



Corrosion Studies with the Atomic Force Microscope, Part I: Characterization of Potential Inhomogeneities on Passive Surfaces by Surface Potential Imaging (a.k.a., Scanning Kelvin Probe Force Microscopy)

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Introduction

Atomic Force Microscopy (AFM) offers 3 primary modes for imaging: Contact mode, TappingMode, and Torsion Resonance Mode (TRmode). Each primary mode enables numerous other modes, which we collectively refer to as secondary modes or derivative modes. Surface potential imaging, or Scanning Kelvin Probe Force Microscopy is a derivative of TappingMode AFM that is described in detail elsewhere.¹ What makes surface potential imaging different from most other derivative AFM modes is that, it furnishes reliable, repeatable *numerical* values of a quantity other than topographic dimensions, and maps that quantity across the sample surface area, simultaneously with topography. That quantity is the electrostatic potential of a small area—immediately underneath the AFM tip—on the sample surface, and it is measured relative to the potential of the AFM tip.

This application note first compares AFM-based surface potential measurements with electrochemical potential measurements made in bulk electrolytes, and shows the correlation. It then shows how the information in AFM surface potential images and electron micrographs of the same area of a sample surface may complement each other.

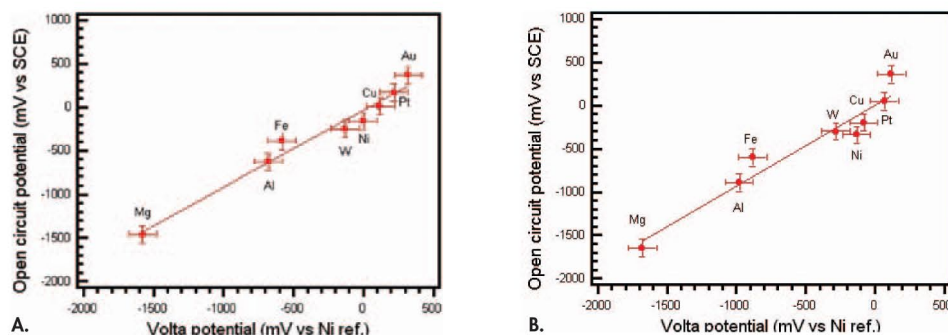


Figure 1. Correlation of AFM Surface Potential Measurements in air ("Volta potential") with open circuit potential measurements in electrolytes for different metals A) in de-ionized water, B) in 0.5M NaCl. See text. Reproduced by permission of The Electrochemical Society.³

The application note also shows how AFM surface potential measurements and electron scattering data correlate.

In short, the images and data presented here help establish the value and usefulness of AFM in corrosion science research, by illustrating that the qualitative and quantitative results stemming from the unique capabilities of AFM surface potential measurements and imaging correlate with results from other analytical techniques.

Correlating AFM surface potential measurements in air with open-circuit electrochemical potential measurements in electrolytes

In order to establish that the quantitative output of AFM-based surface potential measurement is meaningful for corrosion studies, in the sense that it correlates with measurements made with other techniques, we compared AFM-based surface potential measurements in air

with electrochemical potential measurements in bulk electrolytes, as described next.

Samples of different metals were immersed for 30 minutes in either de-ionized water (DI-H₂O) or a 0.5M aqueous NaCl solution. The stabilized open circuit potential was then measured for these samples versus a reference saturated Calomel electrode (SCE) using a potentiostat. The samples were then removed from the electrolytes, rinsed with DI-H₂O, and air-dried prior to AFM surface potential imaging and measurements with a Veeco Instruments Dimension 3100 SPM. The AFM tip was coated with a metal layer.² The potential of the tip was calibrated by measuring the surface of a pure Ni sample after exposure to water; this surface was found to provide reproducible measurements.

