

Electropolishing Stainless Steel Implants

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ABSTRACT: Virtually every manufacturer of AISI Type 316L stainless steel surgical implants uses electropolishing as a surface finishing procedure, but little research has been devoted to the basic chemistry, techniques, and possible benefits of the process. The electrochemical reactions that take place in the electropolishing cell are discussed, as well as the physical techniques used to electropolish stainless steel. Data on the corrosion resistance of electropolished stainless steel is compared to conventional passivation treatments.

KEY WORDS: electropolishing, stainless steels, corrosion resistance, oxide layer, implant materials, degradation, fatigue (materials)

The electropolishing process was first described by Jacquet in 1936 [1].² He observed polishing of metallographic copper specimens when an anodic current was applied in orthophosphoric acid. In 1936 to 1937, Faust discovered mixtures of orthophosphoric and sulfuric acids produced a superior polishing effect on stainless steel [2]. He described the metal surface to be highly lustrous and free from scratches and the "piled" layers characteristic of mechanically polished surfaces [3]. These solutions patented in 1943 form the basis for contemporary electrolytes used to electropolish AISI Type 316L stainless steel implants.

The amount of basic research aimed at understanding electropolishing, the techniques involved, and the possible benefits of the process seem less than warranted, considering the wide-spread use in research and industry. Surveying the literature available on electropolishing, one finds only brief references to the increase in corrosion resistance of electropolished surfaces. Only recently has the influence of electropolishing on the corrosion resistance of AISI Type 316L stainless steel been presented [4]. The object of this discussion is to present a brief electrochemical description of the process, industrial techniques used, and data on the corrosion resistance of electropolished stainless steel.

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²The italic numbers in brackets refer to the list of references appended to this paper.

Electrochemistry

A typical polarization curve for stainless steel in a sulfuric-orthophosphoric acid electropolishing solution is shown in Fig. 1 [5]. This curve is characteristic of a metal surface that can be passivated [6]. In the active region (*A-B*), the surface is aggressively attacked and etching occurs. At the critical current density (*B*) a thin passive film of slowly dissolving oxides begins to form. The curve enters the passive potential range at the Flade Potential (*C*) [7]. The dissolution current in this range is approximately 100 times less than critical current density.

As the potential is increased further, the current density begins to rise (*D*). Surface atoms are oxidized and diffuse into the solution. At high current densities, the dissolution rate is very high and the metal ions are unable to diffuse into the solution rapidly enough to replenish sulfate-phosphate acceptor ions. This is called concentration polarization.

The limiting current density (*E*) is reached when acceptors into the diffusion layer and metal-acceptors out of the diffusion layer are at a maximum. No more rapid flow of ions can occur in this case [8]. Near the limiting current density, ideal electropolishing conditions are established, that is, the metal surface becomes bright and smooth.

Two discrete reactions at the anode surface are responsible for the mechanism of electropolishing. They are

1. The formation of a thick, viscous diffusion layer that controls smoothing of the surface by dissolution of peaks over $1 \mu\text{m}$ (macrosmoothing).

