Morphological Instability Leading to Formation of Porous Anodic Oxides

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Porous anodic oxide films are formed by electrochemical oxidation in solutions in which the oxide is soluble. Pores initiate after an initial stage of barrier oxide growth, due to morphological instability at the oxide-solution interface. This presentation describes our efforts to understand the instability mechanism during constant-current anodizing of Al in phosphoric acid, through a combination of experimental and modeling methods.

Linear stability analysis indicates that the oxide-solution interface is stabilized by oxide formation and destabilized by inward oxygen ion migration (1). Specifically, we show that the interface is stable when the anodizing efficiency $\varepsilon_0$ exceeds the oxygen transport number $t_0$, and that ordered pore patterns can emerge when $\varepsilon_0$ is slightly smaller than $t_0$. In situ measurements of stress transients following interruption of anodizing current reveal relaxations that depend sensitively on the metal thickness consumed during anodizing. We present evidence that the relaxations are controlled by a disordered metal layer adjoining the metal-oxide interface containing nanoscale voids (3-5). Such interfacial void layers are present in Al irrespective of surface treatment. For small oxidized metal thickness, compressive stress relaxations are detected, because the voids help relieve tensile stress in the metal produced by anodizing. On the other hand, oxidizing a metal thickness greater than 20 nm incorporates the voids in the oxide, and the stress relaxations become tensile (voids relieve compressive stress in the oxide). Modeling analysis suggests that interfacial voids control the initiation of pores. When the void layer is present at the metal-oxide interface, the resulting high local current density at the metal-oxide interface significantly decreases $t_0$. Since $\varepsilon_0$ is then larger than $t_0$, the anodic film is stable despite the small efficiency of 0.3-0.4 during the initial stage of anodizing (6). When the void layer is fully incorporated into the oxide, $t_0$ reverts to the typical value of 0.6; as a result, the morphological instability initiates since $\varepsilon_0$ is smaller than $t_0$. This instability produces the “incipient pores” observed during the initial stage or porous oxide formation.

We present evidence that the initiation of the larger pores comprising the steady-state porous anodic oxide layer is due to a second instability, which is triggered by the buildup of stress in the metal. This second instability produces characteristic patterns of ridges and scalloped depressions at the metal-oxide interface. Since this second instability occurs in systems where no flow of oxide is detected, it is not associated with oxide flow (7). Oxide flow initiates in some systems due to localized stress generation associated with the high current density in the oxide at the pore base. Flow may play a significant role in the mechanism of self-ordering of pores.

References