The AFM-based surface potential measurements are plotted in Figure 1, along the left-right axes, versus the open

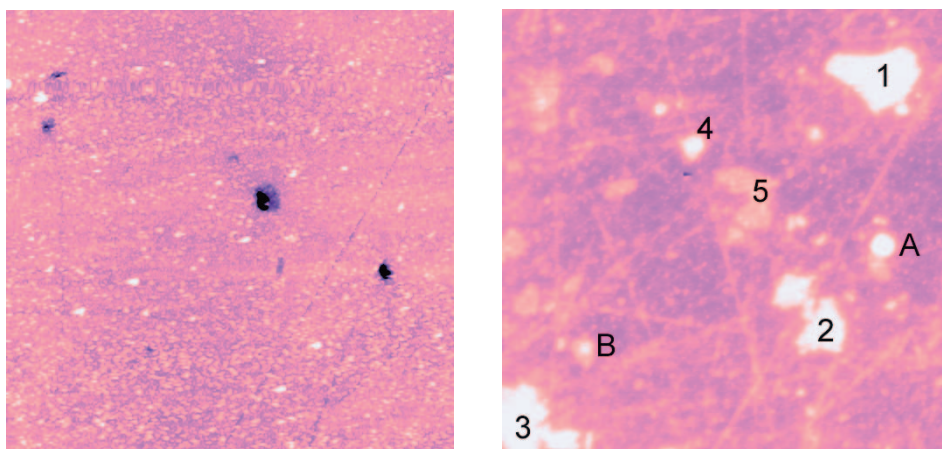


Figure 2. AFM Images of an AA2024-T3 alloy sample. Inter-metallic particles are visible as brighter areas (higher potentials) in the surface potential image (right). Topography (left) does not distinguish between the matrix and the inter-metallic particles. 60 μ m scans. Reproduced by permission of The Electrochemical Society.⁴

circuit bulk electrolyte measurements for DI-H₂O, and for the NaCl solution. The AFM measurements correlate linearly with the open circuit potentials, and can be associated with the Volta potential of the samples. The open circuit potentials measured in 0.5M NaCl are shifted in the active direction (i.e., they are lower) by around 200mV compared with measurements made in DI-H₂O.

These plots establish that surface potential *measurements* made with the AFM are reliable for establishing the relative nobility or activity of species, and can be compared with open-circuit potential measurements made of the same species in bulk electrolytes. The main difference is that AFM surface potential measurements may have very high in-plane (X,Y) resolution, allowing for deep sub-micrometer mapping of regions with different potentials, as we describe next.

AFM provides high-resolution surface potential measurements

A unique feature of AFM surface potential imaging is that it maps the potential locally, with a resolution that can extend down to the nanometer-scale in the plane of the sample surface. Figure 2

shows the surface of an aluminum-based AA2024-T3 alloy, commonly used in airplanes and extremely susceptible to corrosion. The left and right images are TappingMode AFM topography and surface potential maps, respectively, of the same area, 60 μ m on a side. Lighter shades of color in surface potential images correspond to higher potential values. On this sample, inter-metallic particles that are not evident in the surface topography are seen in sharp contrast to the embedding matrix in the surface potential image, which is captured simultaneously with the topography map. The surface potential image pinpoints the location and boundaries of inter-metallic particles. These particles measure from sub-micrometer to as large as 20 μ m across, and here they exhibit a higher potential than the alloy matrix. These potential differences are responsible for enhanced corrosion due to galvanic coupling between the different areas. The cathodic reaction rates are enhanced at these particles, while dissolution is stimulated at lower potential sites in the matrix or at active particles.

The surface potential image can also shed some light on the significance of the features in the TappingMode AFM

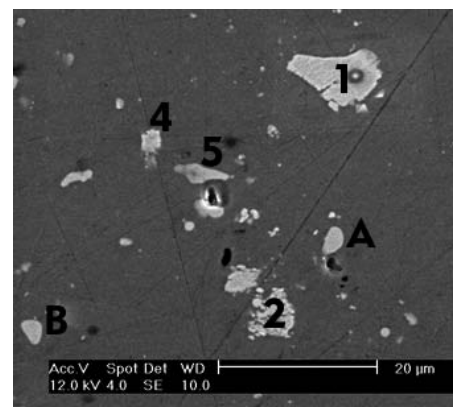


Figure 3. SEM image of approximately the same area as in Figure 2. EDS analysis indicated that particles 1-5 are Al-Cu(Fe,Mn) inter-metallics, and that A, B are Al-Cu-Mg inter-metallics. Reproduced by permission of The Electrochemical Society.⁴

topography image. In Figure 2, several pits are visible in the topography image (left): one associated with the inter-metallic particle 5 in the surface potential image, and one with particle A. This sample's surface was prepared by non-aqueous polishing to minimize corrosion during preparation, and was examined in the as-polished condition. The pits evident in the topography image formed during polishing (despite the non-aqueous polishing medium), because the sample is extremely susceptible to corrosion during the polishing process. The measured potential distribution (right) provides important information regarding the most likely locations for the anodic and cathodic reactions on the surface during subsequent exposure to a corrosive environment.

