Surface Enhancement and Characterization of L-605 Cobalt Alloy Cardiovascular Stent by Novel Electrochemical Treatment

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Smooth surface is prerequisite for all implantable medical devices to increase biocompatibility. Electropolishing is an effective process for improving surface smoothness of the cardiovascular devices. In this study, electropolishing was employed on laser cut L605 Co-Cr alloy cardiovascular stents to increase surface smoothness. Acid descaling was used as a pretreatment before electropolishing for effective removal of metal oxides generated due to laser-cutting process. Effect of temperature during electropolishing on the rate of material removal was also evaluated. Passivation was carried out after electropolishing of stent to enhance its corrosion resistance in biological environment. The stent was characterized by Optical Microscopy for strut dimension analysis, Scanning Electron Microscopy and Atomic Force Microscopy for its surface smoothness, gravimetric analysis for evaluation of material removal uniformity, EDAX analysis for elemental composition and balloon expandability. It was found that elemental composition of stent remains unaltered after series of chemical treatments including the acid descaling and the electropolishing. Surface roughness of stent after electropolishing was reduced to significant level and such electropolished stents also demonstrated uniform expansion under specific required conditions.

Introduction

L605 (ASTM F-90) biomaterial is a nonmagnetic wrought Co-Cr-W-Ni alloy with high corrosion resistance [1]. It has a long clinical history in orthopedic implants, dental implants and more recently in cardiovascular stent applications, where its high density favors radiopacity, high elastic modulus, limiting recoil and strong tensile properties allows stent designs with thinner struts. It has clinically proven that thinner stent struts offers reduced restenosis rates after angioplasty [2].

Coronary stents have emerged as an effective treatment for occlusive vascular diseases to restore blood flow perfusion to the downstream tissues. The stent is mounted on a balloon catheter and delivered to the site of blockage. When the balloon is inflated, the stent expands and is pressed against the inner wall of the coronary artery. After the balloon is deflated and removed, the stent remains in place, keeping the artery open. Hence, the stent expansion defines the effectiveness of the surgical procedure. Therefore uniform opening of the stent strut is major concern for successful PTCA procedure. These can be achieved by uniformity of material removal in electropolishing process. The use of Cobalt based alloys in balloon expandable stent is rapidly growing world wide. Low thickness stent provides a lower crimped profile, less metal to artery ratio and improved flexibility/deliverability without compromising radial strength.

A roughened stent surface may result in increased frictional obstruction during insertion and excess drag during travel to the stenotic site as well as damaging the endothelium lining of the vessel wall [3]. Surface roughness also influences the amount of protein adherence as it determines the contact area [4]. Immediately following and in concert with the adsorbed proteins after stent implantation, the stent surface properties will determine platelet and leucocyte adherence. As such, the surface properties determine thrombogenicity, inflammation and vascular wound healing. As the surface characteristics influence directly the biocompatibility of the stents, a smooth surface obtained after electrochemical polishing can minimize thrombosis effectively and also has a potential beneficial effect on neointimal hyperplasia [5]. Surface prepared by electropolishing [6-9] have shown improved the performance of stents.

The aim of this research was to prepare smooth surface of L-605 coronary stent by electropolishing and characterize the surface properties of stent after series of fabrication processes. Acid descaling with the application of ultrasonic waves has been effectively utilized to remove laser generate metal oxides and burrs. To improve surface smoothness of the stent, a novel electrolyte and EP process has been investigated for coronary stents. Effect of various process parameters for electropolishing process has been optimized to get smooth and uniform surface. In order to characterize the surface morphology; various sophisticated analytical techniques such as scanning electron microscopy (SEM), and atomic force microscopy (AFM) were explored. Energy dispersive X-ray analysis (EDEX) was used to determine the subsurface composition of metal after different stages of processes. Passivation process has also been carried out as an approach to improve the corrosion resistance properties of metal when it is used as an implantable biomaterial. Expansion properties of investigated stent have been verified after crimping and expanding the stent on balloon catheter and results were collected as SEM micrographs.

