

PULSE AND DC ELECTROPOLISHING OF STAINLESS STEEL FOR STENTS AND OTHER DEVICES

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Abstract— This paper describes optimized conditions for the electropolishing of austenitic type 304 and 316L stainless steels in commercially-available EPS 4000 solution (based on a mixture of phosphoric and sulfuric acids) for use in cardiac stenting applications. Electropolishing parameters such as electrolyte temperature and concentration, current density, polishing duration, use of pulsed current and ultrasonic agitation have been explored and optimal conditions have been found. Quality of the polishing was determined on the average surface roughness, amount of thickness reduction, and overall surface appearance. Samples polished in an ultrasonic bath with pulsed currents of 50 Hz, and 60°C achieved the lowest surface roughness with little or no evidence of surface defects which were present in other recipes. Similar results were seen in both types 304 and 316L stainless steels.

I. INTRODUCTION

Since the beginning of the twentieth century, electropolishing has extensively been used as a tool for removing surface abrasions on metals. In the biomedical field, electropolishing is especially useful for the surface treatment of stainless steel cardiac stents. Planar stents seen in Fig. 1 have been fabricated out of stainless steel 304 by means of micro-electro-discharge-machining (μ EDM) [1]. However, the nature of the μ EDM process leaves behind sharp edges and creates burrs on the surface of the stent, and if internally implanted without proper surface treatment, it could induce thrombogenicity and neointimal hyperplasia [2].

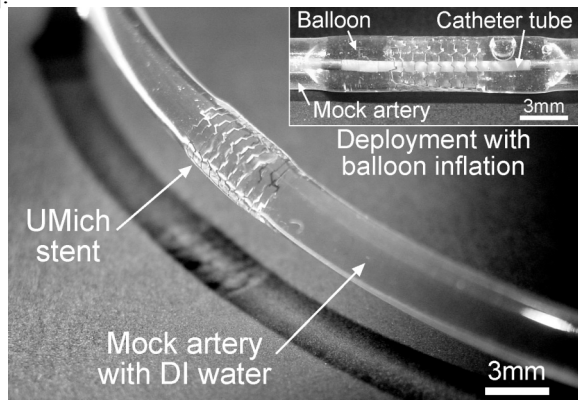


Figure 1. Planar Stent fabricated using μ EDM [1].

Cardiac stents are typically implanted in arteries using balloon angioplasty as a method of treatment for several arterial disorders. These include the re-narrowing of arteries (restenosis), formation of blood clots (thrombosis), extravascular tissue growth (proliferation), and the deposition of more plaque on the arterial wall [3]. Our objective is to find the optimal conditions for electropolishing stainless steel so as to reduce the likelihood of the aforementioned disorders from occurring while retaining or improving the mechanical strength of the stent itself.

II. BACKGROUND

Since stainless steel is primarily composed of iron, there has been much success in producing a more polished surface via oxidation-reduction chemistry. Electropolishing is generally performed in an aqueous acidic bath under carefully controlled conditions [4]. There are many factors that affect whether electropolishing occurs and the quality of the polished piece. Such factors include current density, concentration and temperature of solution, polishing duration, frequency of applied current, and the method of agitation [5, 6, 7]. These parameters must be adjusted to achieve the optimal result depending on the application.

Dissolution of the anode is greater at its asperities due to a higher current density at these locations. This dissolution of the metal creates a viscous film adjacent to the metal's surface, which in turn aids the electropolishing process by masking the recesses of the surface, and allowing the peaks to be etched faster [5]. Due to these uneven etch rates the surface becomes polished. However, there is a net thickness reduction, which presents a major challenge to the electropolishing technique. For our purposes, we require a surface roughness of less than 100 nm, while minimizing thickness reduction. Excessive reduction of the thickness would compromise the mechanical strength of the stent itself. The removal of sharp corners and burrs is also very important to the biocompatibility of the polished stent.

III. EXPERIMENTAL RESULTS

The overall surface quality of the electropolished stainless steel can be characterized by three components: (1)

average surface roughness, (2) amount of pitting, and (3) surface brightness. The latter two are qualitative observations while surface roughness can be quantified through use of an interferometer or a surface profiler. Surface roughness measurements describe how well the polishing did at removing surface asperities and making an overall planar surface. Pitting is a result of the evolution of gas bubbles on the metal's surface. Minimizing the formation of bubbles is necessary in order to avoid pitting and achieving a higher quality finish. Lastly, the degree of surface brightness or luster of the sample after polishing determines if the electropolish was successful in creating a surface with a high chromium and nickel content. This is desirable as it improves the corrosion resistance as well as the mechanical strength of the stent.

