In-situ spectroelectrochemical studies of the removal of chlorides from copper

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Abstract

This paper describes corrosion potential measurements of corroded copper samples taken whilst acquiring time-resolved X-ray diffraction or X-ray absorption data in a synchrotron beam line. The surface structure of the samples and its evolution, whilst under simulated conservation treatment in sodium sesquicarbonate, were examined using X-ray diffraction. The fluid chemistry over the sample was monitored during identical experiments using X-ray absorption. All measurements were carried out with the sample immersed (i.e. without the need to expose the sample to air). Processes were followed from initial wetting of the surfaces through to the cessation of measurable change. A webcam was used to make a simultaneous visual record of the sample and its environment. The experiments aim at contributing to the improvement of conservation methods for cupreous artefacts recovered from marine environments.

Keywords: copper, corrosion, marine, conservation, spectroelectrochemistry, X-ray absorption spectroscopy, X-ray diffraction

Introduction

It is well known that cupreous artefacts recovered from marine environments are jeopardized by exposure to air until the chlorides have been removed from the metal (Hamilton 1998). This is usually accomplished by soaking in tap water or dilute sodium sesquicarbonate, for a period of up to several years. Nevertheless, the metals often show some instability, such as the transformation of the natural patina and the development of active corrosion (Horie and Vint 1982; Pollard et al. 1990). As a result, continuous monitoring of the system remains essential. Usually this is done by measuring the chloride level at regular time intervals in the solution. The latter, however, is an indirect method in the sense that it does not provide information on the actual changes on the metal surface. Corrosion potential measurements (Ecorr), on the other hand, are potentially able to provide information on the surface chemistry. One hypothesis might be that, if the corrosion potential does not change as a function of time, the surface composition should be stable. A change of the corrosion potential, on the other hand, could indicate a transformation of the natural patina or the development of active corrosion.

In previous experiments we have evaluated this method using ex-situ synchrotron radiation X-ray diffraction (SR-XRD), which necessitated the transfer of the samples from the solution to air (Leyssens et al. 2004, 2005a, 2005b). In this paper we describe the acquisition of the corrosion potential of a set of corroded copper samples and the analysis of their surface simultaneously in-situ using either SR-XRD or X-ray absorption (XAS). The latter techniques provide respectively information about the presence of crystalline products on the surface and the solution chemistry in the selvedge layer above the sample. The study was carried out using a novel electrochemical cell (eCell) designed for time resolved synchrotron spectroelectrochemistry.
**Experimental**

Circular copper coupons, 12 mm in diameter (ADVENT, purity 99.9 %), were made into electrodes that fit the electrochemical cell described below (see working electrode assembly in figure 1). The electrodes were ground on 1200 grit SiC paper to obtain a fresh surface. Further smoothing of the surface was carried out using a polishing cloth covered with alumina powder of 1 μm particle size. The adherent Al₂O₃ particles on the surface were removed by immersing the samples in an ultrasonic bath containing propan-2-ol for 15 minutes and rinsing them thoroughly with deionized water. The samples were corroded artificially to obtain different chloride-containing corrosion products, including nantokite (CuCl) and atacamite (Cu₂(OH)₃Cl). Details on these corrosion protocols can be found in previous papers by Leyssens et al. (2004, 2005a, 2005b).

eCell is a specialized electrochemical cell compatible with synchrotron radiation X-ray based methods. The cell is made from PCTFE for good chemical resistance and reasonable mechanical stability. It is basically a cylinder 60 mm in diameter and 100 mm high containing a piston which is driven along the bore by a stepper motor through a dynamic seal. The working electrode, whose surface forms the sample for X-ray analysis, is mounted on the piston. It can be moved precisely to translate the reacting surface from an “electrochemical” position, in proximity to a reference electrode, through an annular platinum counter electrode to a “X-ray analysis” position close to a flexible 8 μm thick Kapton window. In the latter position, the path length for X-rays in the electrolyte is a fraction of a millimetre to reduce scattering and X-ray absorption. In order to establish permanent potential control on the electrode surface, a rigid polyethylene tetraphthalate inner window with a rectangular or elliptical hole in the middle is positioned just inside the Kapton, limiting the electrolyte thickness in a reproducible manner to 100-175 μm, depending on its thickness. In this way, the cell can be used down to X-ray energies below 8 keV. The two windows are tightly fastened onto the cell body by an O-ring. The cell is equipped with a silver/silver chloride reference electrode and a platinum counter electrode. Figure 1 shows a cut-away diagram of the cell. The prototype of the cell used is described in more detail elsewhere (Dowsett and Adriaens 2006). The system is complimented by a webcam which allows video or stills of the eCell operation to be observed and captured.

SR-XRD experiments were performed on station 2.3 at SRS (Daresbury Laboratories). A monochromatic beam with a wavelength of 1.6 Å was used. Slits were positioned so that an area of 2 mm² was analyzed. Typically, the detector scanned the 2θ range 24-50° with a step size of 0.02° (counting time 1 s/step). The photon intensity was in the range 10⁹-10¹⁰/s, and each spectrum took 20-30 min to collect. At this stage, therefore, raising and lowering the working electrode was not worthwhile and the sample was kept in the X-ray position all the time. Simultaneously, electrochemical data were collected using a CHI1232 handheld potentiostat (I J Cambria Scientific Ltd.).