Materials and methods

The L-605 Co-Cr alloy (ASTM F 90-07) annealed tubes (outer diameter 1.60 mm, thickness 110-115 µm) were procured from Minitubes, France and used as received. The material composition in wt % as per supplier specification was Cr (19.91), Ni (10.39), W (14.96), Fe (1.80), Si (0.17), Mn (1.21), C (00073), P (0.010), S (0.002) and Co (balance). These tubes were utilized for laser cutting (Star Cut Tube 18, Rofin Laser, Germany) to obtain stents of 16 mm length. Prior to laser cutting, tubes were initially cleaned using deionized water in an ultrasonic agitation bath for 15 min and were dried by hot air dryer (Philips Flex 1000, Japan). PTCA (Percutaneous Transluminal Coronary Angioplasty) balloon catheter used during the study was procured from Natec, Mauritius. It was made up of Nylon-12 material with PTFE coated stainless steel hypotube shaft. Two radiopaque markers were located underneath the balloon, which fluoroscopically marked its working length. Dimensions of balloon used was 3.0 x 17 mm, where 3.0 mm denotes the maximum diameter achieved at nominal inflation pressure and 17 mm denotes usable balloon length between two radio opaque markers. All Ranbaxy make chemicals sulfuric acid, hydrofluoric acid, perchloric acid, nitric acid, iso propyl alcohol and glycerol were of AR grade.

Acid Descaling

Laser micromachining generates slag, unwanted metal oxides and burrs at stent structure edges and inner surface. To achieve high degree of smooth surface after electropolishing, unwanted scale must be removed from the stent. Acid descaling was performed on laser cut stent to remove these slag, metal oxides and burrs. As-received laser-cut stents were first cleaned ultrasonically with deionized water and dried by hot air drier. Acid descaling was performed on the laser-cut stents by immersing them in to descaling solution having HF, HNO_3 and deionized water, at 45 °C for 200 minutes using ultrasonic waves operating at 43 kHz. Thermostat of ultrasonic cleaner (Branson 3510-DTH, USA) was used to maintain constant temperature of water bath After acid descaling treatment, the descaled stents were cleaned ultrasonically using deionized water for at least 15 minutes to remove traces of descaling agents and were then dried by hot air drier. Composition of the acid descaling solution and electrolyte

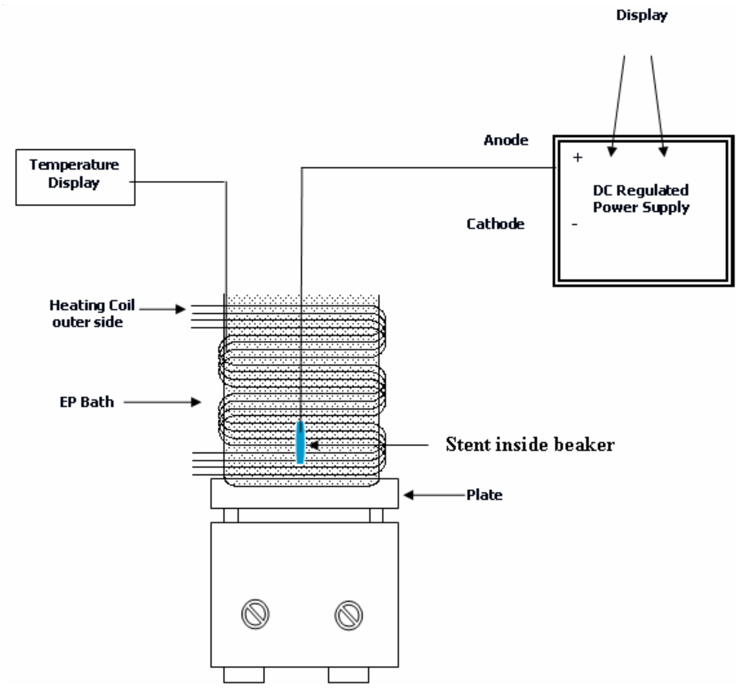


Figure 1: Schematic of electropolishing setup

formulation are 3ml HF, 20ml HNO3 and rest deionised water to make it 100ml.

