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Nano-FTIR microscopy and spectroscopy studies of atmospheric corrosion with a spatial resolution of 20 nm

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ABSTRACT

Since corrosion commonly occurs heterogeneously over a surface, studies on a microscopic level are desired to obtain a complete picture of the process. Here, we demonstrate the capability of nano-FTIR microscopy to spectroscopically determine the nature of different corrosion products and their spatial distribution with a resolution of 20 nm, two-three orders of magnitude better than conventional IR microscopy. A copper surface was exposed to a humid atmosphere containing formic acid, and in addition to cuprite the corrosion product copper formate was observed to form inhomogeneously in particles of some tens to a few hundreds of nm.

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1. Introduction

Copper is a widely used metal in industrial applications such as in electronic components and heat exchangers, due to its excellent electrical and thermal conductivity. However, in many environments copper is susceptible to atmospheric corrosion, which can cause failure of an equipment [1]. In corrosion and oxidation processes the attacks are frequently distributed inhomogeneously over the surface due to imperfections and grain boundaries, for example. Thus, in order to obtain a complete understanding of a corrosion process, it should preferably be studied on a microscopic level. The atmospheric corrosion of copper has been extensively studied in the past [2–6], and several techniques have been employed to investigate the inhomogeneous formation of corrosion products, such as conventional infrared (IR) microscopy (spatial resolution of some or commonly a few tens of μm) [7–11], confocal Raman microscopy (some hundreds of nm) [12–14], and atomic force microscopy (AFM, ~Å) [12,15]. Unfortunately, the techniques able to provide vibrational spectroscopic information about the nature of the corrosion products have a significantly lower spatial resolution due to diffraction limitation than for example AFM, but a drawback with AFM is that it cannot yield chemical information. Hence, it would be desirable to combine the chemical information provided by vibrational spectroscopy with the spatial resolution achievable with AFM. During the last years this AFM/IR combination has been feasible through a nano-FTIR technique, a scattering-type scanning near-field optical microscope (s-SNOM), which provides FTIR spectra with a spatial resolution of ~20 nm [16–20]. In addition, the topography of the surface is simultaneously determined by AFM. The technique works by focusing an IR laser beam at the AFM tip, which acts as an antenna and concentrates the radiation at the apex of the tip [21]. The spatial resolution is dependent on the size of the apex of the tip [22]. To obtain an infrared spectral image of the surface, the sample is moved within this nano focus and the scattered radiation is detected.

Here, it is for the first time demonstrated how nano-FTIR microscopy and spectroscopy can be used to investigate the spatial distribution of corrosion products. The system investigated is a copper surface exposed to an atmosphere containing humid air of 80% RH and 100 ppb formic acid, typical conditions to simulate an indoor atmospheric corrosion process [23]. The concentration of formic acid in many indoor environments is around 20 ppb [24,25], and this simplest carboxylic acid is an important corrosion promoter indoors. Nano infrared spectra and spectral images with a spatial resolution of 20 nm of the corroded copper surface have been obtained, which is two-three orders of magnitude better than with a conventional IR microscope. With this spatial resolution, being significantly better than in earlier vibrational spectroscopy studies of corrosion and oxidation processes, new doors are opened

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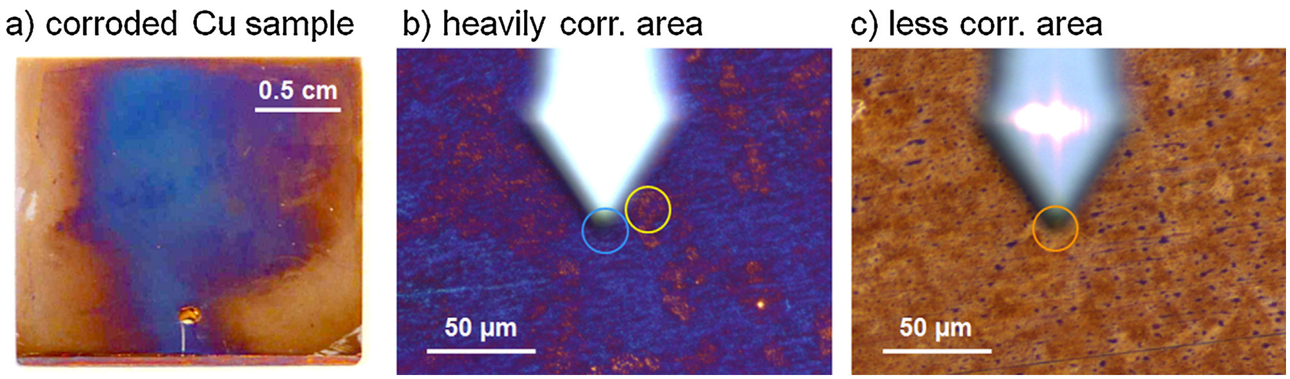

Fig. 1. (a) A photograph of the corroded copper surface. The pictures in (b) and (c) are obtained from an optical microscope integrated in the s-SNOM system and show the (b) heavily and (c) less corroded areas, respectively. The circles in (b) and (c) indicate the areas studied by nano-FTIR microscopy.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the field and will allow future detailed investigations on the nano level of key corrosion phenomena such as pitting, the homogeneity of inhibitor films, and very early corrosion when only tiny amounts of corrosion products have formed.

