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ENVIRONMENTALLY BENIGN ELECTROPOLISHING OF BIOMEDICAL ALLOYS

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ABSTRACT

A process for surface finishing of medical device and implant alloys is described. Unlike conventional electrochemical surface finishing processes, Faraday's pulse reverse process does not require low conductivity/high viscosity electrolytes and does not require the addition of aggressive chemicals such as hydrofluoric acid to remove the passive film associated with electropolishing of passive and strongly passive materials. This paper focuses on pulse/pulse reverse electropolishing of Nitinol and other metals and alloys containing titanium, molybdenum and niobium.

INTRODUCTION

Electropolishing is the process whereby the asperities are preferentially removed by an electrolytic reaction, which may be generally represented as:

$$M^0 \rightarrow M^{+n} + ne^- \quad [1]$$

Furthermore, during anodic metal dissolution (Eq. 1) some metal surfaces can form a passive oxide film, generally described as:

$$M + xH_2O \rightarrow M(O_x) + 2xH^+ + 2xe^- \quad [2]$$

For strongly passivating metals (e.g. titanium, nickel, niobium, and their alloys), continued electropolishing under direct current (DC) electric fields in a simple electrolyte can lead to a roughened surface similar to pitting corrosion. To remove the passive film, aggressive chemicals are added to the electrolyte. For example, in the case of niobium, hydrofluoric acid or fluoride salts are added to the electrolyte to depassivate the surface [1]. In addition to the electrolyte handling and safety issues associated with concentrated hydrofluoric acid, conventional DC electropolishing of niobium presents process control issues, and reject rates may be high [2]. Faraday has developed a pulse reverse electrochemical surface finishing process that eliminates the need for low conductivity/high viscosity electrolytes with chemical depassivation additions, while maintaining or improving process throughput and surface quality.

THEORY

Figure 1 presents a generalized pulse/pulse reverse waveform. The anodic pulse is tuned (on-time, t_a, and peak voltage, V_a) to enhance mass transport and control current distribution. While a priori determination of the on-times and peak voltages is not currently known, guiding principles based on single pulse transient studies have been presented [3]. Generally speaking, for uniform polishing of a surface, for hydrodynamic boundary layers conforming to the roughness features (i.e. a macroprofile) the anodic on-time should be relatively small. For hydrodynamic boundary layers much larger than the roughness features (i.e. a microprofile) the anodic on-time should be relatively large. Furthermore, for oxide forming or passive materials, anodic only pulses lead to a rougher surface due to the non-uniform breakthrough of the passive film [4,5].

In order to depassivate the surface, we intersperse cathodic pulses (on-time, t_c, and peak voltage, V_c) within the anodic pulses, in place of or in conjunction with off-times, t_{off} [6-9]. The off-times are generally inserted between the anodic and cathodic pulses to facilitate replenishment of reacting species and removal of by-products and heat. The cathodic pulse eliminates the need for HF and/or fluoride salts or other chemicals to remove the surface oxide. While the exact mechanism of depassivation is unknown at this stage, we speculate that the cathodic pulses remove the oxide film either by direct electrochemical reduction or indirect chemical reduction, and restore the virgin metal surface prior to the next anodic pulse. The amplitude of the cathodic pulses required for depassivation is material specific, and appears to be based on the strength of the passive film. Some have suggested using non-aqueous or low water content electrolytes to remove the source of oxygen leading to the formation of the passive film [10,11]. However, from an industrial implementation perspective, these processes are difficult to control, due to the hydroscopic nature of the non-aqueous electrolyte.

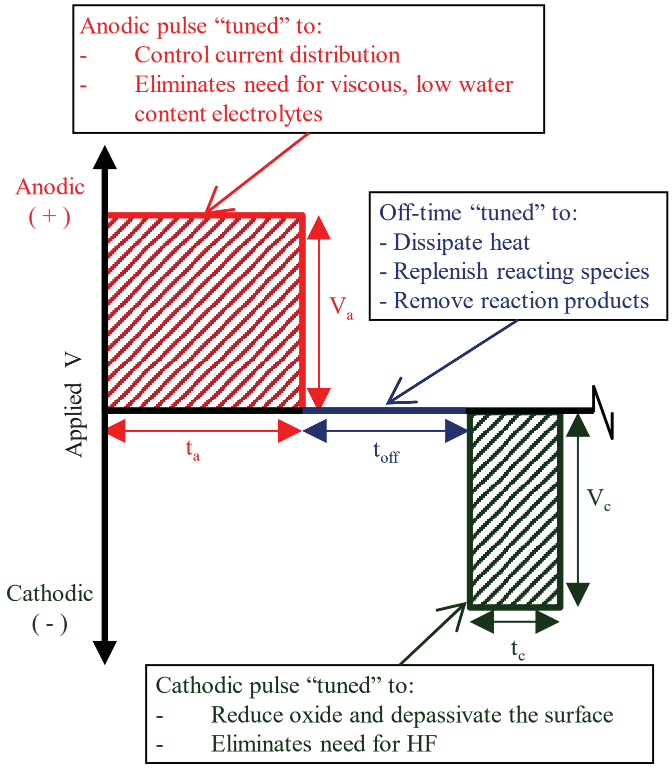

FIGURE 1: GENERALIZED PULSE/PULSE REVERSE WAVEFORM FOR SURFACE FINISHING OF PASSIVE MATERIALS.

