

Small-Scale Pattern Size Control during Metal Electropolishing

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ABSTRACT

In our previous work, we have studied the pattern formation during the electropolishing of both isotropic and anisotropic materials. Both models predict stable hexagonal and striped patterns and are in qualitative agreement with experiments. In this paper, we study the small-scale pattern size control during electropolishing. Our study shows that applied voltage, surface diffusion and surface desorption coefficients play a key role in decreasing the pattern size.

KEY WORDS: Pattern formation; Anisotropy; Interfacial energy; Pattern size;

INTRODUCTION

Electropolishing of aluminum is one of the self-assembly techniques that can produce nanoscale ordered patterns, which have found many potential uses in magnetic recording media, electronic and electrooptical devices. Consequently, a thorough understanding of the mechanism is needed to better predict and control the pattern formation.

Existing theory (Yuzhakov *et al.*, 1997) hypothesized that the onset of the patterns forms as a competition between electrochemical dissolution and surfactant adsorption. We extended the existing theory by including both isotropic and anisotropic interfacial energy. The inclusion of the interfacial energy stabilizes the interface and decreases the dissolution rate. Therefore, the onset of the patterns comes from a competition between dissolution rate, surfactant adsorption, and interfacial energy (Guo and Johnson, 2003a & 2004). We also have modified the evolution equation by including a damping term to account for variations in the bulk concentration. The

addition of the damping term stabilizes the long-wavelength disturbances and allows us to derive the spatiotemporal amplitude equations at the. (Guo and Johnson, 2003b)

Our theory allows us to explore how to control the pattern size during electropolishing. Based on the derived evolution equation, we obtain an equation of pattern wavelength that is a function of applied voltage, interfacial energy, surface diffusion and surface desorption coefficient. Upon deriving the pattern wavelength equation, one can study the effects of different parameters on the pattern wavelength. To verify the stability of pattern formation at such a small-scale size, we perform further linear stability analyses to predict the wavelength of the patterns and weakly nonlinear analyses to predict the effects of the parameters on the stability of the patterns. Studies show that temperature, applied voltage, and surface diffusion and desorption coefficients play a key role in reducing the pattern size.

In this paper, we derive an isotropic governing equation that describes the evolution of the interface over time and space. We further derive an equation of pattern wavelength with interfacial energy, applied voltage, surface diffusion and desorption coefficients included. Upon obtaining the pattern wavelength equation, we study the effects of different parameters on the pattern wavelength. Finally, linear instability and weakly nonlinear analysis are conducted to analyze the stability region of patterns at the small-scale pattern level.

MODELING OF ELECTROPOLISHING

1. Isotropic evolution equation

The existing theory introduced the competitive mechanism between dissolution rate and surfactant adsorption rate. However, it did not account for interfacial energy, which we find has a significant effect on the results. The interfacial energy adds additional stability to the interface by restraining areas of high surface curvature. This results in stabilizing the short wavelength disturbance and modifies the parameter region where stable patterns exist. Furthermore, it is found that the interfacial energy is needed in the model in order to predict stable hexagonal patterns.

The interfacial energy is included in the evolution equation through the total electrochemical free energy. We neglect the role of velocity assuming that the momentum and diffusion boundary layers were much larger than the electric double layer. We further assumed that the double layer thickness and the anodic chemistry were not affected by changes in composition. A long-wavelength expansion of a Debye-Hückel equation is used to derive a relationship between the anode interfacial electric field and the interfacial shape, h . A short-wavelength cut-off mechanism is further introduced to couple with the long-wavelength instability by using a quasisteady equation for the surfactant coverage. Eventually, a dimensionless evolution equation is derived

$$H_\tau - s\nabla^2 H_\tau = -H - (\nabla H)^2 - \left(1 - \frac{p}{s}\right) \nabla^2 H - (1+p)\nabla^4 H - \nabla^2 (\nabla H)^2 + 2\xi (\nabla^2 H)^2 \quad (1)$$

where

$$s = \frac{1-\nu}{\nu}, \text{ and } p = \frac{\nu'}{\nu}$$

$$\xi = \frac{\delta_E^2}{8\nu} \left(\frac{k_d^0}{D_s^0} \right) \left(\frac{\alpha E_0^2}{k_B T} + 1 \right) - \frac{\nu' B_2 \delta_E^2 k_d^0}{4\nu D_s^0}$$