XAS experiments were performed at DUBBLE (Station BM26A, European Synchrotron Radiation Facility, Grenoble). Cu K-edge (8.979 keV) XAS spectra were recorded as a function of energy defined by the stepping of an Si (1 1 1) double-crystal monochromator. The scan time was 20 minutes. Measurements were made in fluorescent mode using the X-ray beam at 80º to the sample surface with a nine channel monolithic Ge fluorescence detector (E&G Ortec Inc.) at 90º to the beam in order to minimize the collected flux of backscattered X-rays. This set-up results in a minimum path length in the fluid of 0.8 mm, but sample roughness can increase this. The electrochemical cell was mounted so that the sample surface was in a vertical plane.
Results and discussion

Figure 2 shows the Ecorr data as function of time for a copper substrate covered with nantokite (acquisition of data starts after evacuation of the experimental hutch which usually takes a few minutes). The corrosion potential first undergoes a strong increase during ~25 minutes after which the value fluctuates slightly between -450 and -470 mV (versus a mercury mercurous sulphate electrode - MSE) during the next 105 minutes. After a period of 130 minutes, it starts to decrease. The arrows across the bottom of the plot show the time correlation with the SR-XRD scans which lasted ~30 minutes each. The latter are plotted in Figure 3 and clearly show the disappearance of nantokite as a function of time. In fact, after 120 minutes of immersion, the nantokite signal has disappeared into the background noise due to scattering in the fluid. The cuprite signal, on the other hand, grows by more than a factor of 2.5 over this
time, from a small level due to the presence of some cuprite on the sample prior to immersion into the sodium sesquicarbonate solution. This is in agreement with previous measurements in which the electrode was removed after 1 day of immersion and measured a few days later using SR-XRD (Leyssens et al. 2004, 2005a, 2005b).

When comparing the SR-XRD results with the Ecorr data, the hypothesis that a stable Ecorr means a stable surface does not seem to be supported. A significant decrease in the amount of nantokite might be expected during the first 30 minutes since the corrosion potential shows a large alteration. In between 30 and 120 minutes of immersion the corrosion potential is more or less stable, implying, according to the hypothesis, no change in the surface composition. The SR-XRD data, however, tell a different story in that nantokite continues to decrease for at least 120 minutes.

In order to study the ongoing processes in further detail, we performed XAS measurements. They provide an independent means of surface characterization as the technique is not only sensitive to the presence and evolution of amorphous surface compounds but will also give information on the presence of potential complex ions in the solution.

The XAS spectra of corroded copper samples, collected during their immersion in the sesquicarbonate solution, all show increasing signals as a function of time. The increase is observed both at the absorption Cu K edge, and in a proportional increase in XANES and EXAFS modulation, but the shapes of the spectra do not appear to evolve strongly, even though the chemical composition of the surface is undoubtedly changing. The effect is largest for the atacamite layer, as described below.

Figure 4 shows the successive XAS spectra recorded for this sample. The copper edge of the first measurement is set to be equal to 1. All subsequent scans are normalized to the edge height of the first scan. Scan number 8 already shows an increase of 4 times with respect to the copper edge of the first measurement. From the ninth spectrum on, the increase between the different spectra becomes rapidly larger: the copper edge of spectrum 12 is ca 30 times as high while the EXAFS modulation has increased significantly in amplitude as well. One underlying effect, which is a continuous increase in the height of the copper edge, results in continuously increasing background slopes in the EXAFS region. The modulation in the EXAFS region also evolves slightly – from the picture presented in figure 5, to one which is extremely similar to the dry corrosion layer. The obvious change in the XANES or EXAFS intensity of the immersed samples could not be observed for the original dry corrosion layers, observed over similar times in air (i.e. there is no increase in signal over time for dry samples). Whilst the spectra are being recorded and any electrochemistry is in progress, eCell makes a continuous visual record of the process using a webcam. Figure 5 shows an example of a webcam image recorded after the sample had been immersed for 30 minutes. The sequence of the webcam images shows the detachment of the atacamite layer from the copper substrate (not shown). A stream of atacamite drifts downwards as the sample surface is in a vertical plane on DUBBLE. Two sorts of detaching material are clearly visible: relatively large crystalline fragments up to 100’s micron in size, and a “smoke-like” blue haze streaming downwards under gravity. The sudden increase in signal as of scan number 9 can in this context be explained by the fact that at this stage more of the atacamite layer gets detached. It should be noticed, however, that the spectrum remains characteristic of atacamite throughout this process.

A possible hypothesis to cover this behaviour would be the presence of small crystalline fragments from the surface – perhaps of colloidal size and supported by Brownian motion. This is further supported by the observation of a slow initial increase in the spectral intensity followed by much more rapid increases, as if the larger solid debris from the surface which have fallen to the bottom of the cell break down into large numbers of smaller particles which would be rapidly transported throughout the cell by Brownian motion. This is exactly what would happen if the crystalline material itself consists of agglomerates of small microcrystals, or had an extensive network of internal grain boundaries which were attacked by the electrolyte over time.

**Conclusion**

In this simulation work it is clear that most of the chlorides are removed from the copper substrate through detachment rather than dissolution or conversion, and that this is partly due to the formation (or thickening) of a cuprite layer at the copper surface. The chlorides (especially the atacamite) spill into the fluid (and can be observed as a “blue smoke”) but retain their characteristic short-range structure, forming, at first, a colloidal suspension which dissolves only slowly. Ecorr does not track the surface chloride coverage as such: it only “sees” the chlorides (in particular atacamite) when they are chemically attached to the substrate and not when they are physically attached. The latter can be misleading when it comes to conservation issues as chlorides may be retained in the surface and give rise to post-treatment reactions. In future this work will be extended to real corrosion layers and cupreous alloys. The search for an effective monitoring technique will continue.
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