Evaluation of anti-corrosion top coatings by scanning electrochemical microscopy (SECM)

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Naval Air Systems Command has a continuing need to provide better anti-corrosion coatings to its primary customer, the US Navy.¹ In an effort to provide more resolution of corrosion events, have proposed using scanning electrochemical microscopy (SECM) to make comparisons of various metal treatment regimens.

SECM is a technique developed in the Bard lab at the University of Texas in the early 80's.² It involves the use of a very small diameter electrode whose electroactive tip is only microns in diameter. The sharpened tip is positioned to within a few tip diameters of a surface which allows the surface to be electrochemically interrogated via a mediator in solution.³ This has been extended to study of both corrosion⁴ and film transport properties⁵. It was studies such as these that led us to attempt to use the SECM as a rapid screening tool for various potential anti-corrosion coatings.

This project seeks to make comparisons of the electrochemical performance of 7075-T6 aluminum with just primer vs. samples with primer and a top coat. The evaluation first, maps the topography of a small section of the surface by using the negative feedback mode at the insulating surface (figure 1). In this mode, the tip is set to oxidize ferrocene methanol which in an aqueous nitrate solution. Diffusion to the tip is blocked and current decreases when the electrode moves close to any feature on the surface in this mode. We use the current convention of (-) as oxidation. Thus in Figure 1, there is a clear feature to the left.

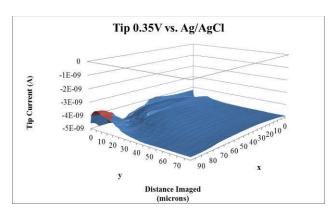


Figure 1: 100 x 100 micron section Solution is 1mM in FcMeOH/0.1 M KNO₃. The Pt tip has a diameter of 25 microns and is 25 microns above the surface.

The substrate generation – tip collection (SGTC) mode is then used to see how effective the surface is at passivating electrochemical activity of the aluminum and slowing diffusion of species to/from the substrate. This is done by setting potentials at the aluminum increasingly higher than the oxidation of the mediator to see if any species reducible by the tip are made. Features in the coating may lead to electrochemical which will make a basis for comparison. Note in Figure 2, the feature from Figure 1 gives rise to slight current perturbations at 0.5V, but more pronounced effects at 1.5V (Figure 3).

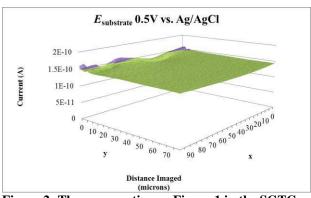


Figure 2: The same section as Figure 1 in the SGTC mode showing little activity.

Identical experiments on samples with the primer and top coat will allow us to evaluate how effective the additional treatment is in stopping any electrochemical activity.

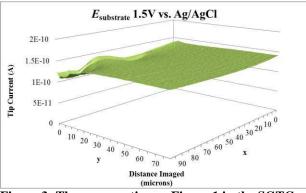


Figure 3: The same section as Figure 1 in the SGTC mode showing clear electrochemical activity at the higher voltage.

² A. J. Bard, Scanning Electrochemical Microscopy, New York, USA, Marcel Dekker, Inc., 2001.

³ L. Diaz-Ballote, M. Alpuche-Aviles, D. Wipf, "Fastscan voltammetry-scanning electrochemical microscopy," J. Electroanal. Chem., vol 604, pp. 17-25, 2007.

⁴ D. Walsh, L. Li, M. Bakare, K. Voisey, "Visualisation of the local electrochemical activity of thermal sprayed anti-corrosion coatings using scanning electrochemical microscopy," Electrochim. Acta, vol. 54, pp. 4647-4654, 2009.

⁵ M. Williams, J. Hupp, "Scanning Electrochemical Microscopy Assessment of Rates of Molecular Transport through Mesopourous Thin-Films of Porphyrinic 'Molecular Squares'," J. Phys. Chem B, vol. 105, pp. 8944-8950, 2001.

¹ D. Forman, E. Herzberg, J. Tran, A. Kelly, P. Chang, N. O'Meara, "The Annual Cost of Corrosion for Navy and Marine Corps Aviation Equipment" LMI Government Consulting, Report MEC70T3, May 2008.