ν denotes the ratio of the activation energy of the dissolution to the adsorption while ν'

represents the ratio of interfacial energy to the activation energy for the adsorption. The symbol ξ represents the dimensionless applied voltage.

2. Mathematical analysis of the model

A linear instability analysis of eqn. (1) shows that interfacial energy changes the linear stability criteria by making the region of unstable wave vectors smaller, and reducing the maximum growth rate. A weakly nonlinear analysis shows that the interfacial energy significantly alters the parameter regions where stable striped and hexagonal patterns can exist. In particular, we found that the interfacial energy needs to be included in the model to predict stable patterns. A numerical simulation of the evolution equation also predicts the stability and existence of stable striped and hexagonal patterns. The results are shown in Figure 1.

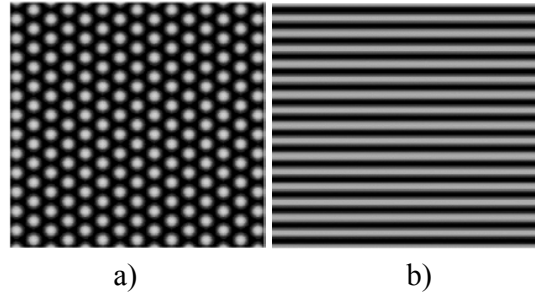


Figure 1. Stable hexagonal and striped patterns from the nonlinear simulation with interfacial energy. $p = 1071/5329$, $s = 9/16$, and $\xi =$ a) 0.2 and b) 0.6.

SMALL-SCALE PATTERN SIZE CONTROL

The objective of this paper is to study how to control small-scale pattern size during electropolishing of aluminum. We have derived the evolution equation that describes the evolution of the interface over time and space. The pattern wavelength can then be defined as

$$l = \frac{2\pi}{q_m} \sqrt{\frac{\nu}{1-\nu}} \sqrt{\frac{D_s^*}{k_d^*}} \exp\left(\frac{\beta\alpha U^2 a^2}{2\delta_E^2 k_B T} - \frac{\beta' \gamma \delta_E \nabla^2 h}{RT}\right)$$

(2)

where

$$\nu = \frac{\beta_r \delta_E \exp\left(-\frac{\alpha U^2 a^2}{2\delta_E^2 k_B T}\right)}{\alpha U a K_a^*},$$

$$\frac{D_s^*}{k_d^*} = \frac{\delta_E^2 \left(\frac{\alpha U^2 a^2}{\delta_E^2 k_B T} + 1\right)}{8\nu \xi_r \exp\left(\frac{\beta \alpha U^2 a^2}{\delta_E^2 k_B T}\right)} \text{ and } \beta_r' = \frac{Z}{C_M \delta_E}.$$

Here U is the potential difference, a is a parameter determining the potential distribution across the anode, γ is the interfacial energy, β is an unknown positive coefficient measuring how the combined activation energy of diffusion and desorption depend on the electric field, K_a^* is the fieldless adsorption-desorption equilibrium constant, C_M is the mole concentration of aluminum, Z is the metal ion charge, and ξ_r is a parameter used to calculate the value of D_s^*/k_d^* . The Debye length δ_E is estimated from the Poisson-Boltzmann equilibrium of the Debye-Huckel theory

