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Electropolishing of 316LVM Stainless Steel Cardiovascular Stents: An Investigation of Material Removal, Surface Roughness and Corrosion Behaviour

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Smooth surface of a cardiovascular stent is an important factor in determining biocompatibility. Electropolishing is an effective method for improving surface smoothness of the stents. In this study, electropolishing has been employed on laser cut SS316L cardiovascular stents to increase surface smoothness. Acid pickling has been used as a pre-treatment for electropolishing followed by passivation to enhance its corrosion resistance in biological environment. Stent has been characterized by strut dimension analysis, Scanning Electron Microscopy for its surface smoothness, gravimetric analysis and potentiodynamic corrosion analysis. It was found that surface roughness after electropolishing has been reduced to significant level and also long-term corrosion behavior of stent material in simulated biological fluid (PBS) is very stable.

Introduction

Metallic coronary stents are included in category class III medical device [1]. The stents are used to scaffold a biological lumen, mostly diseased arteries after Percutaneous Transluminal Coronary Angioplasty (PTCA) and to maintain the patency of a blood vessel immediately after vascularization treatment [2,3]. Compared to balloon angioplasty, PTCA with stenting improves the safety and efficacy of the intervention, especially by preventing the abrupt vessel closure. The stents are made from surgical grade materials like 316LVM Stainless Steel, L605 Cobalt Chromium alloy and Nickel Titanium alloy etc. It is inevitable for such stents to have smooth and athrombogenic surface to enhance biocompatibility. Such stent surface is obtained by electropolishing treatment. The surface of the stent must be extremely smooth so that the stent can be inserted easily and travel through the tortuous vessel pathway prior to implantation. Surface roughness influences the amount of protein adherence, as it determines the contact area of the stent with coronary artery [4]. As such, the surface properties of the stent determine post stent implantation complications like thrombogenicity and tissue reaction i.e., the nature of the metal surface is crucial to blood compatibility [5,6]. A smooth surface can help prevent the activation and aggregation of platelets, which is recognized as one component of the thrombosis process. It is inevitable to have smooth and finished surface of the stent. Electropolishing minimizes thrombosis effectively and provide potential beneficial effect on neointimal hyperplasia [7]. The aim of this work is to characterize the electropolished SS316LVM stent for it's surface smoothness and corrosion resistance after different stages of production.

Materials and methods

316LVM Stainless Steel (ASTM F138) annealed tubes were procured from Minitubes, France and used as supplied. The material composition in wt % reported was Cr (17.00–19.00), Ni (13.00–15.00), Mo (2.25–3.00), Mn (<=2.00), Si (<= 0.75), C (<=0.03), P (<=0.025), S (<=0.01) and Fe (balance). These tubes were utilized for laser cutting (Star Cut Tube 18, Rofin Laser, Germany) to obtain stents of 16 mm length and 1.720 mm outer diameter and wall thickness of 110-115 microns. All Ranbaxy make chemicals sulfuric acid, hydrofluoric acid, nitric acid and ortho phosphoric acid were of AR grade.

Acid Pickling

Acid pickling was carried out to remove slag and metal oxides attached after laser micromachining of stents. As-received lasercut stents were first cleaned with deionized water spray and dried by hot air drier. Acid pickling was performed on the laser-cut stents by immersing them in an acid solution having HF, HNO_3, and H_2O, at 45°C for 15 minutes by ultrasonic cleaner [8]. Thermostat of ultrasonic was used to maintain constant temperature in ultrasonic water bath (Branson 3510-DTH, USA). After Acid pickling treatment, the pickled 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 dryer (Philips Flex 1000, Japan). Composition of the acid pickling solution is as follows; HF 1ml, HNO_3 9ml and DI water 90 ml.

Electropolishing

Electropolishing is the process of obtaining better smoothness on the surface of the stent by anodically polarizing in highly conductive electrolytes. The stent is made polarized by desired level of DC current or voltage. This polarization provides anodic leveling and anodic brightening [10], due to difference in the dissolution rates of the peaks and valleys on the rough surface, current distribution and mass transport. By anodic polarization, the peaks and valleys are removed at the different rates (anodic leveling) and the smoothness is achieved up to the desired level. A smooth electropolished surface, which appears bright to the naked eye, results from a combination of these two factors [11].