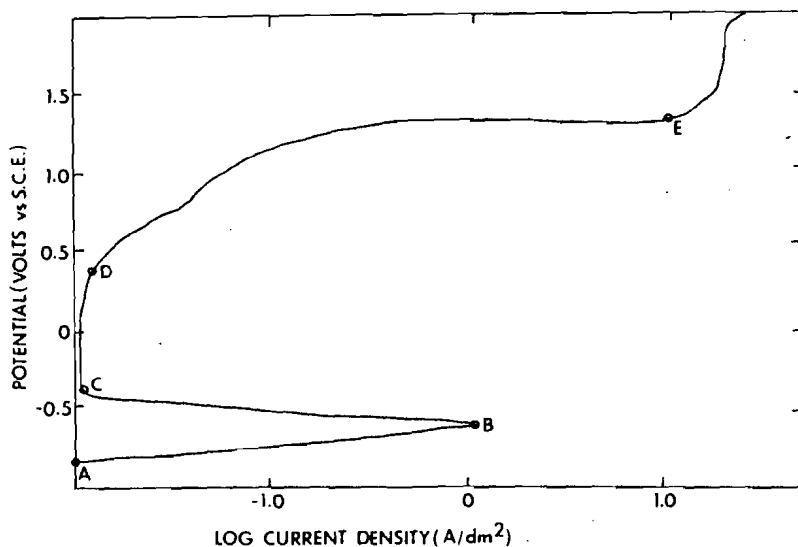


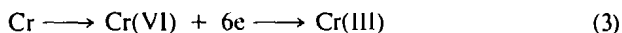
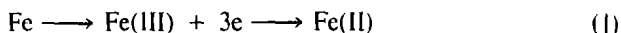
FIG. 1—Typical anodic polarization curve for iron + 18% chromium alloy, 40°C, in a sulfuric-orthophosphoric acid electrolyte.

2. The formation of a thin solid film on the surface that controls brightening or dissolution of peaks down to $0.01 \mu\text{m}$ (microsmoothing) [9].

The viscous film surrounding the anode has a high ohmic resistance that is proportional to the film thickness. Macroscopic peaks are less shielded by the film, therefore receive a higher microcurrent density than the valleys. They dissolve at a faster rate and macrosmoothing occurs, Fig. 2 [2]. The thin solid film is only a few atomic layers thick and is theorized to protect the surface from preferential attack of high energy sites [9]. The random removal of metal ions due to cation vacancies in the film causes brightening of the surface.

At the high potentials involved in electropolishing AISI Type 316L stainless steel, metal ions diffuse into the solution in the highest valent state Eqs 1 to 3 [10].

Surface Anode Reaction \longrightarrow Solution \longrightarrow Cathode Reaction



These cations are soluble and migrate in the electrolyte to the cathode, where reduction and precipitation occurs. The dissolved metal content of an electro-

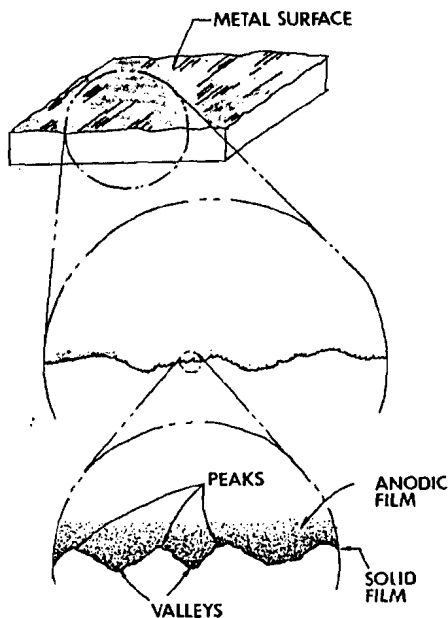


FIG. 2—Pictorial representation of the anodic film formed during electropolishing.

polishing solution usually increases with time since the efficiency of the reduction process is less than 100%.

Industrial Physical Techniques

Most electrolytes used in industry to electropolish stainless steel are based upon the sulfuric-phosphoric acid formulas developed by Dr. Faust [2]. Some proprietary solutions include organic compounds such as hydroxy-acetic acid, lactic acid, and diethylene glycol monobutyl ether. The composition of electrolyte usually determines the operating parameters such as temperature, current density, specific gravity, and time, but the techniques illustrated in this discussion are useful for any electropolishing system.

The industrial electropolishing cell is normally a chemical pure lead-lined steel tank, ranging in size from one gallon to several thousand gallons. The tank is electrically insulated from the floor and surrounding environment. Heat is provided by a thermo-regulated lead steam coil or an electric quartz immersion heater. A direct current power supply is used to provide sufficient current and potential for the electropolishing process. The power supply may be as simple as a manual powerstat type or versatile as a solid-state type with automatic constant current, voltage stabilization, ampere-minute timing, etc. Choice of a power supply is usually determined by the degree of process control required. Agitation of the electrolyte is necessary to prevent streaks from the gas evolved on the workpiece.

The agitation should be enough to disburse the gas bubbles, but should not disturb the thick diffusion layer surrounding the anode. Experience has shown that an oscillating anode rod will provide sufficient agitation without disturbing the anodic film.

