Life Expectancy of Plasma Electrolytic Oxidation Electrolyte for Aerospace Applications

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IBC Coating Technologies, Inc. has been developing and utilizing Plasma Electrolytic Oxidation coatings and is interested in characterizing the bath life. In determining bath life, various characterization techniques were used including optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), hardness testing, and X-ray diffraction. Using these techniques, structure-property relationships relevant to bath life were identified.

This work is sponsored by IBC Coatings Technologies INC, Lebanon, IN

Project Background

Plasma electrolytic oxidation (PEO) is a next generation coating process that submerges a metal substrate such as aluminum, magnesium, or titanium in an aqueous electrolyte bath in which a voltage is applied. This creates localized micro-plasma discharges on the surface of the substrate and facilitates the growth of a ceramic oxide layer. PEO coating results in improved tribological properties and can be grown to several hundreds of microns in thickness. Literature has analyzed several factors that affect the coating characteristics, but little has been done to analyze the electrolytic bath itself. The goal of this research is to determine the life expectancy of the electrolytic bath and develop structure-property relationships that relate bath use to film structure and performance in the PEO coatings.

Materials

Nine sample pucks of PEO coated 7075 aluminum were provided by IBC Coatings Technologies. The pucks were from various stages of the electrolytic bath life ranging from 0-101 amp-hours per liter (A*hrs/L).

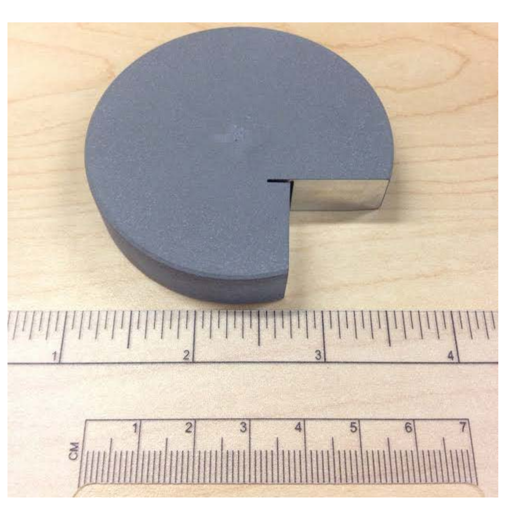

Figure 1. Photograph of sample provided by IBC.

Coating Thickness

Due to the surface roughness of the coating, the coating thickness can be measured in a multitude of ways. Measurements were obtained by determining the lowest point in the surface and measuring to the substrate. This eliminated some of the variation caused by the surface roughness in the top layer.

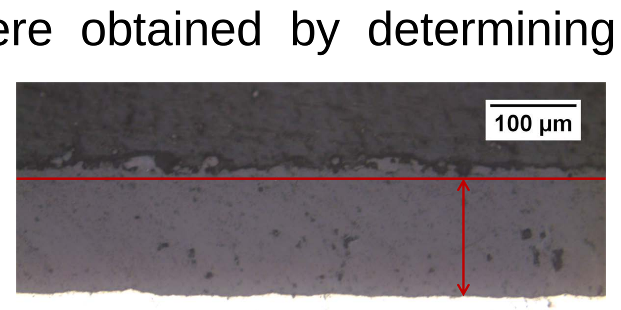

Figure 2. Micrograph of cross-section showing method of thickness measurements.

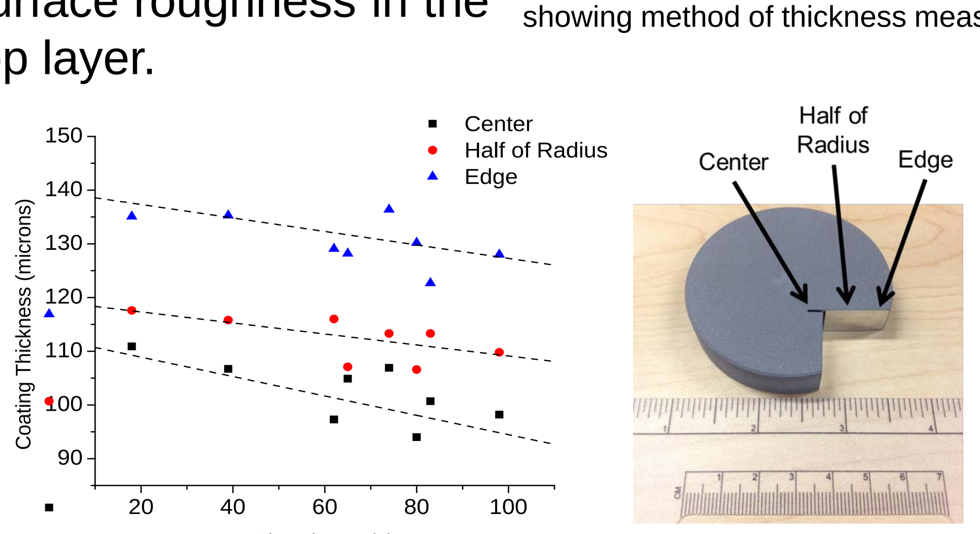

Figure 3. Plot of coating thickness as a function of bath life at varying locations on the puck, shown in the schematic. Each point represents a three A*hrs/L period in the bath.