A. Procedure

The electropolishing experiments were performed on multiple samples of type 304 and 316L austenitic stainless steels, with thicknesses of 50 and 100 microns, and an initial surface roughness (R_a) of 220 and 110 nm, respectively. The samples were diced into sizes of 5mm x 5 mm and then cleansed in an ultrasonic bath of acetone. The samples were fastened to a Teflon jig, which houses electrical connections for both the anode and cathode, and then polished in 500 mL of EPS 4000 electropolishing solution (which is based on a mixture of phosphoric and sulfuric acids, distributed by Electro Polish Systems, Brown Deer, WI, USA) at nominal temperatures that were between 60°C and 70°C and a current density of 323 mA/cm². Agitation in the electropolishing tank was achieved by using a hot plate with stirring capability, set at a nominal rate of 150 RPM. After polishing, the samples were rinsed in a series of baths of (1) acetone, (2) isopropyl alcohol, (3) DI water, and finally dried using compressed nitrogen.

B. Effect of Pulsed Current and Ultrasonic Agitation

A pulsed current was applied to different samples at varied frequencies and duty cycles. From Fig. 2, it is evident that surface roughness increased while frequency was increased. This was possibly because at higher frequencies, the duration of the current pulse is not long enough to reach the sufficient steady state for proper polishing to occur. From Fig. 3, increasing the frequency led to an increase in thickness reduction. Figures 2 and 3 show more thickness reduction and surface polishing occur when the duration of the pulses is longer. With a longer duration, the sample's surface becomes more planar as the slag and sharp edges are removed, resulting in lower surface roughness values. However, this means that more material is lost and therefore the thickness will be decreased.

Changing the duty cycle also affected the surface roughness and thickness. Reducing the duty cycle decreased the thickness reduction but the surface remained relatively unpolished. Increasing the duty cycle had the opposite effect on the surface.

Ultrasonic agitation has been noted to reduce the incidence of pitting in electropolished stainless steels [7, 8]. However, ultrasonic agitation was used to replace mechanical stirring and under the same conditions it showed no drastic improvement in surface roughness reduction. The same experiment was tried with a pulsed current at 55.5 Hz, 100 Hz, and 500 Hz. The results show a reduction in surface roughness of approximately 0.05 microns on average, comparing pulsed with mechanical stirring (discussed later) and pulsed with ultrasonic agitation.

In general, all of the samples that used ultrasonic agitation showed a drastic decrease in the amount of pitting on the surface. In addition, the surface appeared much more bright compared to samples with a pulsed current and mechanical stirring. Ultrasonic agitation is one method of obtaining a very uniform and quick removal of gas forming on the surface of the anode. Both ultrasonic and mechanical agitation appears to have similar effects on surface roughness in DC experiments. With a pulsed current, ultrasonic agitation clearly has an advantage. The reason for this result may be because during the pulse "off" time, more of the gaseous layer on the anode is removed. Mechanical stirring does not exhibit this behavior in pulsed current experiments.

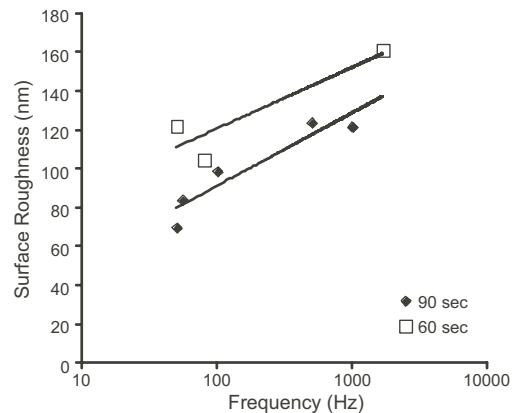


Figure 2. Surface roughness against frequency and duration.

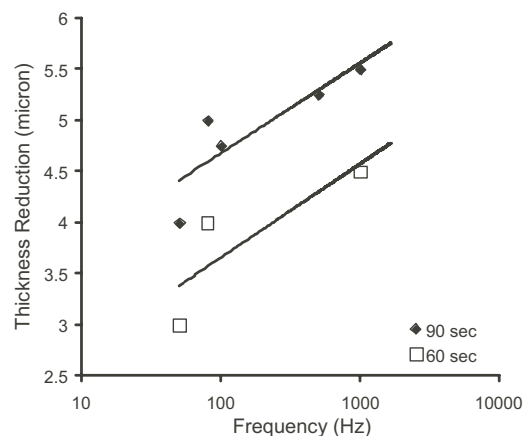


Figure 3. Thickness reduction against frequency and duration.