Copper rods, insulated from the cell, are used to provide power to the electrodes. Cathode materials are normally chemical pure lead or stainless steel. A bare copper fixture can be used to hold the stainless steel implant in most cases, but more often it is coated with an acid-resistant plastisol. Actual contact to the implant is made with a titanium spring clip, using special care not to scratch the implant when attaching it to the fixture.

The implants are cleaned in accordance to ASTM Recommended Practice for Surface Preparation and Marking of Metallic Implants (F 86-76) after they are placed on the fixture. Before entering the electropolish cell, the parts should be relatively dry to prevent water contamination of the electropolishing solution. The fixture is connected to the anode rod, the motor-drive to oscillate the rod is turned on, and the power supply is switched on to the proper operating output. Time for electropolishing is usually determined by the dimensional tolerances and surface finish of the implant prior to electropolishing.

When electropolishing is complete, the power supply is switched off and agitation ceased. The fixture is removed from the solution and a yellow film covering the implants is observed. This is part of the thick, viscous film mentioned earlier. The best method found to remove this high viscosity film is by

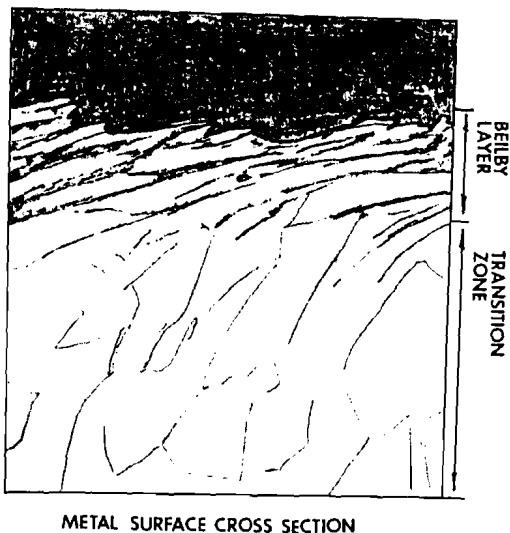
placing the fixture in a fogging spray of dilute electropolish solution (dragout) [11]. The implants are rinsed in clean water and dried. Once again care must be taken not to scratch the implant when removing them from the fixture.

There is very little documentation concerning quality assurance and process control for electropolishing. In some cases, the recommended practice is to discard the solution when the metal content exceeds the level specified for the electrolyte. The chemistry involved in the process causes an increase in the metal content, a slight decrease in water content from hydrolysis, and increases in water content from water adhering to the work-piece (drag-in) to the tank. A better approach to process control may be to monitor the specific gravity and the metal content. Using this method, decisions to decant part of the solution or add water can be made. Quality assurance for electropolished parts has yet to be determined. Suggested methods include nondestructive visual tests, destructive electrochemical testing, cross-sectioning for microscopic examination, or copper sulfate passivation tests. Clearly, better quality assurance procedures will be determined from additional research in electropolishing.

Corrosion Resistance

The increase in corrosion resistance of electropolished material is of great interest. Aluminum, zinc, stainless steel, carbon steel, and bronze are shown to have a higher resistance to aqueous corrosion than mechanically polished specimens [12]. In 1962, General Dynamics/Astronautics Division in San Diego recommended the use of electropolishing to increase the corrosion resistance of stainless steel in propellant system material to the National Aeronautics and Space Administration. Their observations were based on accelerated and actual seacoast exposure tests [11]. Revie and Greene showed electropolished AISI Type 316 stainless steel to be the most corrosion resistant when compared to a sand-blasted, $\frac{1}{2}$ emery polished, and rouge-buffed surfaces [13]. More recently, Sutow has demonstrated the increased corrosion resistance of electropolished AISI Type 316L stainless steel specimens by the more anodic corrosion and breakdown potentials [4].

