

Nanoscale Surface Textures on Aluminum Formed by
Dissolution and Anodic Oxidation Processes

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Various aluminum dissolution processes produce a characteristic surface texture consisting of roughly circular scalloped depressions bordered by ridges (1-3). These “cells” form a mosaic pattern covering the entire surface, in some cases comprising a highly ordered arrangement. Processes resulting in pattern formation include open circuit caustic etching and chemical polishing (dissolution in hot concentrated acid), and electropolishing. The cellular pattern also closely resembles the texture of the metal-oxide interface after formation of anodic oxide films with ordered pore arrays (4-5). Typical cell radii and ridge heights range from 10-100 nm and 1-10 nm (electropolishing) to 100-300 nm and 10-30 nm (caustic etching). As demonstrated in much recent work on porous anodic films, the surface texture can be used as a template for nanofabrication (5).

This work presents a unified modeling approach to simulation of the surface textures formed by open circuit dissolution, electropolishing and anodizing. The model includes ionic conduction in the oxide film, and kinetics of Al^{+3} and O^{-2} ion transfer at the film-solution interface (6,7). The rates of the latter processes depend on the interfacial potential drop, expressed in terms of the overpotential η for O^{-2} transfer. The oxide film geometry on the concave surface of the cells is a section of a spherical shell, as accurately depicted by cross sectional TEM (1,3). This geometry is characterized by the inner and outer radii of the film (r_1 and r_2), and the angle subtended by the spherical section (θ_0). For a given potential, the distributions of potential within the oxide and η along the film surface are calculated. The metal-film and film-solution interface velocities are then evaluated. Geometric parameters associated with stable cellular patterns, in which both velocities are the same and independent of position, are identified. In this way, the physical processes underlying stable cellular patterns are elucidated.

The calculations indicate that negligible current flows to the oxide-solution interface on ridges, as a result of the local small area at the metal-film interface. Thus, chemical dissolution on ridges removes stoichiometric proportions of Al^{+3} and O^{-2} ions there. On the other hand, there is a net influx of O^{-2} ions on the concave surface between ridges, where η is positive. Since the current flux in the film has a component parallel to the surface, these O^{-2} ions are transported eventually to ridges. At steady-state during open-circuit dissolution, incorporation of O^{-2} on the concave surface balances O^{-2} dissolution on ridges.

The criteria for stable patterns during dissolution are as follows. (i) The ratio r_1/r_2 is determined by matching of the metal-film and film-solution interface velocities (8),

$$\frac{r_1}{r_2} = \sqrt{1 - \frac{\varepsilon}{t_0}}$$

where ε is the current efficiency for oxide formation (a function of η) and t_0 is the transport number of oxygen ions in the film.

(ii) r_1/r_2 is also related to η according to the oxygen balance mentioned above. (iii) The angle θ_0 is determined by the requirement of a uniform metal-oxide interface velocity, based on the current distribution along this interface. This requires that θ_0 is approximately the same all three types of cellular pattern, in agreement with experiment. Further, the film thickness $r_2 - r_1$ is determined by the potential, which is constrained by equality of the cathodic and net anodic currents.

During anodic oxidation, chemical dissolution of oxide is typically slow. The rate of O^{-2} incorporation on the concave surface exceeds that of chemical dissolution on ridges, leading to the development of pore walls. Requirement (ii) is replaced by a balance between the overall rate of Al^{+3} dissolution and the rate of mass transport in solution.

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REFERENCES

1. C. E. Caicedo-Martinez et al., *Surf. Interface Anal.*, **34**, 405 (2002).
2. F. B. Cuff and N. J. Grant, *J. Inst. Met.*, **87**, 248 (1958-59).
3. G. E. Thompson and G. C. Wood, in *Treatise on Materials Science and Technology*, Vol. 23, J. C. Scully, Editor, p. 253, Academic Press, New York (1983).
4. H. Masuda and K. Fukuda, *Science*, **268**, 1466 (1995).
5. O. Jessensky, F. Muller, and U. Gosele, *Appl. Phys. Lett.*, **72**, 1173 (1998).
6. T. Valand and K. E. Heusler, *J. Electroanal. Chem.*, **149**, 71 (1983).
7. K. J. Vetter and F. Gorn, *Electrochim. Acta*, **18**, 321 (1973).
8. H. Wu, X. Zhang and K. R. Hebert, *J. Electrochem. Soc.*, **147**, (2000).

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