$$\delta_E = \sqrt{\frac{\epsilon RT}{2F^2 Z_0^2 C_{eff}}}$$

Here Z_0 is the solution ion charge, C_{eff} is the effective ion concentration on the surface, and ϵ is the permittivity of the medium. From Eq. (2), it is clear that the values of U , D_s^*/k_d^* , T , γ , and C_{eff} are predominant factors in reducing the wavelength while reducing the effective polarizability difference α , and parameter a could lead to smaller patterns in a narrow region. In particular, It is found that changing the value of D_s^*/k_d^* may significantly reduce the pattern wavelength. Figure 2 shows that the pattern wavelength for the range of 45 V to 65 V is around 100 nm when ξ_r is 0.68. However, the pattern wavelength can be significantly reduced to near 10 nm if ξ_r is chosen big enough. To verify that the pattern formation is indeed stable at such a length scale,

we perform a linear instability and weakly nonlinear analysis.

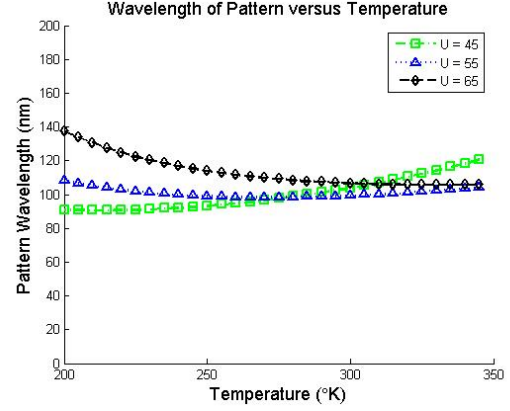


Figure 2. Pattern wavelengths of various applied voltage are around 100 nm when ξ_r is 0.684.

1. Linear instability analysis

Linearizing eqn. (1) and substituting a normal mode $H \sim \exp(\lambda\tau + i(kx + ly))$ yields the growth rate

$$\lambda = \frac{\left(1 - \frac{p}{s}\right)q^2 - (1+p)q^4}{1 + sq^2} \quad (3)$$

The wavenumber at maximum growth rate q_m is therefore given by

$$q_m^2 = \frac{\sqrt{1 + s + s^2} - 1}{s} \quad (4)$$

Equation 4 shows that the wavenumber with the maximum growth rate changes with the interfacial energy.

2. Weakly nonlinear analysis

The expansion of the interfacial height in terms of the various modes is given as follows

$$H = \sum_{j=1}^6 [W_j \exp(i\mathbf{k}_j \cdot \mathbf{r}) + V_j \exp(2i\mathbf{k}_j \cdot \mathbf{r}) + U_j \exp(i\mathbf{k}_{2j} \cdot \mathbf{r})]$$

Here W_j represents the unstable modes, V_j represents the stable harmonic modes, and U_j

represents the stable resonant modes. Substituting H into the linearized equation and following the standard procedure to isolate the most unstable modes, yield the following amplitude equations.

$$\begin{aligned} \frac{dW_1}{d\tau} &= \gamma_0 W_1 + \gamma_1 W_2^* W_3^* - \gamma_2 |W_1|^2 W_1 - \gamma_3 (|W_2|^2 + |W_3|^2) W_1 \\ \frac{dW_2}{d\tau} &= \gamma_0 W_2 + \gamma_1 W_3^* W_1^* - \gamma_2 |W_2|^2 W_2 - \gamma_3 (|W_3|^2 + |W_1|^2) W_2 \\ \frac{dW_3}{d\tau} &= \gamma_0 W_3 + \gamma_1 W_1^* W_2^* - \gamma_2 |W_3|^2 W_3 - \gamma_3 (|W_1|^2 + |W_2|^2) W_3 \end{aligned} \quad (5)$$

The amplitude coefficients γ_0 , γ_1 , γ_2 , and γ_3 depend on the maximum growth rate q_m , applied voltage U , D_s^*/k_d^* , temperature T , interfacial energy γ , ion concentration C_{eff} , and other parameters. Once a parameter is changed, the amplitude coefficients change, which changes the stability of the patterns. Our study shows that when D_s^*/k_d^* is decreased to 1.45×10^{-17} at the temperature of 120 °K, an extremely small pattern wavelength of less than 15 nm can be achieved. Figure 3 plots the pattern wavelengths versus D_s^*/k_d^* under various applied voltages. Linear instability and weakly nonlinear analysis shows that both stripes and hexagons exist but only hexagons are stable at such a small wavelength sale. It is also found that the applied voltage has an obvious effect on