Electropolishing

In order to achieve smooth surface, improved fatigue resistance, low friction, improved wetting and bonding properties of a very clean surface, material must under go surface treatment process which can produce defect free surface, remove irregularities, appropriate leveling and smoothness. Electro-chemical polishing is the process of obtaining better smoothness on the surface of the stent by anodically polarizing it in highly conductive electrolytes. It is classified into two processes: anodic leveling and anodic brightening [10]. A negatively charged ionic layer, usually referred to as "Anodic Layer" is formed at the surface of the work-piece mounted on the anode, which is positively charged and chromic ions are concentrated in this layer. The electrochemical reactions are as follows [11, 12].

Anodic: Metal - Electron(s) = Metal Ion

$4OH^- - 4\text{Electrons} = 2H_2O + O_2$

Cathodic: $2H^+ + 2\ \text{Electrons} = H_2$

Total Reaction: Metal Ions + Electrons = Metal

Important parameters which affect the electro-polishing process are current density, composition of electrolyte, temperature, process time, hydrodynamics of electrolyte and the area of substrate to be electropolished [13].

Schematic of electropolishing set-up and stent arrangement is shown in figure 1. A glass container was used as the electrolytic polishing cell (100 mm diameter and 500 mm high). A DC rectifier (Testronix 92D) was used for power supply (30V and 10A maximum). The descaled stent was connected to anode and a 304 stainless steel circular ring (diameter: 90 mm, thickness: 1 mm) was used as the cathode. The distance between these two electrodes was fixed at 45 mm. Electropolishing process was performed with continuous stirring of electrolyte by magnatic paddle. Optimized electropolishing parameters are Stent size 16mm; Volume 9V;

Current 0.24A; Temperature of 55ºC and Time of 300s. The temperature of the electrolyte was maintained by heating coil. After electropolishing process the stent was removed from the bath, rinsed with deionized water spray several times and dried with hot air drier.

Effect of Electropolishing Temperature on Material Removal

Electropolishing temperature remarkably influences the material removal rate. To analyze the effect of temperature on electropolishing process of stents, descaled stents were electropolished at different electrolyte temperature (45º, 50º, 55º, 60º and 65ºC) and reduction in stent weight was compared for each process temperature by gravimetric analysis. All other parameters (current, voltage, time, stent size) were kept constant during the analysis.

Gravimetric Analysis of Stents

Gravimetric analyses of each stent after laser-cutting, acid descaling and electropolishing was performed by an electronic analytical balance (Citizen CX-265, Germany, and Accuracy: 0.01 mg). Dimension measurement of each stent was carried out using a light optical microscope (OLYMPUS SZX 12) attached with CCD camera, which was calibrated with 1/100 mm calibration strip (Model OB-MM, Olympus, Japan) before the analysis. Percentage weight loss and width reduction of each stent was estimated by the following formula.

%Weight loss = (weight before EP – weight after EP)/ weight before EPx100

%Width Reduction = (width before EP – width after EP)/width before EPx100

For a batch, 10 stents were analyzed as above and average of the data was considered.

Passivation

Passivation process was employed after electropolishing to enhance corrosion resistance of the stent. The purpose was to enhance spontaneous formation of the protective passive film in order to achieve Cr_2O_3 enriched layer on the stent surface to improve corrosion resistance of stent under biological environment [14]. Passivation was carried out on electropolished stent using aqueous solution of 25% (v/v) nitric acid in deionized water for 30 minutes. Stents were immersed in the passivation solution which was kept in a beaker maintained at 75°C using constant temperature water bath. To prevent photolytic degradation of nitric acid, glasswares used for passivation process were of amber color. After 30 minutes, the stents were taken out and washed thoroughly with deionized water several times then with 25% sodium carbonate solution to neutralize acid traces. Again stents were rinsed with deionized water for complete removal of sodium carbonate. Finally the stents were stored till further investigation separately in a closed glass container filled with isopropyl alcohol to avoid microbial contamination.

