Investigation of filiform corrosion on coated carbon steel by Scanning Kelvin Probe Force Microscopy

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Filiform corrosion is usually encountered on steel, aluminum, and magnesium underneath organic or metallic coatings in a humid air environment. Corrosion initiates in the presence of soluble ionic species at defects in the coatings and propagates at the metal/coating interface as worm-like filaments. The growth pattern, behavior, physical dimension and velocity of filaments have been reviewed in great detail [1-3]. The average width of filaments is only 0.05 mm to 0.3 mm for steel and 0.5 to 3 mm for aluminum but they can reach considerable length and compose intricate patterns [1]. A mechanism based on a differential aeration cell or oxygen concentration cell proposed by Kaesche [4] is the most satisfactory in explaining the reported characteristics of filiform corrosion. In this mechanism oxygen diffuses through the tail and leads to the separation of anodic and cathodic reaction zones. The primary cathodic region is near the back of the head (at the head/tail boundary) where oxygen is supplied and the primary anodic region is at the front edge of the head of the filament.

Although there is experimental support for this mechanism, there are still uncertainties on the exact location or shape of the cathodic and anodic sites. A more descriptive microscopic picture of local reaction sites in the head or near the head has not been presented yet. The mechanistic study of filiform corrosion by conventional electrochemical techniques is difficult because of the relatively small width of the filaments and the presence of the coating. For instance, the high resistance of organic coatings is the principle obstacle to the use of electrochemical impedance spectroscopy (EIS). EIS also fails to identify the corrosion site. Few techniques have spatial resolution abilities to image real-time events in areas 100 micrometers in diameter or less.

The Scanning Kelvin Probe (SKP) has been used for some time to measure the potentials of various metal surfaces. The applicability of the technique in the corrosion field has been demonstrated for metals covered with a thin layer of electrolyte or polymers [5-9]. SKP can provide information about Volta potentials distribution with a lateral resolution of approximately 50 μm. Although spatial resolution can be improved through tip size reduction and better distance control, very high spatial mapping with SKP has not been fully demonstrated yet.

Atomic Force Microscopy (AFM) is a powerful method for the characterization of surfaces with very high spatial resolution. Techniques associated with AFM have been used to generate considerable understanding of the corrosion behavior of aluminum alloy 2024-T3. Scanning Kelvin Probe Force Microscopy (SKPFM) was used to produce maps of the Volta potential distribution across surfaces of AA2024-T3 in air [10-12]. This technique provided clear evidence regarding shape, position, compositional inhomogeneities and local practical nobility of intermetallic compounds with submicron resolution. Potentials associated with cathodic and anodic reactions in filiform corrosion are expected to vary by several 100 mV and could be sensed by SKPFM with very high lateral resolution. SKPFM measurements during the delamination of ultra thin (20nm -100nm) plasma polymers on gold designed samples have shown a loss of spatial resolution up to 10 μm attributable to sample/tip separation and electrical charging of the coating. [13] Resolution remains nevertheless sufficient to provide a more detailed map of local oxygen concentration cells.

The aim of this study is to provide more information about the mechanism of filiform corrosion on coated steel using SKPFM and its high spatial resolution. SKPFM was used to spatially map variations in Volta Potential on the surface of coated plain carbon steel undergoing filiform corrosion. Different segments of filaments about 100 μm wide were investigated under epoxy coatings with a thickness of approximately 300 nm at 93% RH. Potential profiles showed regions of lower potential in the head consistent with anodic dissolution of steel while tails exhibited higher Volta potentials. Volta potential maps of regions less than 100 μm x 100 μm and topographic features will be presented.

[1] R.T. Ruggeri and T.R. Beck, *Corrosion*, **39**, 452 (1983).
[2] A. Bautista, *Progress in Organic Coatings*, **28**, 49 (1996).
[3] M.J. Schofield, J.D. Scantlebury, G.C. Wood and J.B. Johnson, *Proc. 8th Int. Cong. Met. Corr*., Mainz, 1047 (1981).
[4] H. Kaesche, *Werk. Korros.*, **11**, 668 (1959).
[5] M. Stratmann and H. Streckel, *Corros. Sci.*, **30**, 681 (1990).
[6] M. Stratmann and H. Streckel, *Werk. Korros.*, **43**, 316 (1992).
[7] N. Le Bozec, D. Persson, A. Nazarov, and D. Thierry, *J. Electrochem.Soc.*, **149**, B403 (2002).
[8] W. Schmidt and M. Stratmann, *Corrosion Sci.*, **40**, 1441 (1998).
[9] G. Williams, H.N. McMurray, *J. Electrochem. Soc.*, **148**, B377 (2001).
[10] P. Schmutz and G. S. Frankel, *J. Electrochem. Soc.*, **145**, 2295 (1998).
[11] P. Schmutz and G. S. Frankel, *J. Electrochem. Soc.*, **145**, 2285 (1998).
[12] P. Leblanc and G. S. Frankel, *J. Electrochem Soc.*, **149**, B239 (2002).
[13] E. Hornung, M. Rohwerder, and M. Stratmann, *Elektrochemische Verfahren fur neue Technologien*, GDCh-Monographie, **21**, 22 (2000).