The inclusion of cathodic pulses and off-times in the waveform suggests that the overall process would be much slower than a conventional DC process, which is undesirable for industrial implementation. However, the maximum instantaneous current density available during the anodic pulse is higher than the DC limiting current density. Specifically, the ratio between the limiting current density realized in the pulsed electropolishing process, i_p, versus that in steady state, i_{lim}, is:

$$i_p / i_{lim} = [\delta_p/\delta (1 - \gamma_a) + \gamma_a]^{-1} \quad [3]$$

where δ_p is the pulsating diffusion layer thickness, δ is the steady state (DC) boundary layer thickness, and γ_a is the anodic duty cycle, or the ratio of the anodic pulse and the total period of the waveform. Ibl and colleagues [12,13,14] discussed a "duplex diffusion layer" consisting of an inner pulsating layer and an outer stationary layer. Modeling work by Landolt also suggested the existence of a pulsating diffusion layer [15]. By assuming a linear concentration gradient across the pulsating diffusion layer and conducting a mass balance, Ibl derived the pulsating diffusion layer thickness (δ_p) as [13]:

$$\delta_p = (2Dt_{on})^{1/2} \quad [4]$$

where D is the diffusion coefficient and t_{on} is the pulse length. When the pulse on time is equal to the transition time (τ), the concentration of reacting species at the interface drops to zero precisely at the end of the pulse. An expression for τ is provided in the following equation:

$$\tau = ((nF)^2 C_b{}^2 D)/2i_p{}^2 \quad [5]$$

More exact solutions are given by integrating Fick's diffusion equation:

$$\delta_p = 2((Dt_{on})/\pi)^{1/2} \quad [6]$$

$$\tau = \pi((nF)^2 C_b{}^2 D)/4i_p{}^2 \quad [7]$$

Yin [16] using a similar approach as Ibl, derived the same equation for the pulsating diffusion layer for "pulse-with-reverse" electrochemical processes.

Per equation 3, since δ_p must be smaller than δ, higher instantaneous limiting current densities can be achieved in pulsed processes. The extent of this increase is based on the δ_p/δ ratio, which is directly influenced by the anodic pulse on time. A higher limiting current density relates directly to a higher instantaneous metal removal rate. Therefore, the overall removal rate of a pulsed process can rival or exceed that of a DC process despite a duty cycle that is less than 100%, while enjoying enhanced process performance. The waveform is designed such that the anodic pulse compensates for off-times and cathodic pulses such that the average material removal rate (net anodic current density) is equivalent to or greater than DC electropolishing.

In summary, while conventional electropolishing uses a high viscosity electrolyte to focus the current distribution under mass transport, and HF to remove the oxide film, pulse reverse electropolishing is based on non-viscous water electrolytes and 1) uses the anodic pulse time and amplitude to focus the current distribution (without the need for a viscous solution) by qualitatively considering the effect of pulse anodic on-time to pulsating boundary layer thickness and the pulse amplitude on the transition time, 2) uses a cathodic pulse to remove the oxide film and eliminate the need for HF, and 3) uses an off-time to dissipate heat. This paper describes case studies of electropolishing of alloys such as Nitinol, other titanium alloys, stainless steels and alloys containing molybdenum and niobium.

CASE STUDIES

Electropolishing of Nitinol

Faraday is investigating electropolishing of Nitinol and other materials as they pertain to medical devices, for example, stents, catheters and orthopedic cables. Conventional electropolishing is done in high concentration acid mixtures including sulfuric, phosphoric and hydrofluoric acids, and industry would like to use an environmentally benign solution. Conversely, Faraday's electropolishing studies on Nitinol have been conducted in dilute sulfuric acid solutions, demonstrating the technical feasibility of eliminating toxic and environmentally harmful solutions from the manufacture of medical stents and other medical devices. The preliminary work was done using flat coupons to develop electrolytes and processing parameters for various medical grade alloys. Subsequently, we have transitioned to wire and shape sets fabricated from Nitinol and other alloys.

On flat coupons, the best electropolishing parameters to date in a 17 w/w% H_2SO_4 electrolyte has resulted in a final surface Ra of 0.19 µm, which meets industry requirements for conventional surface finishing. Preliminary work on wires and shape sets is promising, and surface evaluation and corrosion resistance testing is underway. Work is ongoing to further improve the surface finish, and transition the technology to medical devices and implants fabricated from Nitinol.

