

Flow of Viscous Surface Layer during Electropolishing of Tungsten Wire

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ABSTRACT

We investigated the mechanism of mass transfer during DC electropolishing of a tungsten wire in 2M KOH electrolyte solution. It appears that a viscous layer formed by the products of electrochemical reaction on anode surface has distinguishable optical and physicochemical properties. The viscous fluid flow is initiated by formation and detaching of a small droplet at the wire tip. Therefore, according to Tate's law, effects of surface tension and gravitational forces exerted on the film are comparable. Using high speed flow imaging, we estimated the density of this layer as $\rho \approx 1075 \text{ kg/m}^3$ and its interfacial tension as $\gamma \approx 5.82 \cdot 10^{-6} \text{ N/m}$.

Keywords: electropolishing, tungsten, surface tension, density, viscous fluid

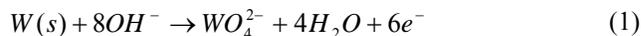
1 INTRODUCTION

Metal wires with nanotips are widely used as atom probes [1], charge sources in scanning tunneling microscopes [2-4] and nanoindentation tips [5]. These ultrasharp wires are produced by conventional cutting [6], DC and AC electropolishing [2, 4, 7, 8] occasionally combined with ion milling [3], chemical etching [9] and other methods [10]. Among the listed methods, electropolishing is considered as the most inexpensive, easiest to implement, and most reliable technique for obtaining sharp tips with nanoscale radii of curvature.

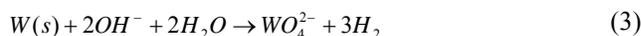
During DC electropolishing, necking of a tungsten wire anodically connected to a power supply takes place in a vicinity of electrolyte-air interface, this being accompanied by continuous decrease of a current in the circuit. When the neck breaks under weight of the lower wire part, the current disappears [2]. The resulting tip shapes are dependent on meniscus surrounding wire submerged into electrolyte solution [2, 7, 10]. The products of electrochemical reaction on anode in a form of viscous fluid flow down continuously during tungsten electropolishing and shield the lower part of immersed wire, while lower rates of polishing of the upper wire part are ascribed to insufficient concentration of hydroxyls at the volume enclosed by meniscus [2, 7].

Electrochemical dissolution of tungsten involves anodic reaction of oxidation of metal atoms to their ions. Reaction

on cathode corresponds to reduction of water with hydrogen and hydroxyls as products. These reactions follow Equations (1) and (2), respectively [2, 11]:



And overall reaction in the electrolytic cell can be written as:



Equation (1) is rather oversimplified, yet reflects the mechanism of electrochemical reaction. A sequence of complementary reactions were suggested in the References [11, 12]. For alkaline solutions with pH greater than 12, the reaction on anode results first in creation of a tungsten oxide WO_3 followed by formation of WO_4^{2-} ions which are considered as the reaction products. Diffusion of hydroxyls to anode surface was suggested as a rate-controlling factor for tungsten dissolution [12]. The concentration of WO_4^{2-} ions might approach the saturation limit, hence the surface film is expected to have distinguishable physico-chemical properties [13]. While importance of the surface layer on electropolishing process has been discussed for a long time, and some hypotheses were put forward [7, 13, 14], the mechanism of mass transfer has never been studied.

In this paper we investigate the mechanisms of fluid flow observed during electropolishing as the thin film formed at the tungsten wire due to electrochemical reaction is crucial for the process of the tip sharpening. Using high speed flow imaging and measuring the flow parameters, we conclude that the film flow is caused by capillary action of a thin film and free convection of the heavy ions.

2 EXPERIMENTAL PROCEDURES

The materials used in this study were 99.95% commercial pure tungsten wires (Type 1A ASTM F288-96) supplied by Small Parts Inc., Miramar, FL with diameters of 0.3, 0.5 and 0.7 mm. The wires were cut to necessary lengths using ordinary metal cutter.

Schematic illustration of electropolishing equipment is shown in Figure 1. The tungsten wire was anodically connected to DC Instek PSS-2005 programmable power supply obtained from Tequipment.NET, Long Branch, NJ.