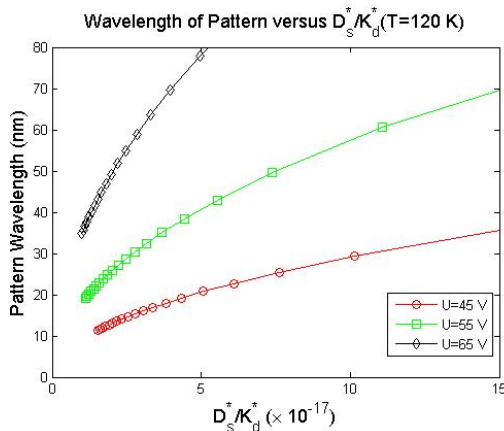


Figure 3. Pattern wavelengths can be dramatically reduced to less than 15 nm at the voltage of 45 V.

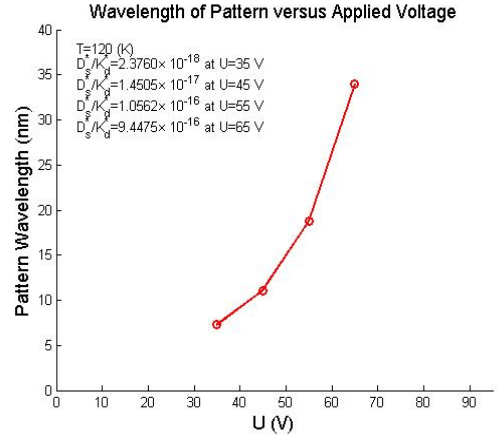


Figure 4. Applied voltage can be adjusted to create smaller patterns.

controlling pattern wavelength, as shown in Figure 4.

However, as shown in Figure 5, pattern wavelengths are not very sensitive to changing the fieldless adsorption-desorption equilibrium constant K_a^* , when K_a^* is less than 1. Therefore, small patterns can be achieved by adjusting the applied voltage, electrolyte compositions, temperature, different metal/electrolyte systems that change the interfacial energy, and special surfactants that give very low diffusion coefficient and high desorption rate.

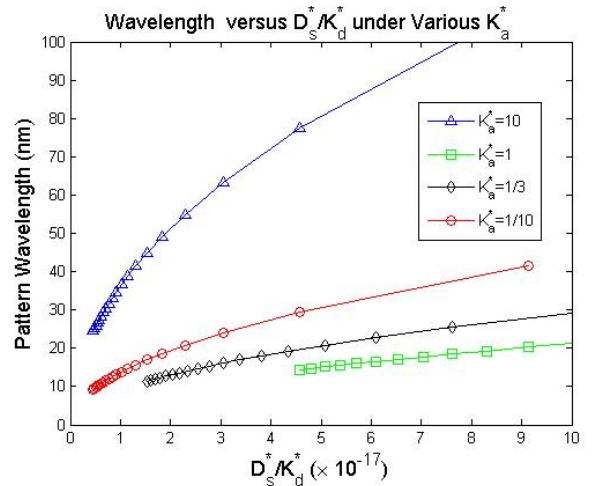


Figure 5. Pattern wavelengths are not very sensitive to changes in the fieldless adsorption-desorption equilibrium constant K_a^* that are less than 1.

SUMMARY

We have studied the small-scale pattern size control during the electropolishing of a metal. A linear instability analysis and a weakly nonlinear analysis are employed to study the effect of changing variables on the pattern wavelength. In particular, it is found that the choice of surfactant can significantly change the pore size due to the surfactant's surface diffusion and desorption coefficients.

ACKNOWLEDGMENTS

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