

## AFM Study of the Behavior of Near-Surface Voids in Aluminum During Anodic Oxidation

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Positron annihilation spectroscopy (PAS) was previously used to detect near-surface voids 10-100 nm in size in aluminum metal, either near or adjoining the metal-oxide film interface (1,2). The internal surface of the voids was shown to be free of oxide, suggesting a high reactivity upon exposure during dissolution. Voids were present in as-received annealed foils, and are formed by several dissolution processes. Surface cavities were found in atomic force microscope (AFM) images after chemically stripping the oxide film; the cavity depth and area coverage from AFM corresponded quantitatively with PAS measurements. Thus, cavities may originate from voids. The morphology and distribution of surface cavities strongly resembled those of corrosion pits formed by anodic etching in chloride solutions. Voids are therefore of potential significance as initiation sites for pitting corrosion.

In the previous AFM experiments, metallic voids may have been enlarged significantly by dissolution after they were exposed in the oxide stripping bath. Thus, the AFM images after oxide removal provide only limited information about the void size, morphology and location on the metal surface. In the present work, aluminum foils containing near-surface voids were anodically oxidized, so that a significant portion of the void-containing layer was reacted to form oxide. On the basis of previous transmission electron microscopy (TEM) results, metallic voids should be incorporated into the oxide layer (3-5). The anodic films were dissolved to various depths with phosphoric acid, and their surfaces were then examined by AFM for evidence of voids. Since oxide dissolution is relatively very slow, the morphology of oxide voids revealed by this procedure may closely resemble that of metallic voids prior to anodic oxidation.

Aluminum foils were annealed and of 99.98 % purity (provided by Nippon Chemi-Con). Prior to oxidation, foils were treated by immersion for various times in 1 M NaOH at open circuit, to generate a layer of interfacial voids 20-40 nm thick (1). Anodic oxidation was at 2.5 mA/sq. cm. in borate buffer, to voltages of 27, 53, 80 and 106 V (oxide thickness approx. 1.4 nm/V). Oxide stripping was carried out in 5 % phosphoric acid at 80 C. Oxide surfaces were imaged in contact mode (DI Nanoscope III).

Oxide films dissolved uniformly and at a constant rate in the stripping bath, as confirmed by measurements of initial voltage upon re-anodizing of partially stripped films. When oxide film dissolution was carried out beyond a critical depth, circular cavities, of order 10 nm depth and 50 nm diameter, were found on the film surface. Taking into account shape change during dissolution, these features may have originated from roughly spherical 10 nm radius voids, as found in the prior TEM study (3,4). Cavities were located preferentially on submicron-high ridges. Cavities were only found when the dissolution depth was greater than a critical value corresponding to approximately 40% of the total oxide thickness. Since this fraction agrees with the cation transport number in the oxide, the defects forming cavities are generated continuously at the metal-oxide interface during film growth. The concentration of cavities in the inner part of the film depended strongly on NaOH treatment time; the trend was the same as that of the void volume fraction prior to oxidation (1). This suggests that the cavities initiate from metallic voids incorporated into the oxide during film growth; the cavity morphology would then correspond to that of a metallic void. Similar conclusions about void formation during anodic oxidation were reached in an

earlier PAS study (6). Formation of voids at asperities may be explained by a locally elevated electric field in the film, or by tensile strain in the film over the asperity, leading to enhanced rate of metal ion transport.

### ACKNOWLEDGMENTS

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