Scanning Electron Microscopy and EDAX analysis

Evaluation of the qualitative surface morphology and elemental analysis was performed using Scanning Electron Microscopy (Philips XL30 ESEM TMP). It is preferable that the processes involved in the manufacturing of stent should not alter the chemical composition and thus mechanical performance of the alloy used to prepare the stent. The elemental analysis by EDAX was carried out simultaneously to evaluate material composition after different stages of stent fabrication and chemical surface improvisation processes.

Atomic Force Microscopy

The surface topology and quantitative roughness measurements were performed on acid descaled and electropolished stent by Atomic Force Microscopy (AFM). Roughness was measured by means of AFM instrument di-CP II, Veeco Asia. The samples were placed on platform of evaluation device and analysis area was monitored by attached CCD camera during the analysis. Entire analysis setup was kept on antivibration device for the accurate measurement of roughness. The evaluation area for AFM analysis was 30x30 micron.

Balloon Expandability of Stents

To examine expandability of the stents after surface treatment, they were expanded using commercial PTCA balloon catheter. Passivated stents (16mm long) were crimped on the 3.0x17mm balloon by means of automatic crimping machine SC 500 (Machine Solutions Inc, USA). The crimped stents were expanded by inflation device (Medtronic, Skimed- Sedat, USA). The pressure gauge was attached with the expansion device to measure the pressure applied to the balloon. Sterile water was used to inflate balloon for expansion of stents at nominal pressure of 6 bar as prescribed in compliance chart provided by balloon manufacturer. The balloon was kept dilated for approximately 45–60 sec and then deflated. The crimped and dilated stent symmetries were inspected by scanning electron microscopy.

Results and Discussion

Effect of Electropolishing Temperature on Material Removal

As shown in table 4 it can be seen that material removal rate increased with increase in process temperature. The rate of material removal was controlled between 50-60º C. Fig. 2(a) and 2(b) indicates optical images of the stent electropolished at 40 and 65ºC temperature respectively. Electropolishing at lower temperature resulted rough surface where as EP at high temperature resulted uncontrolled material removal with the uneven surface smoothness. Therefore temperature was optimized at 55ºC for the electropolishing process. Surface quality as well as dimensional data also supports this temperature range of electropolishing process as revealed by SEM analysis.

Table 4: Material removal rate at different temperature

Temperature (°C)	Initial Weight (gm)	Final Weight (gm)	Weight Difference (gm)
40	0.0212	0.0176	0.0036
45	0.0214	0.017	0.0044
50	0.02139	0.01657	0.00482
55	0.02139	0.01635	0.00504
60	0.02143	0.01594	0.00549
65	0.02142	0.01427	0.00715

Gravimetric Analysis

Table 5 represents the average data of gravimetric analysis of 10 stents and Table 6 represent those of strut widths / width reduction and wall thickness reduction of the laser cut, descaled and electropolished stent.

As shown, the laser cut stent has an average weight of 23 mg and a strut width of 101.5 µm. After acid descaling, there was a weight loss of 6.95 % and the stent strut width was decreased by 6.40 %. The reduction in stent weight and dimension is due to the removal of metal oxides and excess slag formed during laser cutting of stent. Due to electrochemical polishing, the weight and strut width of the stent decreased by 28.59 % and 40.88 % respectively. Therefore, after electropolishing the final average dimension of the stent strut was decreased to 60 µm from 105 µm. Figures 3, 4 and 5 illustrate uniform reduction in weight, strut width and wall thickness after each process. The data revealed that the rate of removal of material after electropolishing is excellently controlled.

