



In Situ Investigations of Corrosion via SPM

Application Note

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Metals, minerals, and plastics are all subject to the destructive power of corrosion — affecting billions of dollars of repair and replacement costs per annum. It is not, however, a one-sided battle. Public and private sectors combat corrosion by pouring billions of dollars into research aimed at developing advanced corrosion-resistant materials, corrosion-resistant paints and coatings, and corrosion inhibitors.

Corrosion is an interfacial phenomenon, occurring at solid surfaces in contact with gases or liquids. Although it often has macroscopic consequences, corrosion typically begins at the atomic level. These factors make corrosion processes ideal candidates for study via *in situ* scanning probe microscopy (SPM), a highly sensitive surface technique that can be utilized in the presence of a wide range of corrosive solutions and gases. The versatility of *in situ* SPM enables direct, real-time observation of corrosional processes with atomic or near-atomic resolution, often providing valuable kinetic information as well as important structural data.

The use of *in situ* SPM as a key research tool for studying corrosion has been steadily gaining popularity over the past several years. Researchers have utilized SPM to

investigate the structure of a variety of noble metal surfaces (1) and passivated surfaces (2, 3), electrochemical SPM to investigate the rate and mechanism of corrosion, and scanning tunneling microscopy (STM) to investigate the adsorption, orientation, and ordering of corrosion inhibitors on copper and silver surfaces (4). Information about the coverage and adherence of paints and other coatings is also easily accessible via use of these techniques.

Agilent's product line is uniquely suited to the *in situ* investigation of corrosion, providing a number of features designed specifically for these studies. For instance, Agilent's specially engineered electrochemical cell has a large volume-to-surface area ratio. The open design of the cell accommodates a large ring counter electrode, thus ensuring uniform distribution of current. Furthermore, removal of precipitates and gas bubbles can be accomplished by exchanging the solution in the cell without disrupting the experiment. Additionally, the Agilent environmental chamber can be used to control the amount of dissolved oxygen in the electrolyte or to introduce reactive gases. These features, combined with easy optical access, precision temperature control plates, and a truly modular design, make Agilent SPM systems an ideal choice for corrosion studies.

This application note describes three specific examples in which SPM has been used to study various aspects of metallic corrosion. More information about studies of corrosion using SPM can be found on Agilent's website or by contacting Agilent directly.

Corrosion of Steel

A study was conducted to investigate the effects of a sodium chloride solution on 304 stainless steel. In preparation, the sample was cut from a 304ss rod, polished to a roughness of less than 30 nm over 15 microns, and sonicated in deionized water for 20 minutes. The sample was transferred to the electrochemical cell and studied.

Figure 1A shows an image of the steel surface immediately upon immersion into 100 mM NaCl in purified, distilled water. The large inclusion in the bottom-left corner of the image was most likely a result of the polishing process. The sample was continually monitored while being held at open circuit in the corrosive solution. Images at 30 minutes (Figure 1B) and 150 minutes (Figure 1C) show the rapid dissolution of the inclusion and the corrosion of the surrounding stainless steel, suggesting that corrosion proceeds through a pitting mechanism.



Selective Dissolution of Aluminum

The tip-induced, selective dissolution of an aluminum foil is shown in Figure 2. The aluminum sample was imaged in 100 mM NaCl at high contact force, causing the formation of a recessed region. The dissolution mechanism is not simply rubbing away of the top layers of aluminum as one might assume from the image, as evidenced by the fact that the dissolution does not occur in the absence of chloride. Instead, the mechanism is thought to be a two-step process in which the passivating layer is first broken and then the chloride ions react with the underlying aluminum (5). Such experiments may represent a convenient method for studying the stability and strength of passivating coatings.

Kinetics of Aluminum Corrosion

Figure 3 shows a sequence of atomic force microscopy (AFM) images for the dissolution of an aluminum thin film in 100 mM sulfuric acid. In the preparation of the substrate, aluminum (99.999%, Puratronic) was deposited using physical vapor deposition onto mica in vacuum (base pressure = 5×10^{-9}). Imaging began immediately upon addition of 100 mM H₂SO₄ to the electrochemical cell; no efforts were made to eliminate oxygen from the electrolyte. The corrosion rate at open circuit was slow enough to capture a long image series that demonstrates the kinetics of aluminum corrosion, which proceeds through an apparent step dissolution process within terraces as well as at step sites and defects. Future studies will concentrate on the effects of corrosion inhibitors on the dissolution process.