Coating thickness increases as a function of radial distance from the center. The thickness measurements taken from half of the radius are used to represent the coating thickness of the sample. Thickness tends to gradually decrease with increasing bath life.

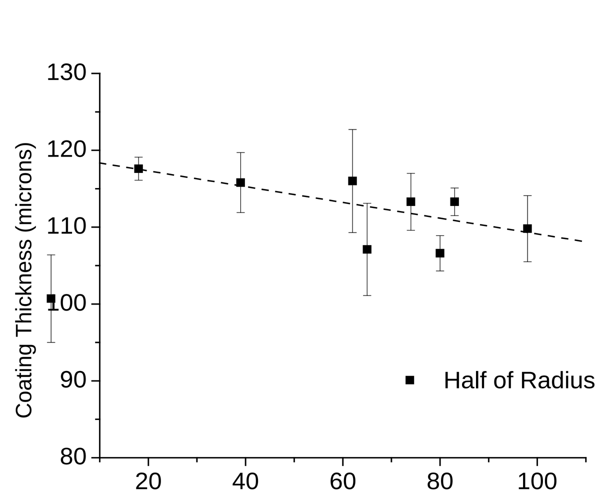

Figure 4. Plot of coating thickness versus bath life. Each point represents a three A*hrs/L period in the bath.

Coating Structure

Three different layers were discovered when analyzing the cross-sections of the samples using scanning-electron microscopy (SEM). The first is a barrier layer just above the substrate, the second is a middle layer which makes up most of the coating, and the third is a top layer with varying surface roughness. Mechanical ion slice testing revealed that visible features throughout the coating are not pores but rather a result of cracking that occurred during sample preparation.

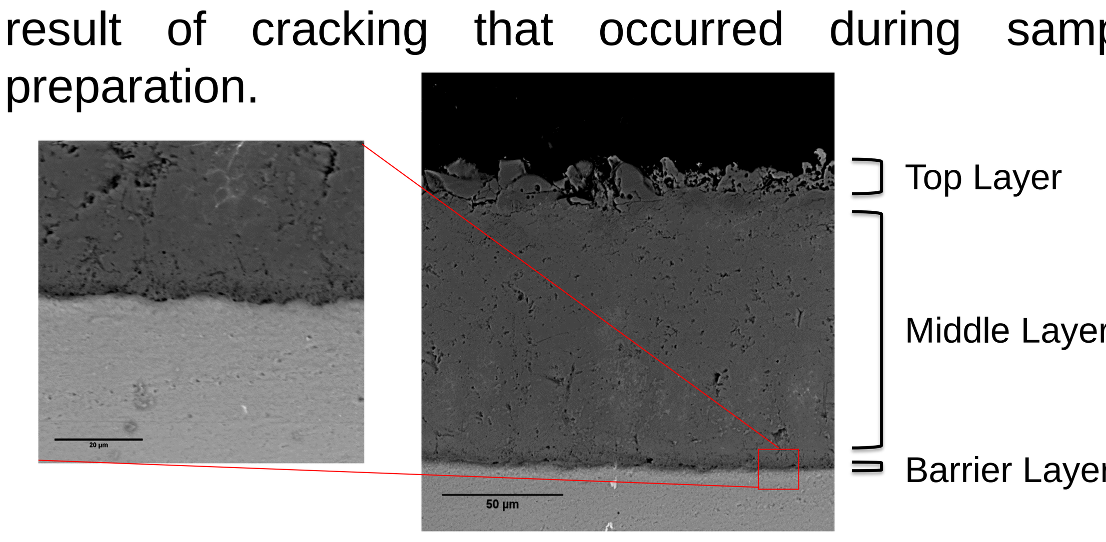

Figure 5. SEM image of 0-2.5 A*hrs/L sample with zoomed in image of the barrier layer at the coating substrate interface

Polarized light microscopy revealed a unique cellular-like structure that was difficult to detect under non-polarized imaging. The cause of this structure was determined to be a chemical or density difference, as this structure was visible in back-scattered SEM imaging but not in topographical analysis.