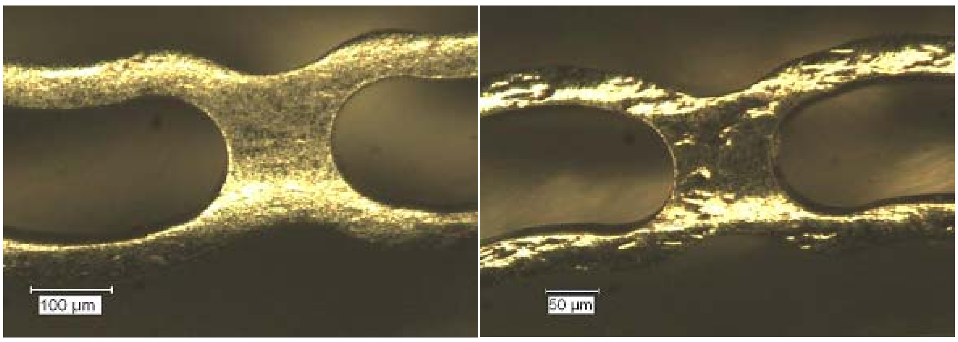


Figure 2(a): EP Surface at 40 °C; 2(b): EP Surface at 65 °C

Table 5: Average data of gravimetric analysis

Stent	Weight (mg)	Weight loss (%)
Laser Cut	23.01	---
Descaled	21.41	6.95
EP	16.43	28.59

Scanning Electron Microscopy

Fig. 7 (a), 8(a) and 9 (a) depicts inside surface of the stent while Fig. 7 (b), 8(b) and 9(b) represents stent cutting zones of the laser cut, descaled and electropolished stent respectively. As oxygen was used to assist the laser micromachining, formation of metal oxides and slag were prominent in presence of elevated cutting temperature (refer Fig. 7 (a) and (b)). As compared to outer surface, higher amount of metal oxides are found on cutting edge and inner surface. Acid descaling process was performed to remove these slag and metal oxides from the surface of the stent. Fig. 8 (a) and (b) shows descaled stent in which slag and metallic oxides have been successfully removed. However surface is appeared to be rough and sharp edges were observed on descaled stent which may damage the coronary artery during stent implantation and that's why electropolishing is necessary to perform. Descaling formulation and process has effectively removed metallic oxides from stent without creating any adverse effect. Fig. 9 (a) and (b) represents smooth surface after electropolishing without any surface defects or irregularities. This shows effective improvement of the surface characteristics by electropolishing of the stent. SEM image of electropolished stent reveals smooth stent edges so the no arterial damage will occur during stent navigation and implantation.

EDAX Analysis

In EDAX analysis element with an element number below 8 could not be detected, no carbon was detected in the results due to the limitation of the applied analysis method. Moreover, the expected concentration of C, Si, P and S is too low to be detected by EDAX so they were not identified. Table 7 shows the result of the composition analysis obtained using EDAX. Fig. 10 (a), (b) and (c) supports the data of laser cut, acid descaled and electropolished stent respectively.

As represented in Table 7, presence of oxygen in laser-cut stent is due to oxides generated during laser cutting process. In acid descaled stents, absence of oxygen confirms effective removal of oxides by acid descaling treatment. Further no amount of fluorine content on stent surface reveals absence of acid traces after descaling. Electropolished samples shows little amount of oxygen which represents formation of oxide film on the stent during passivation effect of electropolishing process. Therefore EDAX analysis reveals that there is no significant change in elemental composition of stent after acid descaling or electropolishing process.

