Characterization of Anodic Aluminum Thin Films Through Nanoindentation

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Summer 2004

Introduction
The Structure of Anodic Aluminum Films
Aluminum is anodized to provide increased corrosion protection. Increased wear resistance, and for decorative purposes. The typical structure of a decorative anodized aluminum film is composed of three layers. The first layer lies in contact with the aluminum and is composed of a dense compact layer of Al2O3. This layer is commonly referred to as the barrier layer and the sealing layer on the other. The pores are commonly filled with dye or other performance enhancing compounds. The sealing layer is composed of böhmit and seals and the additives inside the pores.

Why nanoindentation?
Traditional indentation methods of using Vickers indenter failed due to the brittle nature of the film. At a load of 50 grams both radial and circumferential cracks form, while a load of 25 grams caused the film to delaminate from the substrate. Testing conducted at lower loads produced indents that were inadequate in size to be measured accurately. Even if the films did not undergo failure the thickness of the films that were to be measured were of a similar thickness as the resulting Vickers Indents.

DSM Nanoindentation Method
Since the film’s properties continuously change through the thickness of the film it was necessary to extract an elastic modulus and hardness value from each indent. The Dynamic Stiffness Measurement allows for accurate measure of mechanical properties of films using a single indent. This is achieved by imposing a sinusoidal force signal to the loading portion of the loading-unloading curve providing stiffness and displacement data continuously up to the maximum load.

Methods
All the films that were grown and investigated in this project were grown using industrially accepted procedures on 6001 aluminum in an electrolyte of sulfuric acid. The Elastic modulus and hardness of the cross-section of seven locally grown samples and one industrially grown sample were measured using the DSM technique. The first film was not dyed and remained unsealed; the second sample was sealed for five minutes at a temperature of sixty-five degrees Celsius. The third sample was sealed for fifteen minutes at sixty-five degree Celsius. The forth and fifth sample were both sealed for five minutes but at a temperature of fifty degrees and seventy-five degrees Celsius respectively. Sample six was the same as sample two with the exception of an industrial grade organic dye that was added prior to sealing. The seventh sample was sealed under identical conditions to sample six but the film was grown at .68 amps rather than the .34 amps of all the other samples.

Follow the initial film preparations the samples were sectioned and mounted in Epontol. The samples were mechanically ground and polished with particular care to allow for maximum edge retention. Even small amounts of rounding off excluded large portions of the films from testing.

All seven samples were indented in a grid of evenly spaced indents, such as the one imaged on the right, to allow the properties at a given film depth to be accurately mapped for each sample.

Results
To verify the accuracy of the nanoindentor to the cross-section of the anodic aluminum system an industrially grown standard was intended and compared to the results of Alcalá et al. This work studied the mechanical properties of anodic aluminum barrier films grown in an electrolyte of ammonium pentaborate and shows values of 140 GPa for the elastic modulus and 8.5 GPa for hardness. The maximum values for the industrial grown film were 73.4 GPa for hardness and 100 GPa for the elastic modulus of the barrier layer portion of the film. Variations are related to differences in anodizing conditions. The values of hardness and modulus in the aluminum portion of the sample were comparable to that of the accepted values of aluminum. The porous portion of the film showed a linearly decreasing trend until the extreme outer portion of the film. It is expected that this decrease is the result of a change in porosity as the film thickens and is to be the subject of future work. The sharp change in properties seen after the ten micron mark is likely due to the böhmit sealing layer.

Nanoindentation of the films grown in the lab follow the expectations associated with the accepted structure of anodic aluminum films and that demonstrated by the industrial standard. The measured value for the elastic modulus of the aluminum substrate was centered on the accepted value of 70 GPa. The maximum values for the industrially grown films were increased by approximately 12 µm thick; the other six samples were around 10 micron. This indicates that for the same growth time higher amounts of round off excluded large portions of the films from testing.

Effects of Dyeing on Hardness
The effects of dyeing were illustrated by comparing the unsealed sample with a sealed sample and a sample that was dyed and sealed. The dye was shown to have a similar effect on the mechanical properties as sealing and temperature with the effects of the sealing process out weighing that of the dye.

Effects of Current Density on Hardness
Increased current density during film growth has shown an increase in film properties in the porous layer. When current is doubled during film growth the hardness and modulus of the barrier layer and bulk aluminum remained unchanged when compared with the dyed and sealed and the unsealed sample. The properties of the porous layer still decrease across the layer as the distance from the barrier layer increase but the change is less negative. Sample seven was measured to be approximately 12 microns thick; the other six samples were around 10 microns. This indicates that for the same growth time higher current densities grow thicker films. This film also does not show the characteristics of poor edge retention seen in the other sealed samples nor does it show the dramatic softening at the extreme edge of the sample that was noted in the industrial grade film. The changes in the properties are expected to be due to a change in porosity in the film due to the increased current density and will be investigated in future work.

Conclusions
The mechanical properties as a function of sealing procedures used to prepare decorative anodized aluminum in this work showed no time or temperature dependence. However, the process of sealing caused an overall decrease in hardness of the films. This decrease in hardness was more extreme as the distance from the substrate increased and resulted in poor edge retention during polishing. There was little difference under these sealing conditions between the any of sealed samples with one exception.

The sample anodized at a higher current density showed an increase in hardness across the thickness of the porous layer while the barrier layer and bulk aluminum remained unchanged. This film proved thickest for the same growth time and is suspected to be less porous, leading to the increase in hardness and modulus through the porous layer. The films grown in this study are not uniform as a function of position through the film. The properties of anodic aluminum films can be controlled with anodizing procedures but sealing time, temperature, and dyeing have no apparent effect on the films grown here, while increased current density increases the hardness and stiffness of the films.

Acknowledgements
This work was supported through the National Science Foundation: Division of Materials Research REU site program under grant number 0139125.