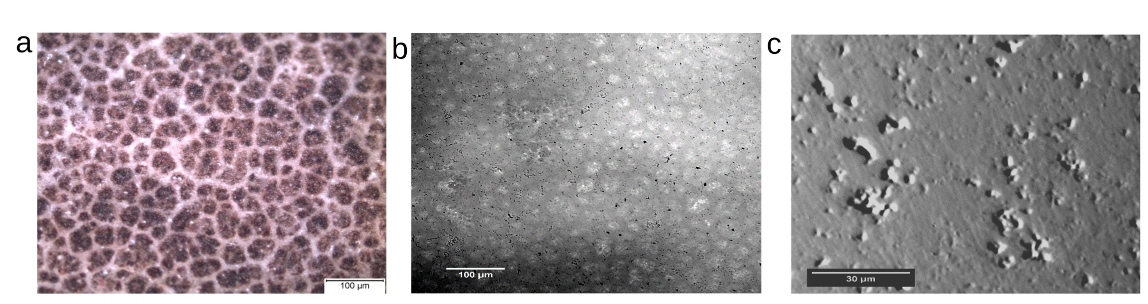

Figure 6. a) Darkfield image of 39-42 A*hrs/L sample, b) SEM backscattered electron image of 39-42 A*hrs/L sample, and c) SEM topographical image of 39-42 A*hrs/L sample. Thickness of the cell boundaries appears to decrease as a function of position in film.

The top surface and cross sections of the samples were analyzed using energy dispersive X-ray spectroscopy (EDS). Line scans as well as mapping of the cellular-like structure determined that an increase in copper and iron content was creating this structure. EDS also resulted in a trend of increasing magnesium from the barrier layer to the top layer of the coating.

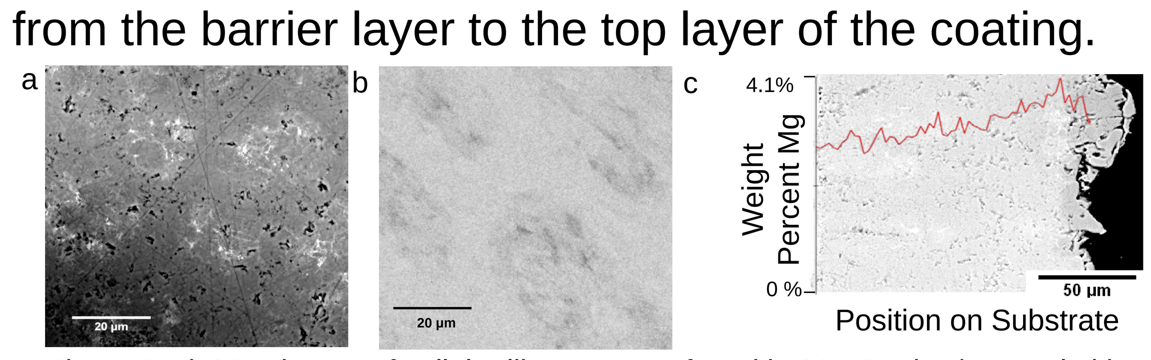

Figure 7. a) SEM image of cellular like structure found in 39-42 A*hrs/L sample b) EDS copper scan of image 7a c) plot of magnesium concentration in 0-2.5 A*hrs/L sample

X-Ray Diffraction

XRD spectra from the 18-21 and 98-101 A*hrs/L samples conclude that the overall structure of the material remains the same. There is little to no variation to this structure as the bath life increases.

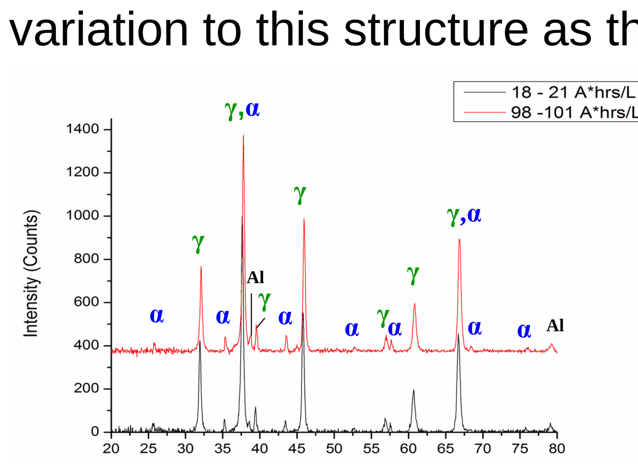

Figure 8. XRD spectra of 18-21 and 98-101 A*hr/L sample

The coating is mainly gamma alumina with the presence of alpha alumina and aluminum. Reference intensity ratios resulted in 84.3% γ-Al_2O_3 in the 18-21 A*hrs/L sample and 84.7% γ-Al_2O_3 in the 98-101 A*hrs/L sample.