An indigenous Electropolishing set up and stent arrangement is shown in fig. 1. A glass container was used as the electrolytic polishing cell (110 mm diameter and 200 mm high). A DC rectifier (Testronix 93C) was used for power supply (30V and 10A maximum). The pickled stent was used as an anode and a 304 stainless steel was used as the cathode. The distance between these two electrodes was fixed at 50 mm. Electropolishing parameters used are stent size - 16mm, voltage - 9.5 V, current 0.44 A, temperatutre - 75C, and time - 180 s. The electropolishing solution consists of H_2SO_4 and H_3PO_4 each at 50%(v/v). The temperature was controlled by a heater cum magnetic stirrer equipped with thermostat device. After electropolishing process the stent was removed from the bath, rinsed with deionized water spray several times and dried with hot air drier.

Gravimetric Analysis of Stents

Gravimetric analyses of each stent after laser-cutting, acid pickling and electropolishing was made by an electronic analytical balance (Citizen CX-265, Germany). Dimension measurement of each stent was carried out using a light optical microscope (Carl Zeiss, Stemi 2000C) 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 EP

Reduction = (width before EP – width after EP)/width before EP

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

Passivation

Corrosion resistance of passivated stent is mainly due to passive film of Cr_2O_3 on outer surface. This film is very stable and self repairing in nature when exposed to the chemical species present in the aggressive medium. Passivation is the process of removing exogenous iron or iron compounds from the protective surface of stainless steel by means of a chemical dissolution i.e. making the passive film free from impurities and improving the

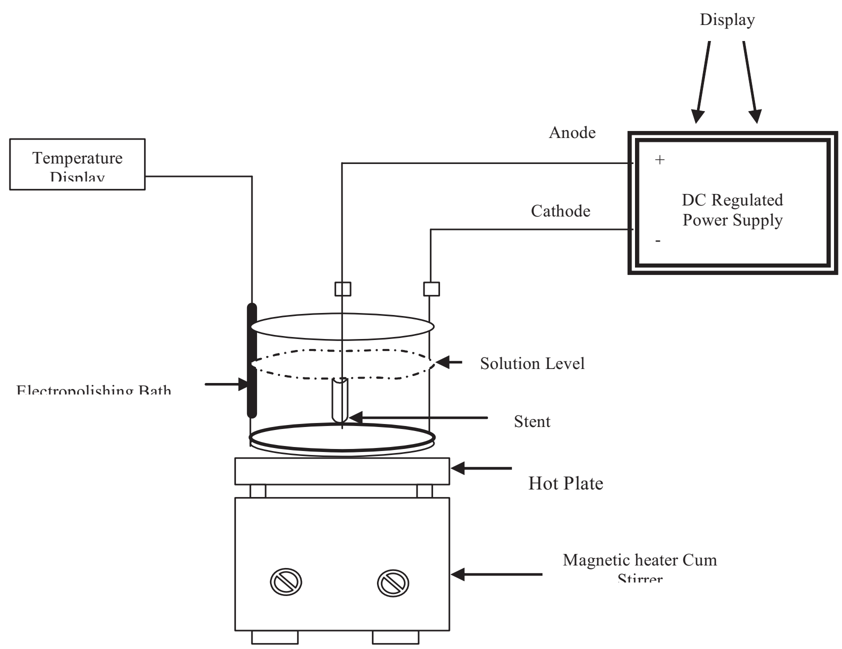

Figure 1: Schematic of electropolishing setup

quality of the passive film. The purpose is 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 highly corrosive biological environment [12]. Passivation was carried out to all electropolished stents using passivation solution containing 25% (v/v) Conc. Nitric acid and 75% (v/v) deionized water for 30 minutes. Water bath was used to achieve temperature 75 °C in the passivation solution. Further the stents were washed with deionized water several times then with 25% sodium carbonate water to neutralize acid traces and again washed with deionized water for complete removal of sodium carbonate. Finally the stents were stored separately in a closed glass container filled with Isopropyl alcohol to avoid microbial contamination for long term storage.

Roughness Measurements of Stents

Roughness measurements were performed on acid pickled and electropolished stents. Evaluation of the surface morphology was carried out by Scanning Electron Microscopy (Philips XL30 ESEM TMP) and Atomic Force Microscopy (AFM). Quantitative roughness was measured by means of AFM (di-CP II, Veeco Asia, Singapore**).** The evaluation area for AFM analysis was 1 micron.