Table 6: Average data of dimensional changes

Stent	Strut Width (µm.)	Wall thickness (µm.)	Width Reduction (%)	Wall thickness Reduction (%)
Laser Cut	101.5	115	---	
Descaled	95	110	6.40	4.34
EP	60	60	40.88	40.88

Table 7: Weight % data for stent cutting zone

Element	O	Cr	Fe	Co	Ni	W
Laser Cut	10.5	19.22	1.57	50.62	7.95	10.14
Descaled	0	22.91	1.07	53.84	6.94	15.23
Electropolished	4.32	21.37	2.17	52.14	9.38	10.63

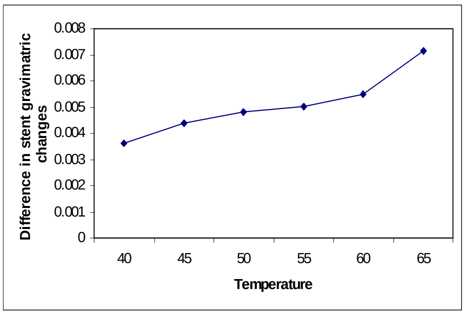


Figure 3: Temperature effect Vs gravimetric analysis

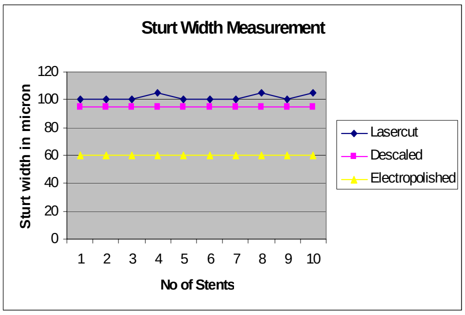


Figure 5: Plot of stent width after Laser cutting, Descaling and Electropolishing

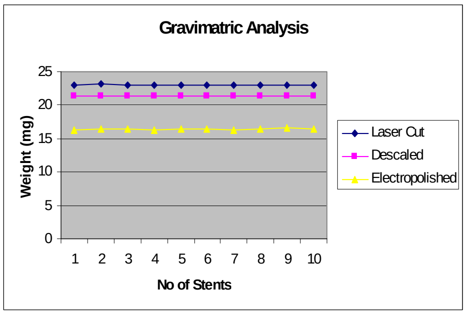


Figure 4: Plot of stent weight after Laser cutting, Descaling and Electropolishing