For the positively charged electrode, cathode, austenitic non-hardenable chromium-nickel stainless steel 314 was used. All experiments were conducted in 2M water solution of potassium hydroxide (KOH). Container for electrolyte was an ordinary laboratory 150 ml glass beaker. Vertical position of the wire was precisely controlled by a calibrated microscope stage not shown in Figure 1.

We collected the data on wire diameter, depth of immersion into electrolyte, its concentration, voltage, current, and time of electroetching. Electroetching was performed in a constant-voltage mode with a current over time change being recorded by a specifically designed Labview application. At a moment when the current reached zero, the applied voltage was automatically shut off to prevent further polishing of the upper wire part. The electropolishing process was recorded using DALSA 4M-60 camera pointed at the angle of $\approx 14^\circ$ to the electrolyte surface with a focus on the wire-electrolyte interface and surrounding meniscus.

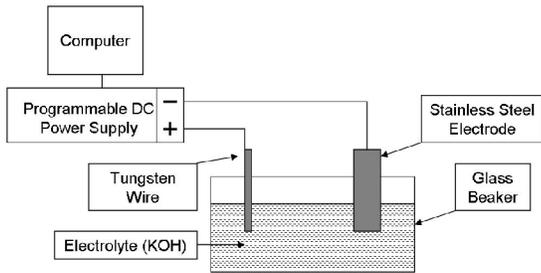


Figure 1 Schematic Illustration of Electroetching Process

Viscous liquid film flowing downward along the anode surface is created during electrochemical dissolving of tungsten. To assess the properties of this fluid, the flow was recorded at 100 fps using Motion ProX3 high speed camera (Princeton Instruments). During electropolishing process, we observed a sporadically appearing droplets at the wire tip, Figure 2a. When the drop detached from the wire tip, the fluid front was tracked and the traveled distance and time were recorded.

The fluid density in the drop ρ was assessed from a force balance for a drop falling in a viscous fluid under its own weight:

$$\rho \times a \times V = F_{fr} - \Delta\rho \times g \times V \quad (5)$$

where a is acceleration of the viscous fluid droplet, $\Delta\rho = \rho - \rho_{KOH}$ is a density difference between fluid in the drop and surrounding 2M KOH solution, $\rho_{KOH} = 1068 \frac{kg}{m^3}$, and V is the drop volume.

Assuming for order-of-magnitude estimates that the drop is spherical, the friction force can be assessed using the Rybczynski-Hadamard equation:

$$F_{fr} = 4\pi \times r \times \eta \times v \quad (6)$$

where $r = \sqrt[3]{3V/4\pi}$ is the drop radius, v is the drop velocity, and $\eta = 0.001P \cdot s$ is the viscosity of surrounding liquid.

Image of the droplet before detachment from the wire was used to estimate the droplet volume, Figure 2b, by rotating a half of the droplet image using AutoCAD. Surface tension at the viscous film-electrolyte interface was estimated using Tate's law representing a force balance between capillary forces and the droplet weight:

$$\gamma = \frac{W}{\pi \times D} \quad (7)$$

where $W = \Delta\rho \times g \times V$ is the weight of the droplet opposed by buoyancy, and D is the wire diameter.

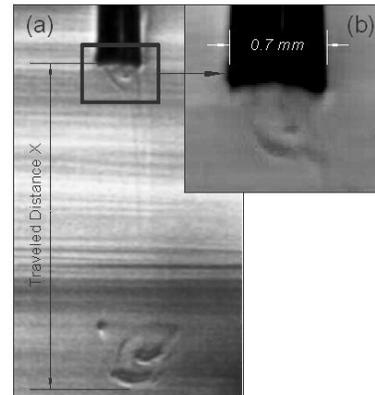


Figure 2 a) Droplet Fall in KOH Solution with Another Droplet Being about to fall from the Tip, b) Magnified Image of the Droplet Before Detachment from the Wire.

3 RESULTS AND DISCUSSIONS

Typically, the upper part of tungsten wire after electropolishing had conical shape, Figure 3a. For example, in Figure 3b we show the tip with a radius of curvature of 115 nm. The lower part of the wire is shown in Figure 3c. An image sequence for a wire dissolution process is presented in Figure 4. The maximum rate of dissolution is observed under meniscus. The part which is below the flat electrolyte-air interface is dissolved at lower rates. Creation of upward pointed meniscus at wire-electrolyte interface indicates hydrophilic properties of the tungsten surface in contact with KOH solution. Equilibrium position of the meniscus is achieved as a balance between capillary and gravitational forces, the former being proportional to the perimeter of contact and, therefore, wire diameter [15]. Bubbles of the emitting hydrogen are occasionally attached

to the tungsten wire, Figures 4b, with their subsequent slow motion along the wire surface toward electrolyte-air interface and presumably cause retardation of anodic reaction.

