ELECTROPOLISHING STAINLESS STEEL IMPLANTS

Charles C. Irving, Jr.
President
Surface Technology, Inc.
7 West Calhoun
Memphis, TN 38103

INTRODUCTION:

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

Very little attention has been devoted to electropolishing in the past
thirty years, and the increase in corrosion resistance of
electropolished stainless steel has virtually escaped attention. Only
recently has the influence of electropolishing on the corrosion
resistance of AISI 316L 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.

ABSTRACT: Virtually every manufacturer of AISI 316L stainless implants uses electropolishing as a surface finishing procedure, but very little attention has been devoted to the chemistry, techniques and 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.

ELECTROCHEMISTRY:

A typical polarization curve for stainless steel in a sulfuric-orthophosphoric acid electropolishing solution is shown in Figure 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, i.e. the metal surface becomes bright and smooth.

POTENTIAL (VOLTS vs S.C.E.)
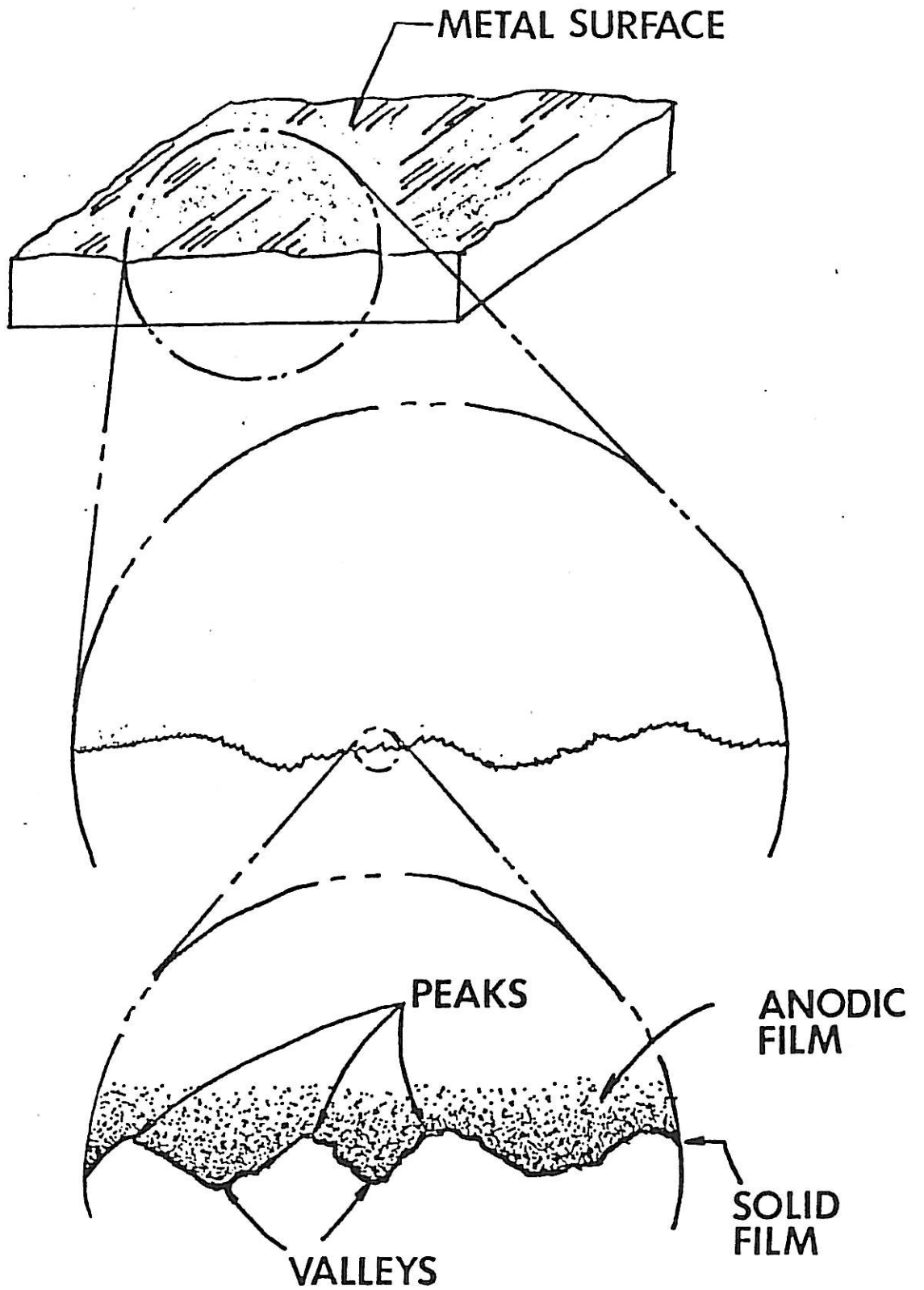
LOG CURRENT DENSITY (A/dm^2)
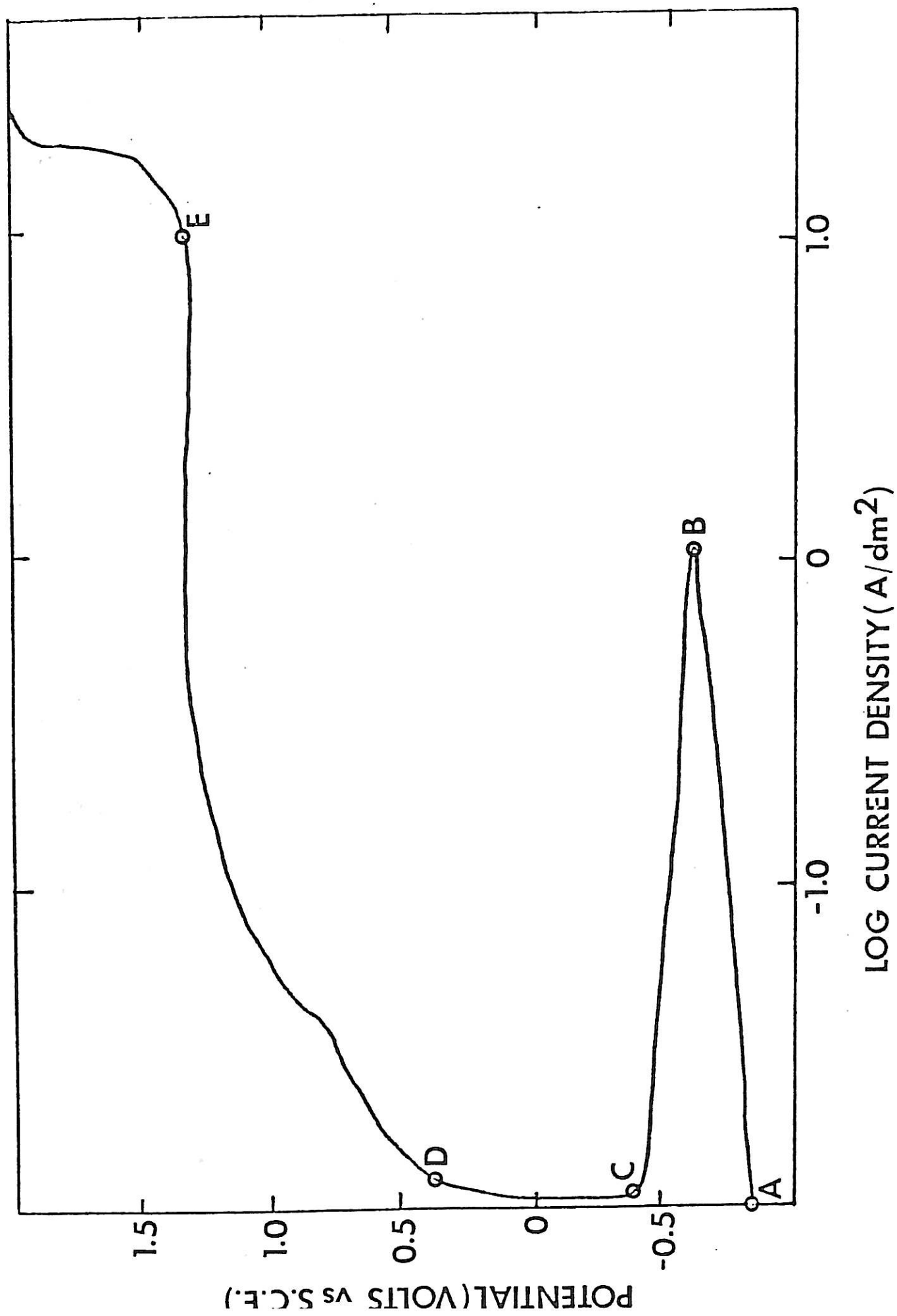
Two discrete reactions at the anode surface are responsible for the mechanism of electropolishing. They are:
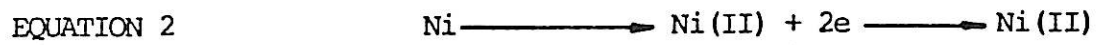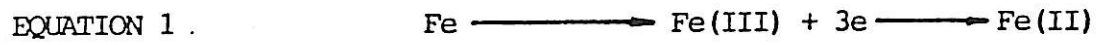
1. The formation of a thick, viscous diffusion layer that controls smoothing of the surface by dissolution of peaks over 1 micron (macrosmoothing.)