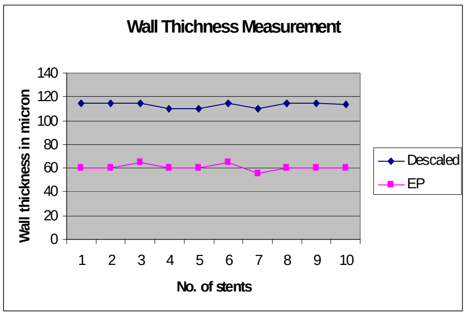


Figure 6: Plot of stent wall thickness after Descaling and Electropolishing

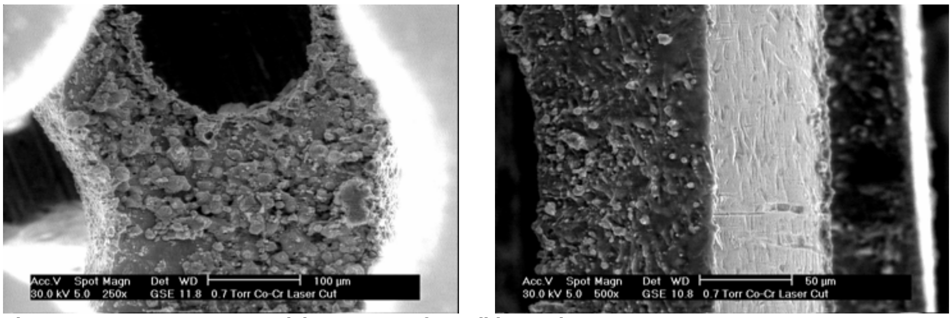


Figure 7: Laser cut stent (a) Inner Surface (b) Cutting Zone

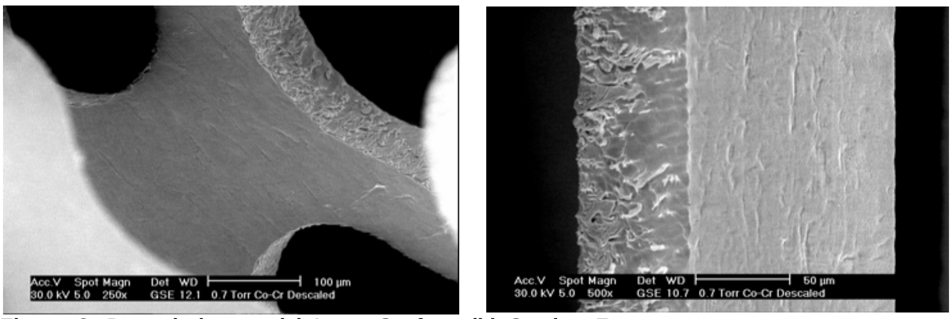


Figure 8: Descaled stent (a) Inner Surface (b) Cutting Zone

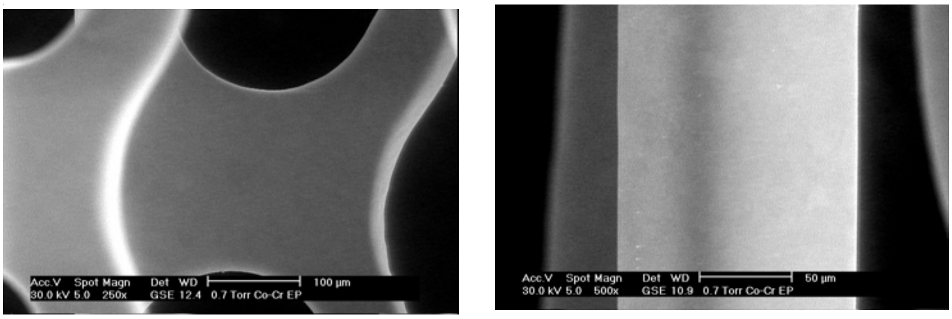


Figure 9: Electropolished stent (a) Inner Surface (b) Cutting Zone

Atomic Force Microscopy

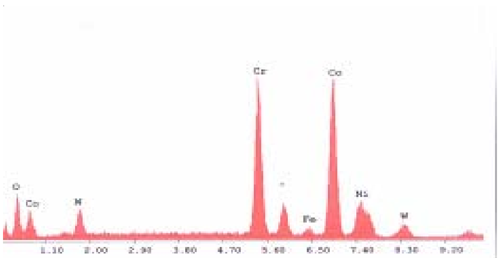
Figure 11 (a) and 11 (b) shows AFM images of acid descaled stent and electropolished stent surface respectively in 30x30 micron evaluation area. Comparison of both the images depicts that electropolished stent has significantly reduced surface roughness compare to acid descaled stent. This also reveals efficacy of electropolishing process to improve surface smoothness. It represents 78.66 % reduction of surface roughness after electropolishing process.

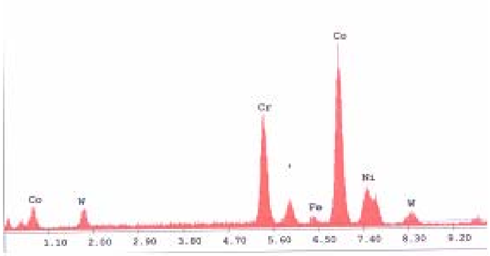
Balloon expandability of electropolished stent

The scanning electron microscopy images of stent crimping on balloon catheter is shown in Figure 12. The stent was found crimped on balloon catheter without overlapping of struts. The crimping profile of stent for 3.0 mm diameter balloon was 0.93 mm measured using contact micrometer. Low crimping profile ensures that stent can easily navigate through small vessels and tortuous blockages. The SEM investigation of expanded stent (Figure 13) revealed that at 6 bar of applied pressure, the stent was uniformly expanded to a diameter of approximately 3.0 mm. None of the struts were disproportionately expanded and appropriate straightening of struts observed between alternate links. Electropolishing process has significant influence on stent expansion properties which is important in stent implantation during angioplasty because uneven material removal can lead to improper scaffolding to artery.