2. Material and methods

Nano-FTIR experiments have been performed on a commercial s-SNOM system (www.neaspec.com) equipped with a broadband DFG laser for spectroscopy and a tunable mid-IR laser (QCL) for IR imaging. Background signal is efficiently suppressed by demodulating the measured intensity at higher harmonics of the AFM tip oscillation frequency, with n indicating the nth harmonic [26]. In the s-SNOM system, near-field amplitude (s_n) and phase (φ_n) images were obtained by interferometric detection using the pseudoheterodyne principle [26]. In spectroscopy mode, interferograms of 600 µm length have been measured with an asymmetric Michelson interferometer, resulting in amplitude and phase spectra of about 8 cm^{-1} spectral resolution [16]. All spectra were normalized to gold.

Copper surfaces of 2 × 2 cm (99.99%, Goodfellow) were abraded in ethanol with SiC paper down to 4000 mesh, and subsequently polished with diamond paste down to 0.25 µm. The samples were then thoroughly rinsed and sonicated in ethanol, dried with nitrogen, and inserted into the exposure chamber. An atmosphere at 21 ± 0.5 °C containing 80% RH and 100 ppb formic acid flowed over the sample surface at a rate of 1.2 L/min. Infrared reflection/absorption spectroscopy (IRAS) spectra were acquired in-situ with a resolution of 4 cm^{-1} and averaged over 1024 scans using a Digilab FTS 40 Pro spectrometer. The p-polarized IR beam was incident to the surface with an angle of 78° from the surface normal and detected with an external MCT detector. A detailed description of the experimental setup[27] and sample preparation[3] is found elsewhere.

3. Results and discussion

As can be seen in the photograph in Fig. 1a, the sample is heavily corroded in the middle (blue color) and less corroded on the sides (still copper colored). Fig. 1b shows the highly corroded central parts, and Fig. 1c the less corroded areas on the sides in 1a, viewed through the light microscope integrated in the neaSNOM system. The heavily corroded bluish areas in 1b (blue circle) also contain less corroded yellowish areas (yellow circle), and the area in Fig. 1c contains tiny darker spots indicating more pronounced local corrosion (orange circle). The circles in Fig. 1b and c indicates the areas which have been investigated with nano-FTIR microscopy.

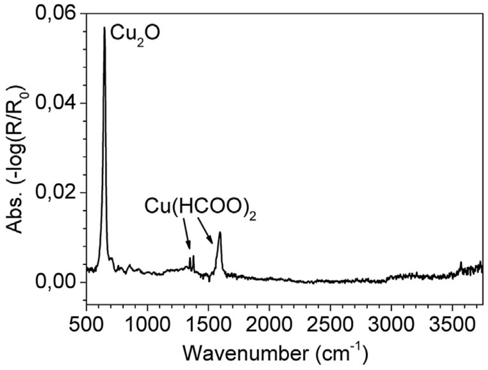

Fig. 2. An IRAS spectrum of the corroded copper surface after 18 h. The spectrum has been background subtracted.

To obtain information about the nature and the amount of the corrosion products, in-situ infrared reflection/absorption spectroscopy (IRAS) was used. Fig. 2 shows the IRAS spectrum after 18 h of exposure, and reveals the formation of cuprite (Cu_2O) at ~650 cm^{-1}, and copper formate ($Cu(HCOO)_2$) at 1350 cm^{-1} (in plane CH bending mode), 1377 cm^{-1} (symmetric carboxylate stretch), and ~1600 cm^{-1} (antisymmetric carboxylate stretch) [3]. Based on earlier studies, the absorbance at 650 cm^{-1} corresponds to an average thickness of ~40 nm cuprite, and the absorbance at 1600 cm^{-1} has been determined to correspond to a layer of copper formate ~4 nm thick [4]. However, the diameter of the IR beam is on the order of a few cm^2, and thus the film thicknesses are averages over a large surface area. To identify and scrutinize the spatial distribution of the two corrosion products on the nano level, IR spectra in the range ~630–1750 cm^{-1} have been acquired on various spots at the surface, and IR images of areas 1 × 1 and 5 × 5 µm^2 have been obtained at the most intense absorption frequency (1600 cm^{-1}) of copper formate. No laser line was available at 650 cm^{-1}, and hence no images highlighting Cu_2O could be obtained.

Fig. 3a shows an AFM topography image of the less corroded area in Fig. 1c (orange circle), and reveals the presence of chunks with a diameter of some tens of nm. The s-SNOM IR amplitude image (s_3) in Fig. 3b and the phase image (φ_3) in Fig. 3c at 1600 cm^{-1} obtained simultaneously with topography reveal that the chunks are enriched in copper formate, leading to a strong phase shift [19]. The amplitude reflects the scattering behavior of the material, and is thus sensitive mainly to the real part of the complex permittivity Re(ε_s). The amplitude image in Fig. 3b thus indicates changes in the refractive index. Hereafter only the phase images will be discussed since they provide direct chemical information, due to the sensitivity of the phase to IR absorption [28]. To determine the spatial

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