C. Effect of Varying Current Density and Temperature

It is known that for many metals and electrolytes in an electropolishing setup, a distinctive ‘plateau region’ in the I-V curve exists [5, 6, 9, 10]. Figure 4 shows the I-V curve for type 304 stainless steel. It has been reported that the optimal current density for electropolishing lies at the end of the ‘plateau region’ in stainless steels [6]. Increasing the current density did result in a smoother and more polished surface while sacrificing more material loss, due to an increase in the mass transport rate.

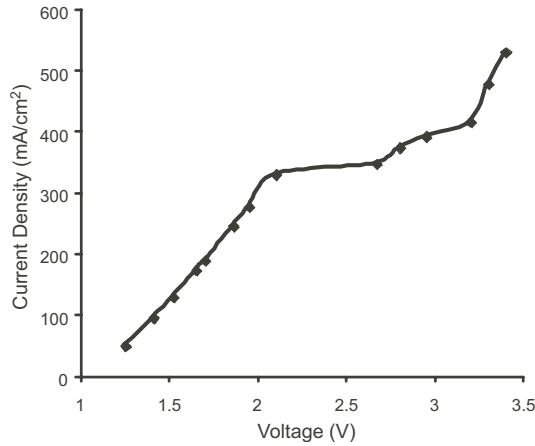


Figure 4. I-V curve for type 304 stainless steel at 150 RPM and 65°C

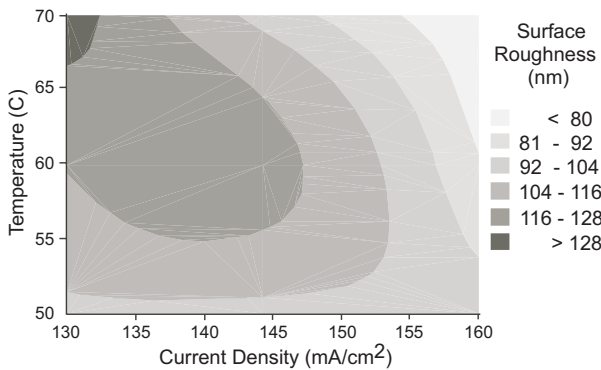


Figure 5. Effect of varying temperature and current density on surface roughness in type 304 SS.

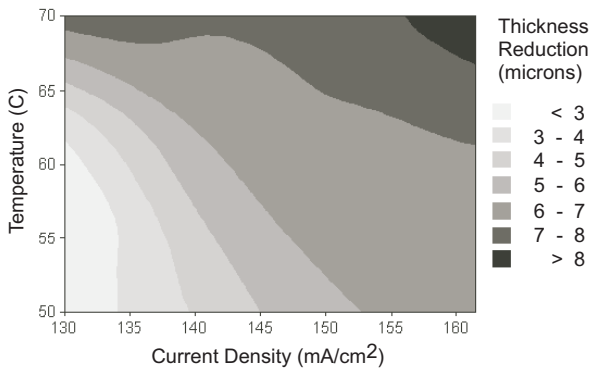


Figure 6. Effect of varying temperature and current density on thickness reduction in type 304 SS.

Figures 5 and 6 shows the contour plots of surface roughness and thickness reduction while varying temperature and current density. The best polishing and the most thickness reduction takes place at higher temperatures and current densities. In our application, it is important to achieve a low surface roughness ($R_a < 0.1 \mu\text{m}$) while keeping the thickness reduction to a minimum. The contour plots identify the regions where acceptable polishing has taken place, and can be used as a tool to obtain optimum conditions for the electropolishing of type 304.

D. Effect of Varying Stirring Speed

The mechanical stirring of the electrolyte by use of a hot plate with stirring capability, can reduce the incidence of pitting and decrease bubble tracks on the surface of the anode [7, 11]. By stirring the electrolyte, the evolved gas on the anode in the form of bubbles is flushed away by agitation before it can leave tracks on the surface.

From Fig. 7, there is a minimum in both thickness reduction and surface roughness as stirring speed is varied. This phenomenon has also been observed in [12]. It is possible that stirring effects may start to increase the surface roughness after a certain point by removing too much of the viscous film which prevents low-lying areas of the surface from being etched. Thus, the best stirring speed conditions must be experimentally determined because geometry of the electropolishing tank, temperature, type of metal, and current density all affect the location of the minima.

