

Internal stresses in ultrathin oxide films: influence on growth and reliability

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Oxide films grown by the anodic oxidation of valve metals are used in several technological applications, including the corrosion protection of aluminum and its alloys. The corrosion protection properties are provided by the ability to grow a very thick porous oxide layer under selected experimental conditions. The sequence of the growth of a porous anodic oxide layer can generally be divided in three successive stages: the growth of a dense oxide layer, the initiation of pores in the dense layer, and finally the growth of a porous oxide layer. In addition to pore initiation, the growth of a dense anodic oxide film can also be terminated by breakdown. Breakdown is detrimental to the mechanical or electrical properties of the oxide. The reasons for the transition from a dense to a porous layer and for oxide breakdown are not mechanistically understood.

Internal stresses present in anodic oxide films during their growth have long been hypothesized to lead to porosity initiation and breakdown. The influence of the internal stress on pore initiation and breakdown phenomena was investigated systematically by correlating their phenomenology with internal stress measurements performed in situ, during the growth of anodic oxide films on aluminum and zirconium. The internal stress was measured with a multiple beam optical sensor, capable of measuring the curvature of anodes with the acquisition rate and resolution relevant for in situ monitoring of the anodic oxidation of metals.

The dependence on the experimental conditions of the internal stress, oxide thickness and pore spacing at the onset of porosity initiation allowed performing a first-order stability analysis of the aluminum oxide/electrolyte interface. The analysis did not support a stress-induced porosity initiation mechanism. Instead, we found that the electric field is the driving force for porosity initiation, the electrostatic energy of the oxide being decreased by porosity initiation.

Regarding breakdown during the growth of anodic zirconia, we found a marked dependence of the onset of the breakdown with the internal stress. The breakdown was attributed to a change of the electronic properties of the zirconium oxide, which lead to a decrease of the ionic current fraction and resulted in oxygen evolution on the anode surface. The increase of the electronic conductivity was found to correlate with an increase of the cubic or tetragonal fraction relative to the monoclinic one. The increase was in turn found to be driven by elastic energy, as the oxide thickness at which breakdown occurred decreased with increasing values of the internal compressive stress directly preceding breakdown. Internal stress therefore plays a key role for the breakdown of anodic zirconia.

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