Spectroscopic Imaging at Localized Corrosion Sites

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Corrosion issues assume great importance for materials and microstructures used in microelectronics and in micromagnetics where critical materials are present in small domains embedded in insulating or dielectric matrices. Localized types of attack have also been studied intensively for metal alloys where the vulnerable domains are associated with inclusions, second phase particles, and grain boundary regions. These sites are studied by both ex situ and (more recently) in situ microscopy techniques to determine the nature of the reactivity of the surface. As the functional domains shrink to smaller sizes, one must use high resolution techniques to reveal the local nature of any corrosion attack. The mapping of properties on a small scale to create an image representing the composite response of a surface has both topographic and chemical components. In the present study we are interested in improving the ability to characterize the chemistry at reacting sites by utilizing spectroscopic methods.

In previous work, localized corrosion of an Al2024 alloy was studied by near-field scanning optical microscopy (NSOM) and SECM and fluorescence microscopy (Alodan, et. al. 1997, 1998; Guillaume, et al. 1998; Büchler, et al. 2000) using fluorescein as a fluorescent probe. Fluorescein decorates the corrosion product deposits formed around anodic sites at surface inclusions, but does not participate to the corrosion process itself (Alodan, et al. 1998). The same fluorescent pattern is achieved if a corroded sample from a solution containing no fluorescein is briefly immersed in a solution with fluorescein (Alodan, et. al. 1997). Dyes forming fluorescent chelates with free Al^{3+}, like morin and quercetin, also yield fluorescent features similar to fluorescein (Büchler, et. al. 2000). The corrosion products are presumably Al-hydroxo polymeric species.

We are interested to extend the range of application of high resolution NSOM imaging from fluorescence detection to fluorescence imaging and chemical mapping. The success of NSOM fluorescence detection of single molecules in an illumination/collection mode (Hosaka, et. al. 2001) and of near-field Raman spectroscopy (Grausem, et. al. 1999) prove that acquisition of very small NSOM signals is possible. However, the design of a near-field scanning fluorescence spectrometer capable of acquiring full spectra in a meaningful time span remains a formidable and expensive challenge. The combination of still not very well understood near-field optical artifacts with the fact that near-field spectra are known to be somewhat different (Narita, et. al. 1998) from far-field spectra make the design of a near-field scanning spectrometer a step-wise process. It is also necessary to verify that, in the case of the dyes used here, the increase in spatial resolution will be paralleled by an increase in spectroscopic information. With such a task in mind, we have designed an optical microscopic system that is able to take fluorescent spectra at individual surface features (e.g., fluorescent disks and rings) in order to assess factors such as degree and variability of chemical shift, fluorescence lifetime, noise intensity and spectrum acquisition time. The exploratory instrument consists of a Leica optical microscope coupled to a fiber optic microspectrometer. In the present paper, we will describe the successful measurement of the fluorescence spectra of fluorescein embedded into the ring of corrosion products at inclusions on Al2024.

The microspectrometer used in the present study is an Ocean Optics USB2000 (Ocean Optics) with a 200nm – 850nm spectral range, a resolution of 0.35nm and a Sony IXL511 2048 elements linear CCD array as a detector. The input is a SMA-terminated optical fiber with a numerical aperture of 0.22 connected to a source-to-fiber collimating adapter. The optical microscope was a Leica DMLM equipped with a 100W Hg(Xe) arc lamp illuminator and a JVC TK-1070U video camera mounted on the auxiliary port. The miniature spectrometer connected to the USB port of a Dell Inspiron lap top computer. To couple the microscope to the spectrometer, we used an eyepiece tube without a lens and mounted the optical fiber collimating adapter (a micro-lens in a SMA mating sleeve) into the tube; the adapter being secured in place with an 1 1/4-inch aluminum washer machined to the tube inner diameter.

The spectrum on a bare surface of polished Al2024 was essentially featureless. The fluorescence spectrum of fluorescein in an isolated inclusion with its ring of corrosion products was blue shifted with maximal position ranging from 506.8nm to 511.5nm. Background spectra were taken at close proximity to the inclusion where the view field appeared totally dark to the naked eye. Interestingly, the latter spectra revealed the presence of a weak fluorescein fluorescence spectrum but not at the same wavelength position. Discussion of the latter observations will be presented.

We conclude that fluorescence spectroscopy of micrometric-size features is possible by a straightforward modification of an ordinary optical microscope coupled to a low-cost miniature fiber optic spectrometer. And finally, we will discuss how the technique is used on our f-NSOM instrument for chemical mapping at high spatial resolution.

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