2. The formation of a thin solid film on the surface that controls brightening or dissolution of peaks down to 0.01 micron (microsmoothing) [9].

The viscous film surrounding the anode has a high ohmic resistance which 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 [2] Figure 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 316 stainless steel, metal ions diffuse into the solution in the highest valent state [10] Equations 1-3. These cations are reduced when they reach the cathode and are precipitated as insoluble salts. The reaction is never 100% complete causing the metal content of the electropolish solution to increase with time.

METAL SURFACE

PEAKS

ANODIC
FILM

SOLID
FILM

VALLEYS

Surface Anode Reaction → Solution ——→ Cathode Reaction

EQUATION 1 .   Fe ———————→ Fe(III) + 3e ———→ Fe(II)

EQUATION 2   Ni ————————→ Ni(II) + 2e ————→ Ni(II)

EQUATION 3   Cr ———————→ Cr(VI) + 6e ———→ Cr(III)

PHYSICAL TECHNIQUES:

The industrial electropolishing cell is normally a C.P. Lead-lined
steel tank. Heat is provided by a thermo-regulated steam coil or an
electric quartz immersion heater. A direct current power supply is
used to provide sufficient current and potential for the electro-
polishing process. Agitation is necessary to prevent gas streaks on
the work, and 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 C. P. Lead or stainless
steel. A bare copper fixture can be used to hold the stainless steel
implant, 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 standard recommended
practice for surface preparation and marking of metallic implants
F-86, 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 will be 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.

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 Dyanamics/ 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 316 stainless steel to be the most corrosion resistant when compared to a sand-blasted, 2/0 emery polished and rouge-buffed surfaces [13]. More recently Sutow has demonstrated the increased corrosion resistance of electropolished AISI 316L 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 Figure 3 [12,14]. The conditions established are ideal for the formation of surface corrosion cells. A related factor discussed by Sutow [4] that would effect the corrosion resistance is the surface roughness factor of 1.1 for electropolished and 3.1 for an austenitic stainless steel surface finished with 2/0 emery paper.

Faust attributes an increased corrosion resistance to a mildly "anodized" stainless steel surface [14]. A study by Ducrocq et al [15] used SIMS and XPS techniques to characterize oxide layers approximately 60 A deep generated by different surface preparations of AISI 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, electropolish) are comparable (50-70 A) 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.)

BEILBY LAYER

TRANSITION ZONE

METAL SURFACE CROSS SECTION

Seo [16] reports the AES analysis of the composition of AISI 316 stainless steel surface films prepared by:

1. mechanical polishing with No. 500 emery paper.

2. chemical etching in a nitric/hydrofluoric acid solution.

3. electropolishing in a perchloric-acetic acid solution.

4. Electropolishing in a sulfuric-orthophosphoric acid solution.

5. treatment in 10% Nitric acid.

6. treatment in 30% Nitric acid.

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. 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 (vs. S.C.E.) in 3.5% saline solution was in directly proportion to the chromium content in the surface layer. Asami also showed the corrosion potential increases with increasing chromium content.

CONCLUSIONS:

Electropolishing is a valuable finishing process for AISI 316L stainless steel implants, but there are many questions to answer:

1. What is the actual composition of the oxide film produced by electrolytes of varying concentrations?

2. Is there an electrolyte that produces an oxide film 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 after electropolishing change the film characteristics?

Figure Captions

FIG. 1. Typical Anodic Polarization Curve for Iron + 18% Chromium Alloy, 40° C, in a sulfuric-orthophosphoric acid electrolyte.

FIG. 2. Pictorial Representation of the anodic film formed during electropolishing.

FIG. 3. Pictorial Representation of the Deformed Surface of a metal subjected to mechanical finishing.

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