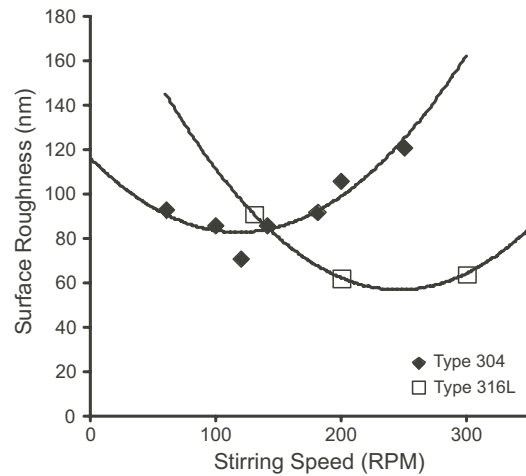


Figure 7. Varying stirring speed for type 304 and 316L SS.

E. Effect of Varying Electropolish Concentration

Relatively high surface roughness resulted diluting the EPS 4000 electropolish solution with deionized water. Solutions of EPS 4000 (60% and 30% vol.) were used to polish for 5 minutes at 70°C and 323 mA/cm². The finish was highly pitted using the 30% EPS solution, with pits appearing as actual craters in SEM micrographs. The cratering effect disappeared with 60% EPS, but the metal grain was highly visible suggesting that electropolishing did not take place.

F. Effect of Varying Anode-Cathode Separation

Anode-cathode separations of 3, 5, 7, 10, 15, and 20 mm were used with type 304 SS and it was found that surface roughness was lowest at 3 mm ($R_a = 72$ nm) and 20 mm ($R_a = 69$ nm), and approximately 100 nm at 10 mm. The thickness reduction appeared to remain constant throughout. The results here are most likely due to the agitation in the electropolish bath. With sufficient agitation, placing the electrodes closer together has been shown to decrease surface roughness, as the current becomes more spatially directed [6]. At large separations (> 10 mm) current density is more uniform over the piece and therefore a smoother surface is achieved [13].

G. Electropolishing of 316L Stainless Steel

Samples of 316L with an initial surface roughness of 110 nm were polished under similar conditions to type 304 stainless steel. It was observed that certain polishing conditions can further improve the surface roughness in 316L. Specifically, it was observed that at 65°C , 323 mA/cm², and 200 RPM, the surface roughness reduced to 62 nm after polishing for 90 seconds. However, other conditions can result in no improvement or even worsening of the roughness. In general, it can be stated that for conditions ranging between $65\text{--}70^\circ\text{C}$, $310\text{--}330$ mA/cm², $150\text{--}200$ RPM, and a duration of 90 seconds, the average surface roughness of the final sample will be $60\text{--}100$ nm.

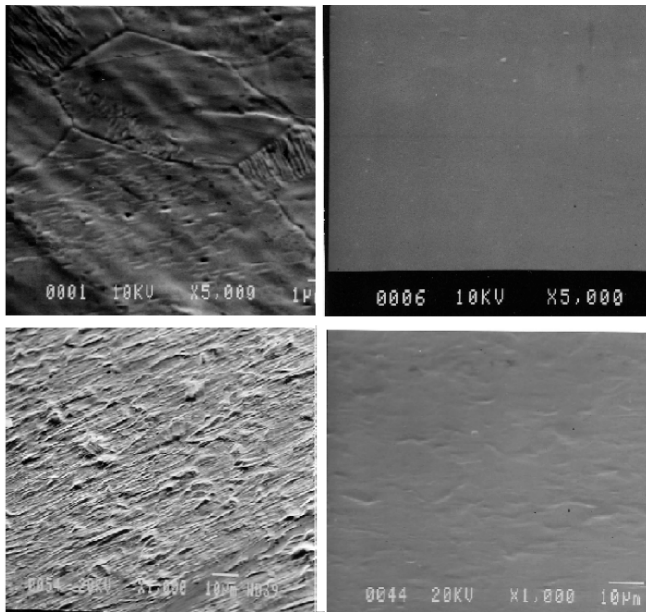


Figure 8. SEM micrographs of 316L (top) and 304 (bottom) stainless steels before (left) and after (right) electropolishing.

IV. CONCLUSION

Optimal conditions were chosen so as to meet the surface roughness and reduction requirements, minimize the amount of pitting, and obtain a surface with high chromium and nickel content. In most cases, surface roughness and thickness reduction are inversely related. Thus, one must

make a trade-off between the two. For our purposes, the best tradeoff happened at a temperature of 60°C , 50 Hz pulsed current at 50% duty cycle, with a density of 323 mA/cm², and duration of 90 seconds. It is possible that lower frequencies may yield improvement, since 50 Hz was the lowest frequency attempted due to equipment constraints. The use of ultrasonic agitation in place of mechanical stirring improved overall surface roughness by 0.05 μm and eliminated almost all evidence of surface pitting and other defects.

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