Hardness Testing

Vickers microhardness testing was performed on polished cross-sections of the PEO coatings using a 50 gram load. Hardness was found to decrease throughout the layers as distance from the substrate increases. Indents in the barrier layer had low hardness values due to the effect of the soft aluminum substrate. Figure 9 displays the average hardness of each sample at varying thickness ranges.

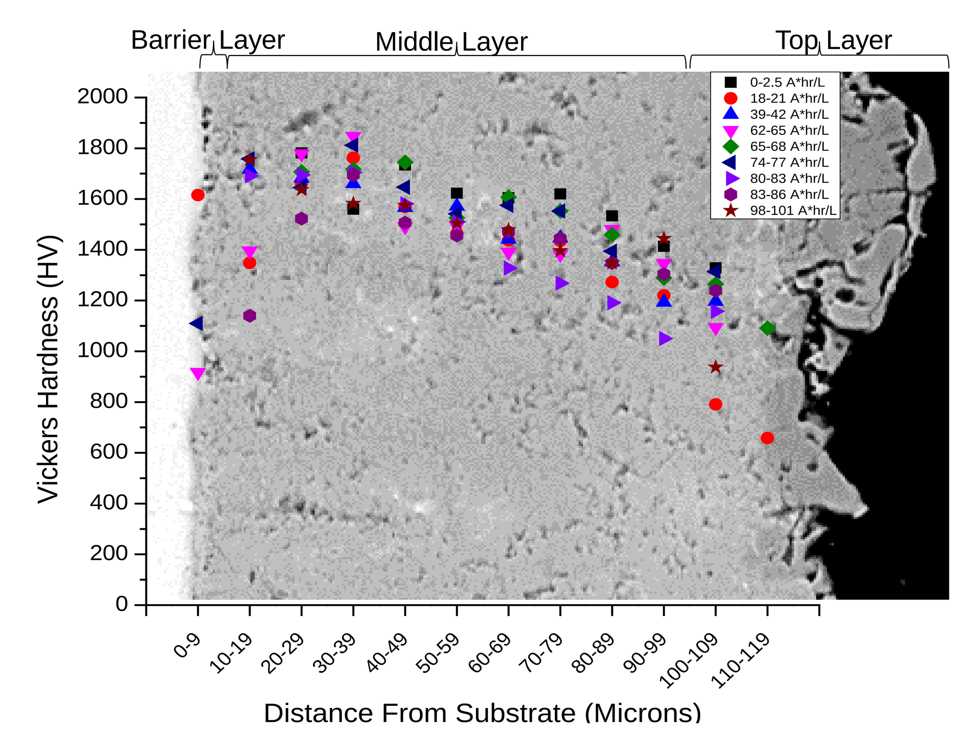

Figure 9. Vickers hardness data of PEO samples plotted with respect to distance from substrate overlaid on a SEM cross-section image of the 80-83 A*hrs/L sample

Data was statistically analyzed in the range of 20-80 microns from the substrate which excludes indents in the barrier layer and the rough top layer. Averages and standard deviations are presented in Table 2.

Two-tailed Mann-Whitney-U statistics test with a 95% confidence interval was used. Samples 80-83, 83-86, and 98-101 A*hrs/L were found to have statistically significant lower average hardness values. The decrease in hardness with respect to bath life could be linked to the changes in cell size.

Table 2. Hardness data collected 20-80 microns from substrate

Sample (A*hrs/L)	Average distance from Substrate	Average Hardness (HV)	# indents
0-2.5	53 ± 19	1653 ± 193	18
18-21	51 ± 17	1547 ± 153	14
39-42	50 ± 17	1563 ± 154	19
62-65	50 ± 18	1579 ± 223	19
65-68	52 ± 18	1638 ± 119	19
74-77	51 ± 18	1628 ± 125	16
80-83	49 ± 17	1517 ± 233	20
83-86	48 ± 17	1518 ± 145	16
98-101	49 ± 19	1523 ± 147	18

*Hardness values in gray are statistically different from hardness values in purple
*Samples not highlighted did not display statistical differences to any other sample

Conclusions

PEO coatings produced throughout a period of 0-101 A*hrs/L show:

- 8% decrease in thickness of coating with respect to bath life
- Presence of a newly identified cellular-like structure that forms due to compositional differences in the PEO film as a result of impurities in the substrate
- Little difference in alumina phase ratios present with 84.3% γ-Al_2O_3 near the beginning of the bath life and 84.7% γ-Al_2O_3 at the end of the 101 A*hrs/L bath life
- Around 7% decrease in average hardness of the coatings with respect to bath life

IBC Coatings Technologies has developed a robust plasma electrolytic oxidation process that produces films with uniform composition, high hardness, and relatively little degradation over 101 A*hrs/L of bath life.