Comparing AFM surface potential imaging with electron-based-probe techniques

Figure 3 is a scanning electron micrograph (SEM) of approximately the same area shown in the AFM images in Figure 2. The contrast in the SEM results from the difference in the electron-scattering properties between the particles and the matrix. EDS

analysis performed on different particles confirmed that the regions of higher potential in Figure 2 are associated with different types of inter-metallic particles: particles 1-5 are Al-Cu(Fe,Mn), and particles A and B are Al-Cu-Mg. In the surface potential image in Figure 2, particles 4 and 5 measure at lower potentials than particles 1-3; so, there are apparently different types of Al-Cu-(Fe,Mn) particles present in the matrix. These are further evidence that surface potential images can complement information obtained from established analytical techniques, and vice-versa.

AFM surface potential imaging reveals effect of processing step

Experiments have shown that the Mg-containing particles will dissolve upon exposure of the polished surface to a chloride-containing solution, but that the attack takes some time to initiate.³ During this initiation time, the potential of these particles decreases to the value of the potential of the matrix.

Surface Potential imaging is extremely sensitive to surface charge. The as-polished AA2024-T3 samples are covered by a native oxide layer formed during polishing and subsequent exposure to air. We imaged an area of a sample surface, and identified in that area several round Mg-containing particles before and after removing some of the oxide with Argon ion sputtering (Figure 4). Auger analysis performed simultaneously with the sputtering showed that the sputtering removed only part (1-2nm) of the surface oxide thickness. The sample was then exposed to air again and the surface potential was remapped with AFM. The surface potential images in Figure 4 show that after removing a few mono-layers of the oxide from the surface, the measured potential of the Mg-containing particles shifted from

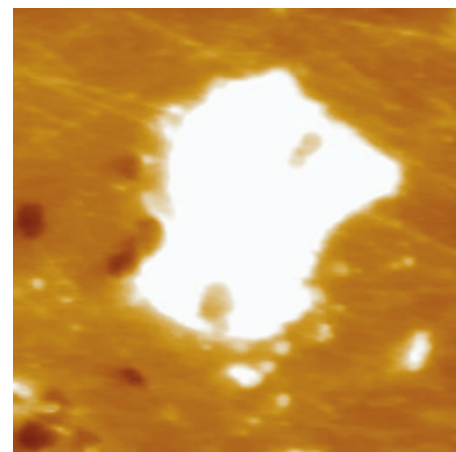
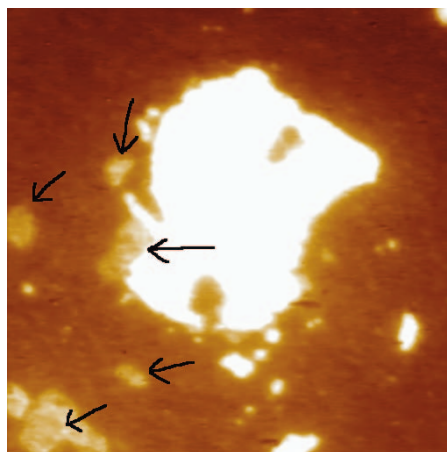
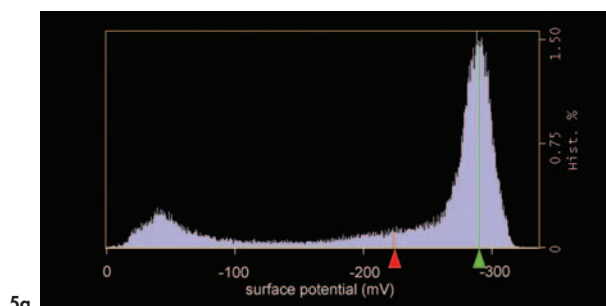