Corrosion Resistance Analysis

Corrosion tests were conducted on each of the laser cut, pickled, electropolished and passivated stents in Phosphate Buffer Saline solution (PBS) at pH 7.4 and 37±1 °C constant temperature [13]. Open circuit potential was used to measure corrosion potential stabilization in PBS solution for 1000 second with respect to saturated calomel electrode. Potentiodynamic plot was obtained using Potentiostat/Galvanostat (make EG & G Princeton Research, USA with M 352 Corrosion Software). Polarization of samples were carried out from -250 mV open circuit potential to 1000 mV with respect to reference electrode, scanning rate was 0.1 mV/Sec and conditioning was done at -1.0 V for 60 seconds.

Table 1: Weights and weight losses changes of stents

Stent	Weight (mg)	Weight loss (%)
Laser Cut	26.11	--
Descaled	24.17	7.43
EP	19.82	17.99

Table 2: Strut dimensions and dimension changes of stents

Stent	Strut Width (μm.)	Reduction (%)
Laser Cut	150.5	---
Descaled	147	2.32
EP	115	21.76

Results and Discussion

Gravimetric Analysis of Stents

Table 1 represents the average data of gravimetric analysis of 10 stents and the Table 2 those of strut widths / width reduction of the laser cut, pickled and electropolished stent. As shown, the laser cut stent has an average weight of 26.11 mg and a strut width of 150.5 ìm. After acid pickling, there was a weight loss of 7.43% and the stent strut width was decreased by 2. 32%. 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 17.99% and 21.76% respectively. Therefore, after electropolishing the final average dimension of the stent strut was decreased to 115 ìm from 147 ìm. Figure 2 and Figure 3 illustrate stable variation in weights and strut width respectively after each process. The data revealed that the rate of removal of material is excellently controlled and material removed from the stent after electropolishing is constant.

Scanning Electron Microscopy

Clearly visible slag material, as shown in fig. 4(a), was formed due to high temperature laser cutting process. Acid pickling process was carried out to remove these slag and metal oxides from the surface of the stent. Fig. 4(b) shows pickled stent in which slag and metallic oxides have been removed. However surface roughness is appeared to be rough and sharp edges were observed on pickled stent which may damage the coronary artery during PTCA. Fig. 4(c) shows 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 less/no arterial damage will occur during stent expansion.

Atomic Force Microscopy

Figure 5 (a) and 5 (b) show AFM images (surface Topography) of acid pickled stent and electropolished stent surface respectively in 1 micron evaluation area. Comparison of both the images shows that electropolished stent surface has very less roughness as compared to that of the acid pickled stent. Fig. 6 shows effect of electropolishing process to improve surface roughness. The observed roughness of pickled stent and electropolished stents are shown in Table 3. This indicates that there was 78.10 % reduction in roughness. By AFM study also it can be said the process of electropolishing is an effective means to improve the surface characteristics.