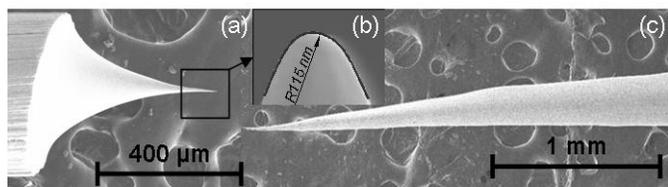


Figure 3 The Upper Part of the Wire at a) Low and b) High Magnification, c) The Lower Part of the Wire

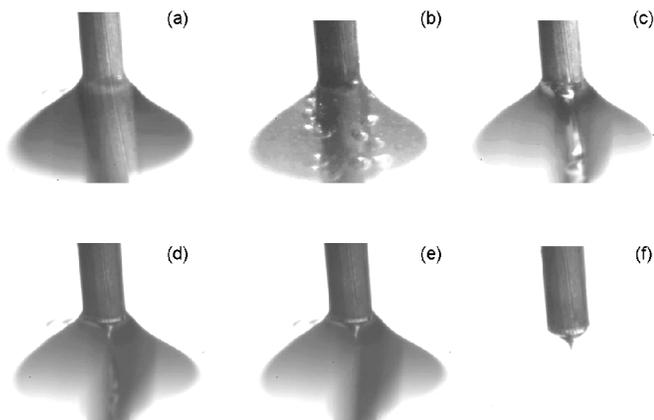


Figure 4 Image Sequence Showing Different Stages of Electropolishing

The distance-time relation for the droplet front was found to be linear, Figure 5, with the velocity being equal to $\approx 3.1 \times 10^{-3} \text{ m/s}$. After approximately 1.5 s, the front started to smear and we cannot apply Eqs. (5)-(6) anymore. Using Eqs. (5)-(7), we estimated the average droplet volume as $V \sim 1.63 \cdot 10^{-10} \text{ m}^3$, the corresponding droplet radius as $r \sim 3.4 \cdot 10^{-4} \text{ m}$, the density difference between liquids in the drop and in surrounding solution as $\Delta\rho \sim 8 \text{ kg/m}^3$. Consequently, the fluid density in the film formed due to electrochemical reaction is equal to 1075 kg/m^3 not differing significantly from the density of surrounding solution. Surface tension of the viscous fluid in contact with 2M KOH solution was estimated as $5.82 \times 10^{-6} \text{ N/m}$. As seen from above, the studied fluid has distinguishable physicochemical as well as optical properties. Moreover, creation of the droplets at the initial stage of electropolishing suggests that the surface tension and gravitational forces causing motion of the film are comparable.

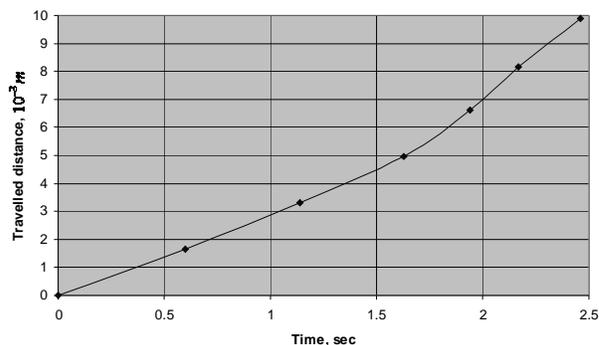


Figure 5 Traveled Distance of the Droplet front vs. Time

4 CONCLUSIONS

In summary, we have presented an experimental method for non-contact measurements of density and surface tension of electrochemical reaction products segregating on the anode surface in a form of thin viscous film. Observations on droplet formation at the wire tip suggest that the effects of surface tension and gravitational forces are comparable. Both of these components should be included into a physical model describing the necking phenomenon during electropolishing.

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