Conclusion

Scanning electron micrographs reveals that acid descaling effectively removed metal oxides generated during laser machining of Co-Cr tubes. The explored electropolishing solution and process conditions significantly improved





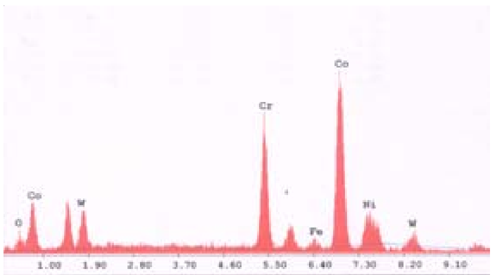


Figure 10: EDAX Analysis, (a) Laser cut stent, (b) Acid descaled stent (c) Electropolished stent

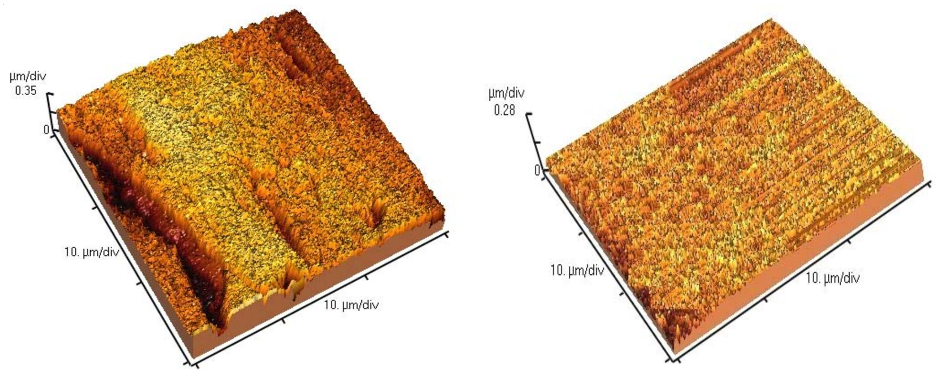


Figure 11: AFM images of stent in 30 X 30 Micron area (a) Acid descaled (b) Electropolished stent

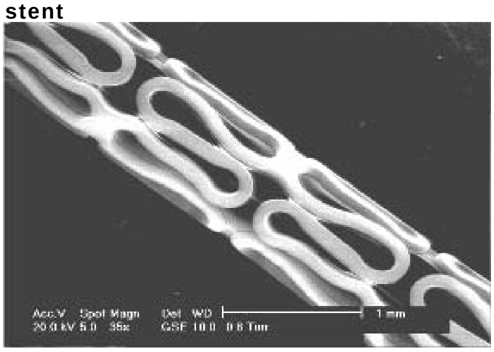


Figure 12: SEM of Balloon crimped stent

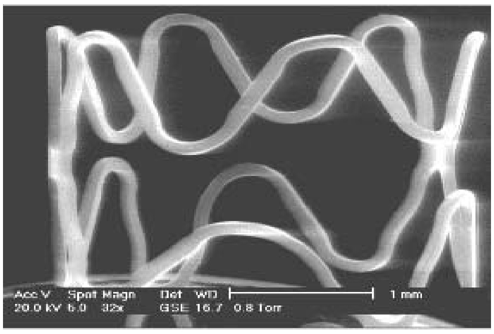


Figure 13: SEM of expanded stent

surface smoothness as confirmed by the SEM and AFM analysis. EDAX analysis reveals no significant change in elemental composition of stent after acid descaling or electropolishing process. AFM analysis shows significant reduction in surface roughness (78.66%) of stent after electropolishing process.

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