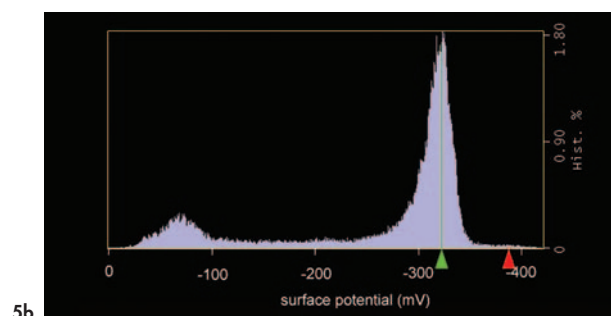
Figure 4. Surface Potential images of inter-metallic particles in AA2024-T3. The arrows point to the location of Mg-containing particles. (Left) before, and (right) after partially removing (about 1-2nm) the native oxide film by argon ion sputtering. 30 μ m scans. Reproduced by permission of The Electrochemical Society.⁵

being more noble than the matrix (higher potential, thus brighter colors in the image), to being more active (darker colors). The location and the boundaries of these particles are visible with sub-micrometer resolution. Surface potential *measurements* using data histograms (Figure 5) quantify the shift in potential to be from about 60mV higher than the matrix to about 60mV lower.

When this sample was exposed to a chloride solution, these particles dissolved immediately with no initiation time required. The redistribution of charge during the partial removal of the surface oxide film and re-growth in air resulted in activation of the particles, and this had an immediate consequence for the corrosion behavior.



5a.



5b.

Figure 5. Histograms of surface potential images in Figure 4. The round Mg-containing particles (correlating approximately to the position of red cursor in histograms) shifted from being about 60mV higher in potential than the matrix (green cursor in histograms), to being about 60mV lower after partial native-oxide removal (bottom histogram). (The peak on the right side in both histograms corresponds to the large, irregularly shaped particle, which is the dominant feature at the center of both images.)

Summary

AFM-based surface potential imaging and measurements are able to reveal details on the surface of a sample in unique ways that are useful to corrosion science research. These images and measurements, often with nanometer-scale in-plane resolution, are complementary to, and correlate with, data from other analytical techniques, including bulk techniques.

Other SPM Techniques for Corrosion Science Research

Soon after the development of AFM and Scanning Tunneling Microscopy (STM), electrochemical environment control of the sample was also introduced, in the form of open or closed liquid electrolyte cells, with electrochemical cell potential control and voltammetry display and analysis software integrated with the AFM (and STM) software. Today, electrochemical AFM and STM, play an important role in corrosion science research. For more information about these techniques, and also about the new, patented Scanning Electrochemical Potential Microscopy (SECPM), we invite you to visit the Veeco Instruments website, or contact us directly.



Footnotes:

1. Please see Veeco Instruments Application Notes "TappingMode AFM Imaging Applications and Technology" (AN 04) and "Electric Force Microscopy, Surface Potential Imaging and Surface Electric Modification with AFM" (AN 27), online at www.veeco.com.
2. Many types of tips have been used and worked well for this kind of measurement. We've used tips coated with CoCr, or NiSi, or PtIr. Even uncoated silicon TappingMode tips work as long as they are made of heavily doped silicon, so that they are quite conductive. Uncoated tips usually cost less than coated tips.
3. P. Schmutz and G. S. Frankel, "Characterization of AA 2024-T3 by Scanning Kelvin Probe Force Microscopy," *Journal of the Electrochemical Society*, 145, 2285-2295 (1998).
4. P. Schmutz and G. S. Frankel, "Corrosion Study of AA2024-T3 by Scanning Kelvin Probe Microscopy and *In Situ* Atomic Force Microscopy Scratching" *Journal of the Electrochemical Society*, 145, 2295- 2306 (1998).
5. V. Guillaumin, P. Schmutz, and G. S. Frankel, "Characterization of Corrosion Interfaces by the Scanning Kelvin Probe Force Microscopy Technique" *Journal of the Electrochemical Society*, 148, B163-173 (2001).

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