence of different surface treatments on the corrosion resistance of NiTi stents. It was found to improve the corrosion behavior of the alloy.

Conclusion

Electrochemical polishing could provide significant improvements in the surface quality of both NiTi and Ta stents under the optimal conditions obtained in this study. Prior to the electrochemical polishing process, a pre-treatment using acid pickling is necessary to remove the rough oxides on the stent struts.

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Contact
Prof. Dr. Ir. Jan Van Humbeeck
Department of Metallurgy and Materials Engineering
Katholieke Universiteit Leuven
de Croylaan 2
B-3001 Heverlee
Belgium
Telephone: +32 16 32 1281
Fax: +32 16 32 1992
E-mail: Jan.VanHumbeeck@mtm.kuleuven.ac.be