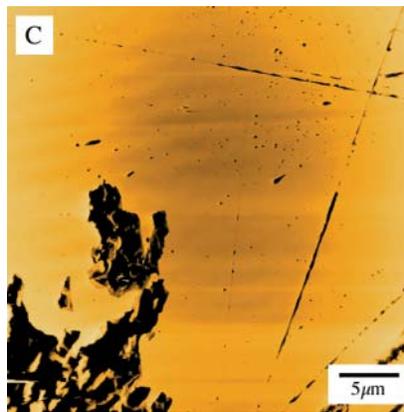
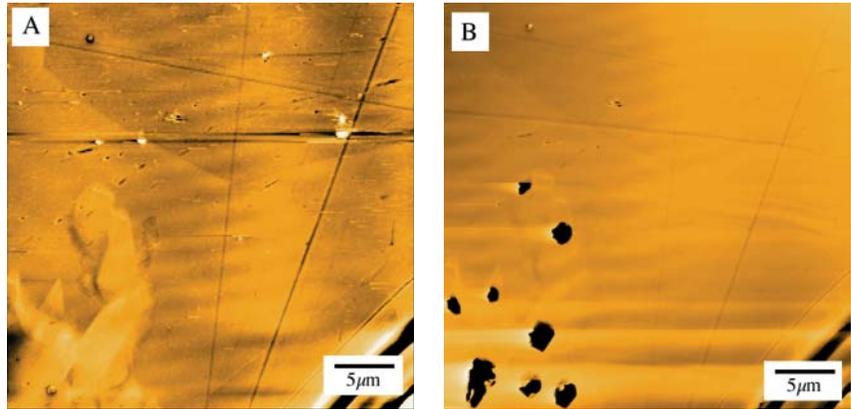


Figure 1. AFM images of the corrosion of 304 stainless steel in sodium chloride solution after (A) 4 minutes (z range = 50 nm), (B) 30 minutes (z range = 250 nm), and (C) 150 minutes (z range = 500 nm). Images courtesy of David Uhl, Arizona State University.

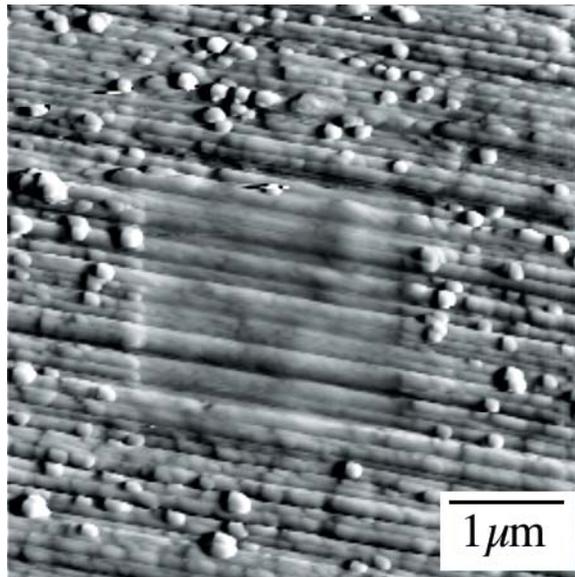


Figure 2. AFM image of the selective dissolution of aluminum in sodium chloride solution. The recessed region in the center of the image had been previously scanned at high force, accelerating the aluminum corrosion. Z range = 1 nm.