Electropolishing of Titanium Alloys

Titanium alloys are used extensively in medical applications due to their biocompatibility. The University of Mississippi Medical Center (UMMC) uses electron backscatter detection analysis (EBSD) on titanium medical grade alloys to determine microstructural properties. EBSD enables sub-micron resolution of the crystallographic orientation of the grain structure, and an understanding of this orientation is believed to be related to biomedical performance of the alloy. UMMC typically uses a perchloric or hydrofluoric acid electrolyte to polish these alloys, and was looking for a more benign method of electropolishing. We electropolished flat coupons of Ti-15Mo and Titanium-Aluminum-Niobium (TAN) alloys in 10 w/w% H_2SO_4 or 150 g/L Na_2SO_4, and achieved a final surface finish for Ti15Mo of an Ra of 0.12 µm and TAN of an Ra of 0.23 µm. UMMC determined that Faraday's electropolishing technology is superior to conventional polishing, in terms of the surface finish attainable and the information that can be derived from the EBSD scan. Figure 2 shows very clear sub-micron resolution grain structure of the beta phase Ti15Mo alloy coupon electropolished by Faraday.

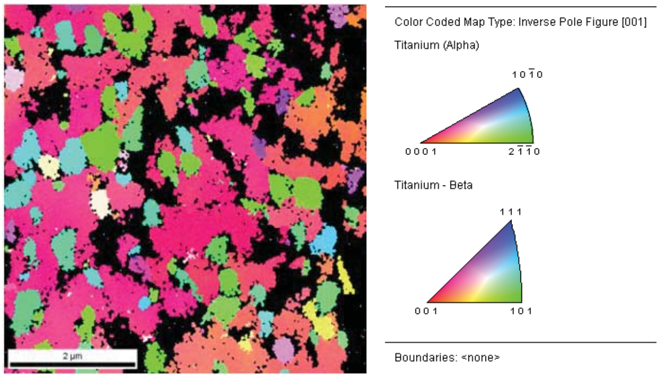

FIGURE 2: DISTINCT EBSD MICROSTRUCTURE WITH CRYSTAL ORIENTATION AT SUB-MICRON RESOLUTION OBTAINED USING FARADAYIC® ELECTROPOLISHING OF A MEDICAL GRADE TI-15Mo ALLOY COUPON.

Electropolishing of Stainless Steels

Stainless steel valves and fittings are used for process fluid control and delivery. The internal valve surfaces must be polished to a mirror-like finish to meet semiconductor performance criteria. Conventionally, the valves were polished using 1) abrasive flow machining (AFM) for bulk removal of tool lines, followed by 2) conventional electropolishing that used a chilled electrolyte consisting of a low conductivity and viscous sulfuric/phosphoric acid and proprietary additives to achieve a mirror-like finish. The AFM media was expensive and the AFM/electropolishing process difficult to control. Faraday developed a replacement process based on FARADAYIC® waveforms in an aqueous NaCl-$NaNO_3$ electrolyte. We used a waveform sequence of short anodic pulses with interspersed cathodic pulses for 30 s followed by a waveform with long anodic pulses and interspersed cathodic pulses for 15 s. We were able to achieve a mirror-like finish and a final R_a of 0.026 µm (Figure 3), which meets industry requirements, for a process time of 45 seconds. By comparison, the conventional electropolishing process alone took two and a half minutes. This process is currently in production at Swagelok Corporation.

FIGURE 3. INTERIOR SURFACE OF A SS316 TUBE BEFORE (LEFT) AND AFTER (RIGHT) FARADAYIC® ELECTROPOLISHING IN A NaCl-$NaNO_3$ ELECTROLYTE.

Electropolishing of Other Materials

We are developing the FARADAYIC® ElectroPolishing process for niobium superconducting radio frequency (SRF) cavities for the International Linear Collider. SRF cavities require a mirror-like finish on the interior surface, and the conventional process utilizes a very aggressive electrolyte of 9:1 98% H_2SO_4:48% HF. Furthermore, the final cavity performance appears to be affected by maintaining an electrolyte temperature during polishing below ~35°C, so extensive electrolyte chilling apparatus is required. Our pulse reverse waveform utilizes a short anodic pulse followed by a short cathodic pulse with a relatively long off-time to facilitate heat removal. Our electropolishing electrolyte is currently aqueous sulfuric acid (5-10 wt%) devoid of hydrofluoric acid and other additives. In coupon studies we achieved a mirror-like surface finish free of defects to a surface Ra of less than 1 nm, and transitioned this process to single-cell SRF cavities, with excellent performance results [17,18]. Furthermore, the conventional process requires that the cavity is held in a horizontal orientation and rotated during polishing, which is not conducive to large scale industrial implementation. By contrast, Faraday's process enables vertical polishing without rotation, with a significantly lower capital equipment cost. Finally, in coupon studies, we have electropolished molybdenum to a mirror-like surface finish, as well as worked on electropolishing of cobalt-chrome alloys and rhenium alloys. We have also done preliminary work on Ti-6Al-4V, and achieved a near-mirror like surface finish. This shows the versatility of the technology, and broad applicability to a wide range of materials.