Several factors contribute to the increase in corrosion resistance of electropolished stainless steel. One of these is undoubtedly the removal of an amorphous, deformed surface called the Beilby Layer. This layer, produced by mechanical finishing, is characterized by crystal fractures and other structural changes. Oxides, polishing compounds, and other materials become embedded in the distorted crystal structure Fig. 3 [12,14]. The conditions established are ideal for the formation of surface corrosion cells. A related factor discussed by Sutow [4] that would affect the corrosion resistance is the surface roughness factor of 1.1 for electropolished and 3.1 for an austenitic stainless steel surface finished with $\frac{1}{2}$ emery paper. Faust attributes an increased corrosion resistance to a mildly "anodized" stainless steel surface [14]. A study by Ducrocq et al [15] used secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) techniques to characterize oxide layers approximately 60 Å deep generated



METAL SURFACE CROSS SECTION

FIG. 3—Pictorial representation of the deformed surface of a metal subjected to mechanical finishing.

by different surface preparations of AISI Type 316L stainless steel. Superficial contamination from the polishing abrasion products was found in the first few angstroms near the surface. The thickness of the oxide layer formed by different polishing procedures (600 grit paper, diamond polishing, and electropolishing) are comparable (50 to 70 Å) and correspond with the thickness after passivation. The composition of the films formed by 600 grit paper and diamond polished are comparable. The films formed by dissolution or passivation are enriched with chromium, but only the film formed by electropolishing was near the composition Cr_2O_3 . All others were mixtures of iron and chromium compounds. (The electrolyte used in this investigation was a non-aqueous, perchloric acid-ethylene glycol monobutyl ether mixture, not commonly found in industry as a result of the hazardous nature of this solution.)

Seo [16] reports the auger electron spectroscopy (AES) analysis of the composition of AISI Type 316 stainless steel surface films prepared by:

1. mechanical polishing with No. 500 emery paper;
2. chemical etching in a 10% nitric acid, 1% hydrofluoric acid solution, 15 min, 323 K;
3. electropolishing for 50 s in a perchloric-acetic acid solution (1:20), 50 V, 6×10^{-2} A/cm²;
4. electropolishing for 50 s in a sulfuric-orthophosphoric acid solution (2:3), 5 to 8 V, 0.5 to 1.0 A/cm²;
5. treatment in 10% nitric acid for 30 min at 333 K; and
6. treatment in 30% nitric acid for 1 h at 333 K.

Unfortunately, the depth profiles for the electropolished surfaces were not presented in this discussion. Surface atomic fraction of chromium and ratio of oxygen to total alloying components in the film were given. This analysis showed the electropolished surface had less chromium on the surface than the samples treated with nitric acid. The conditions specified for electropolishing in a sulfuric-orthophosphoric electrolyte are not what one would expect, even though the temperature is not specified. This composition should be operated at approximately 75 to 90°C with a current density of 0.2 to 0.5 A/cm². An interesting observation of this study was the oxygen ratio of the surface electropolished in the sulfuric-orthophosphoric acid electrolyte was much higher than the nitric acid treated surfaces.

This study and another by Asami [17] demonstrated that the pitting potential versus saturated calomel reference electrode (SCE) in 3.5% saline solution was in direct proportion to the chromium content in the surface layer. Asami also showed that the corrosion potential increases with increasing chromium content.

Summary

Electropolishing is a valuable finishing process for AISI Type 316L stainless steel implants, but there are many questions pertaining to the basic chemistry and result of the process.

1. What is the actual composition of the oxide film produced by electrolytes of varying concentrations?
2. Is there an electrolyte or operating parameters or both that produce oxide films with maximum corrosion resistance?
3. What are the effects of organic addition agents, commonly found in commercial electropolishing solutions, on the film composition and corrosion resistance?
4. Does passivation in nitric acid solutions after electropolishing change the film characteristics?

Conclusions

Electropolishing is finding wide acceptance as a surface finishing technique, but several basic questions remain open. Basic research is needed to determine these answers. References to electropolishing should include the type of electrolyte and the operating parameters, since there may be a correlation between the operating conditions and the oxide film formed. Anodic polarization curves of both the electropolishing process and the corrosion testing may be helpful. More useful surface analytical techniques such as electron spectroscopy for chemical analysis (ESCA) could provide detailed information about the surface after different electropolishing procedures.

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