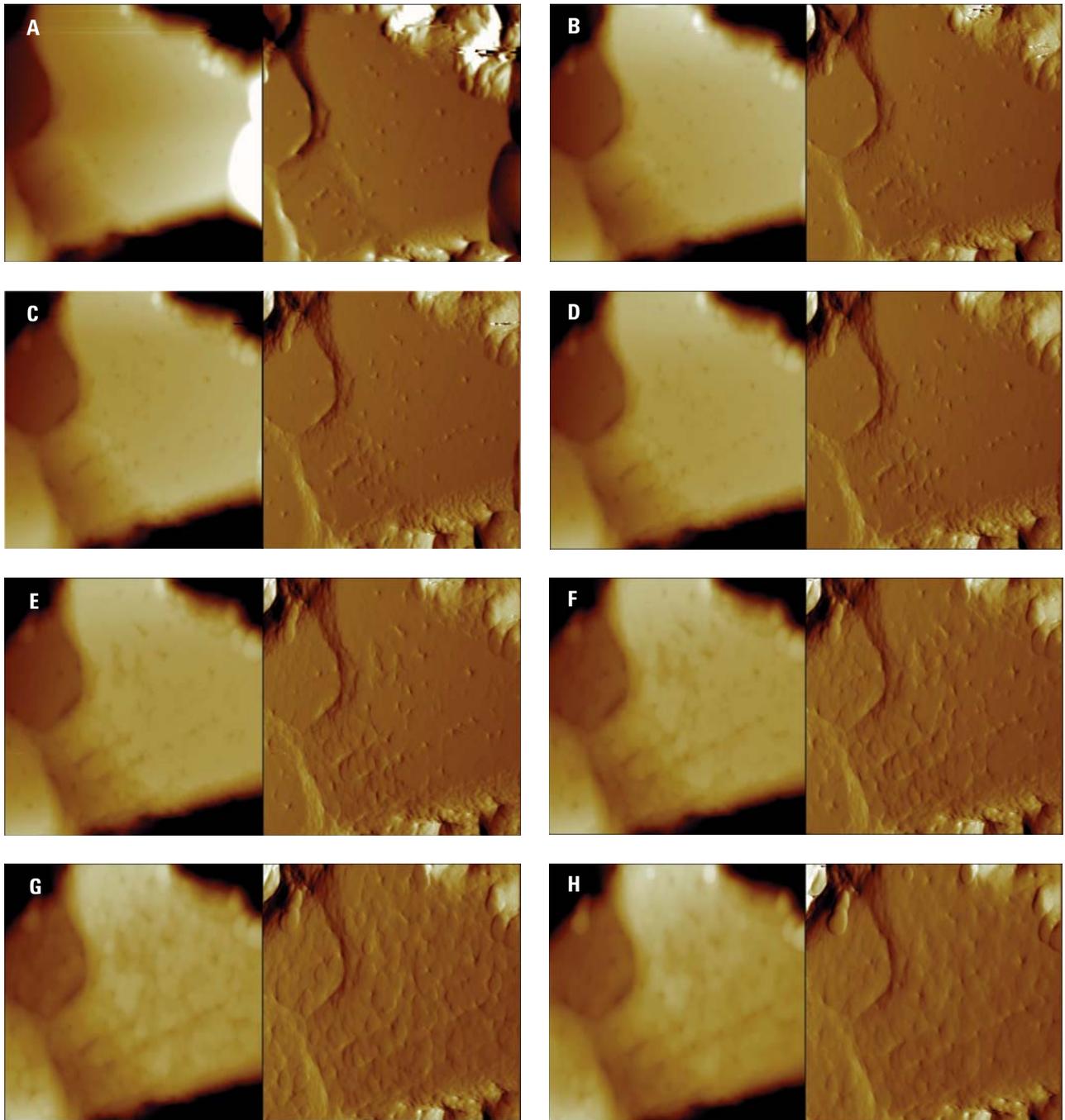


Figure 3. AFM height (left) and deflection (right) images of the corrosion of aluminum in 100 mM sulfuric acid after (A) 0 minutes, (B) 5.5 minutes, (C) 8 minutes, (D) 11 minutes, (E) 16 minutes, (F) 21.5 minutes, (G) 27 minutes, and (H) 43 minutes. Z range for height = 175 nm. Z range for deflection = 5 nm.

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Revised: May 7, 2007

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Printed in USA, June 5, 2007

5989-6895EN



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