CONCLUSIONS

In summary, we have described a pulse reverse electropolishing process that may be applied to biomedical alloys using low viscosity aqueous electrolytes, devoid of aggressive chemicals for depassivating the surface. Consequently, the safety and chemical handling and disposal issues associated with the pulse reverse electropolishing process minimized. In addition, the need for active chilling is minimized by the appropriate use of the off-time and we anticipate that the electropolishing process reproducibility and robustness are greatly enhanced.

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REFERENCES

[1] Tian, H., S. Corcoran, C. Reece, M. Kelly, 2008, The Mechanism of Electropolishing of Niobium in Hydrofluoric–Sulfuric Acid Electrolyte Electrochemical/Chemical Deposition and Etching, *J. Electrochem. Soc.,* **155**, pp D563-568.

[2] Taylor, E.J., 2011, Private communication, stent manufacturer, January.

[3] Taylor, E.J., 2008, "Adventures in Pulse/Pulse Reverse Electrolytic Processes" *J. Appl. Sur. Fin.*, **3**(4), p 178; *Plating & Surface Finishing*, **95**(12), p 24.

[4] Zhou, C., E.J. Taylor, J. Sun, L. Gebhart, E. Stortz, R. Renz, 1997, Electrochemical Machining of Hard Passive Alloys with Pulse Reverse Current, *Trans. NAMRI/SME XXV*, p 147.

[5] Sun, J., E.J. Taylor, M. Inman, L. Gebhart, R. Renz, 2000, Applications of CM-ECM Technology to Metal Surface Finishing, *Trans. NAMRI/SME XXVIII*, p 245.

[6] Sun, J., E.J. Taylor, R. Srinivasan, 2001, MREF-ECM Process for Hard Passive Materials Surface Finishing, *J. Materials Processing Technology*, **108**(3), p 356.

[7] Zhou, C., E.J. Taylor, J. Sun, L. Gebhart, R. Renz, 2002, *Electrochemical Machining Using Modulated Reverse Electric Fields*, U.S. Patent 6,402,931, Jun 11.

[8] Inman, M., E.J. Taylor, A. Lozano-Morales, T.D. Hall, H.M. Garich, 2010, *Electrochemical System and Method for Machining Strongly Passivating Metals* U.S. Patent Appl. No. 13/153,874 Jun 11.

[9] Taylor, E.J., 2003, *Sequential Electromachining and Electropolishing of Metals and Like Using Modulated Electric Fields,* U.S. Patent 6,558,231 May 6.

[10] Piotrowski, O., C. Madore and D. Landolt, 1999, Electropolishing of tantalum in sulfuric acid–methanol electrolytes, *Electrochim. Acta*, **44**(19), pp 3389-3399.

[11] Zhao, X., S. Corcoran, and M. Kelley, 2010, Fluoride-free electropolishing of niobium cavities for next-generation particle accelerators, *6th SRF Materials Workshop*, Tallahassee, FL, Feb. 18-20.

[12] Ibl, N., J. C. Puippe, and H. Angerer, 1978, Electrocrystallization in Pulse Electrolysis, *Surface Technology*, **6**(4), pp 287-300.

[13] Ibl, N., 1980, Some theoretical aspects of pulse electrolysis, *Surface Technology*, **10**(2), pp 81-104.

[14] Ibl, N., 1981, *Proc. 2nd Intl Pulse Plating Symposium*, AESF, Florida.

[15] Landolt, D., 1986, Mass Transport in Pulse Plating, *Theory and Practice of Pulse Plating*, J-C. Puippe and F. Leaman (eds) AESF, Orlando, FL, pp 55-71.

[16] Yin, K., 1996, Duplex diffusion layer model for pulse with reverse plating, *Surface and Coatings Technology* **88**, pp 162-164.

[17] Taylor, E.J., T. Hall, S. Snyder, M. Inman, A. Rowe, 2013, Electropolishing of Niobium SRF Cavities in Low Viscosity Aqueous Electrolytes without Hydrofluoric Acid, *SRF 2013*, Paris, FR, Sept 23-26.

[18] Rowe, A., A. Grassellino, T. Hall, M. Inman, S. Snyder, and E.J. Taylor, 2013, Bipolar EP: Electropolishing with Fluorine in a Water Based Electrolyte, *SRF 2013*, Paris, France, Sept 23-26.