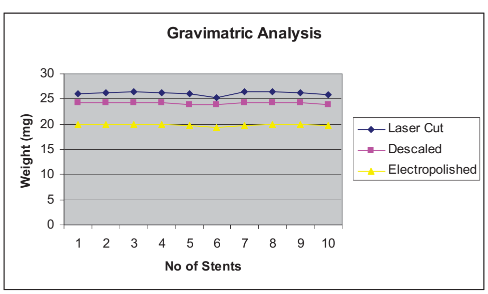

Figure 2: Plot showing variation in stent weight

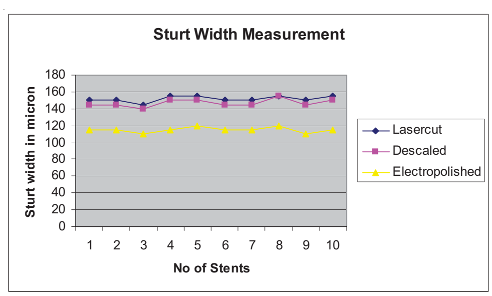

Figure 3: Plot showing variation in stent width

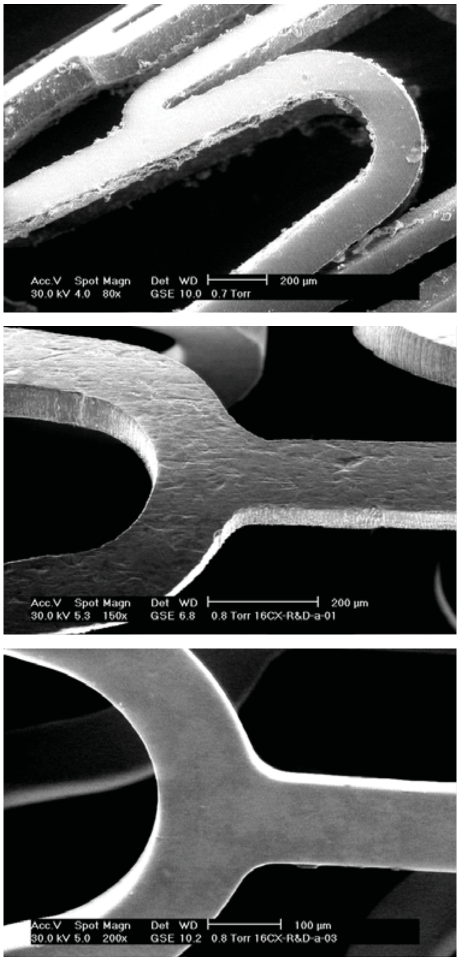

Figure 4: SEM images of (a) Laser cut stent, (b) pickled stent, (c) electropolished stent

Table 3: Values of roughness measurement (5 micron area)

Stent	Ra	Rq	Rp	Rv
Descaled	250 nm	97.56 nm	208.7 nm	-130 nm
EP	14.77 nm	4.895 nm	32.49 nm	-8.921 nm

Table 4: Results of polarization techniques and Corrosion rates

Sample	E_{Corr} (mV)	I_{Corr} $\mu A/Cm^2$	C.R mpy
Laser Cut	-258.6	1.092	0.504
Descaled	-325.9	3.937	1.819
Electropolished	-172.9	8.818	4.069
Passivated	334.6	1.09	0.475

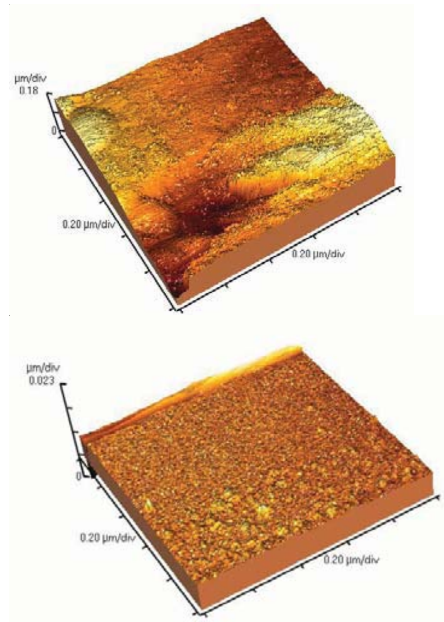

Figure 5: High-resolution AFM images of stents (a) Acid pickled stent (b) electropolished stent

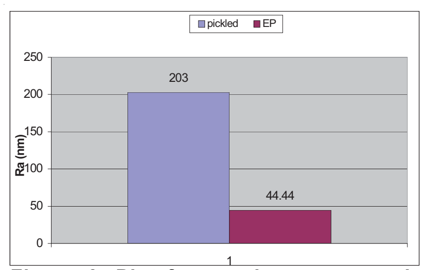

Figure 6: Plot for roughness comparison (5µ area)

Corrosion Resistance Analysis

Figure 7 (E vs t plots) shows that acid pickled (descaled) sample have taken longer time even after 500 second for stabilization of potential which indicated that there was undesired surface roughness. Both electropolished and laser cut samples have shown fluctuations only after 500 Seconds which indicated that the electropolished surface of the stent, having improved surface characteristics, was still sensitive to mild corrosion attack by PBS. The figure also reveled the stability of potential only

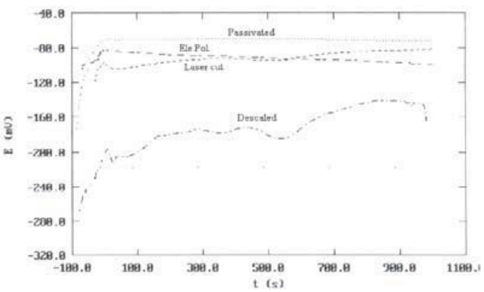

Figure 7: Corrosion Potential Stabilization Curve

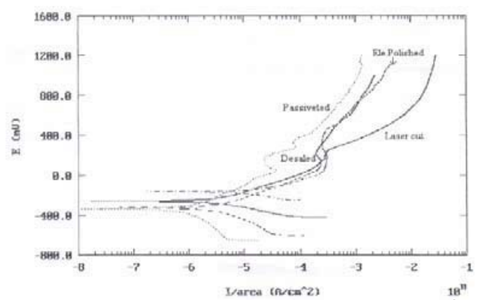

Figure 8: Potentiodynamic test curves for passivity and Corrosion rates

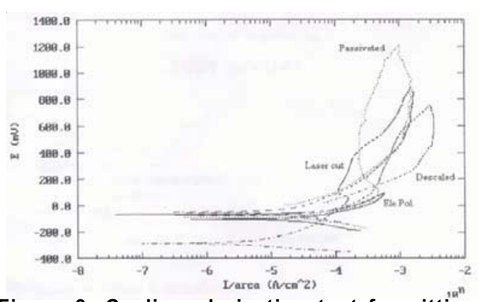

Figure 9: Cyclic polarization test for pitting potential evaluation

up to 500 Seconds even on the laser cut sample possibly due to formation of preventive scales which might have been formed due to laser cutting but there was deviation in potential. The later indicated the presence of roughness due to impurity on the laser cut surface. By acid pickling and electropolishing, the scales created by laser cutting have been removed and the smoothness on the electropolished stent was further at desired level by passivation treatment. This passivation has enhanced the surface characteristics by formation of excellent passive film of $C_{r2}O_3$ resulting in to improved corrosion resistance to the attack by PBS.

Figure 8 shows nobler potentials of laser cut, pickled, electropolished and passivated stents which indicated the improvement in the smoothness of acid pickled samples after electropolishing and subsequent passivation. The potentiodynamic curves also revealed the decrease in corrosion current density (rate) of the acid pickled and laser cut samples when subjected to electropolishing followed by passivation. Both the observation of corrosion potentials and corrosion rates have favored the effect of electropolishing followed by passivation to improve the quality and cleanliness of passive film which was due to excellent corrosion resistance of the passive film.

As shown in Figure 9 the cyclic polarization curve have indicated the Epp (pitting potential initiation) values of passivated, acid pickled and laser cut stent samples as 234, 96 and 107 mV respectively which indicated the highest resistance to pitting attack by passivated sample and the lowest by the acid pickled sample. In case of electropolished sample there was no point of intersection on the anodic polarization curve during reversal which has reflected that electropolished surface has though excellent smoothness on but has no protection to pitting because of the absence of protective oxide film this has clearly shown the need of passivation treatment after electropolishing. Table 4 has revealed most active E_{Corr} (Corrosion Potential) of the acid pickled stent -326 mV to show the roughest surface and most noble +335 mV which indicated the formation of highly protective and passive film. The table also indicated corresponding I_{Corr} (Corrosion Current) and Corrosion Rate (C.R) values which were decreased in case of passivation form 4 ìA/cm^2 to 1.1 ìA/cm^2 and C.R from 2 mpy to 0.5 mpy for pickled and passivated samples respectively. The surface roughness of laser cut sample was decreased compare to electropolished by the shift of ECorr value of -259 to -173 mV. Corresponding change in I_{Corr} and C.R also shown in the table. During electropolishing maximum corrosion rate has been observe as supported by about ICorr 9 ìA/Cm2 and 4 mpy. Due to anodic dissolution as far as corrosion rate is concerned both the laser cut and passivated samples have shown the similar ICorr and C.R values which shows the present protective layer on the surface however there was clear indication the surface roughness in these two types of samples as discussed above by observation of E_{Corr}.

Conclusion

The quality of the surface of 316LVM stainless steel coronary stents was very much improved when subjected to electropolishing followed by passivation. This conclusion has been excellently supported by the data obtained by Scanning Electron Microscopy, Atomic Force Microscopy and Potentiodynemic and Cyclic Polarizations largely and their judicious interpretation. Passivation process has enhanced the corrosion and pitting resistance of the stent in severe blood contacting human body environments.

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