Vol I

Abstract

Archaeological copper-based artifacts recovered from wet and salty environments are often stored or stabilized in sodium sesquicarbonate solutions. Modification of the natural patina and development of active corrosion can occur during these processes, which implies the need for monitoring storage/stabilization processes. The focus of the study consists of examining how corrosion potential (E_{corr}) measurements and voltammetric curves can contribute in providing information on the effectiveness of storage and stabilization treatments. Particular attention is given to side effects such as the transformation of the corrosion layers.

Keywords

corrosion potential measurements, voltammetry, copper, storage, stabilization, sodium sesquicarbonate Electrochemical monitoring of the storage or stabilization of archaeological copper-based artifacts in sodium sesquicarbonate solutions

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Introduction

Archaeological copper-based artifacts recovered from wet and salty environments should not be exposed directly to the atmosphere as the metal usually corrodes at an accelerated rate in the oxygen-rich air (Scott 2002). These objects are usually stored in tap water and stabilized in sodium sesquicarbonate solutions (Oddy et al. 1970, MacLeod 1987a, b). Nevertheless, corrosion layers are transformed during these processes and provoke side effects such as the modification of the natural patina (Pollard et al. 1990, Horie et al. 1982) and the development of new active corrosion. The objective of this research project is to determine whether measurements of $E_{\rm corr}$ can be used to monitor the behaviour of copper-based alloys during their storage and stabilization processes.

Five corrosion products commonly found on real artifacts were considered in this study. Cuprite (Cu₂O) is regularly found on copper artifacts and is a stable product (Scott 2002, De Ryck 2003). Within the copper chlorides nantokite (CuCl), atacamite and paratacamite (both isomers of $Cu_2(OH)_3Cl$) were selected. Nantokite is considered as the main catalytic agent for active corrosion. The presence of this cuprous chloride as a corrosion product adjacent to the metallic surface can create long-term problems for the stability of an object. Bronze disease or pitting corrosion is usually attributed to this corrosion product (Scott 2002). Atacamite and paratacamite are two other important chlorides in bronze corrosion. They are often considered as end products and are formed on top of the active corrosion areas. Atacamite is the most common of the $Cu_2(OH)_3Cl$ isomers, but often alters into paratacamite (Scott 2002, De Ryck 2003). Chalcocite (Cu_2S) is typical of marine artifacts found in anaerobic environments (Scott 2002).

This paper reports $E_{\rm corr}$ vs. time plots performed on artificial coupons (covered or not with corrosion layers) simulating the behaviour of real artifacts immersed in sodium sesquicarbonate solutions. Voltammetric measurements have been performed in parallel to further understand the electrochemical reactions that are taking place during the immersion processes.

Materials and methods

Sample preparation

Before an experiment or a corrosion simulation, the pure copper coupons (Advent, purity 99.9 per cent) were ground first on 1200 grit SiC paper to obtain a fresh surface. To smoothen the surface they were further polished on a polishing cloth covered with alumina powder of 1 μ m particle size. To remove any adherent Al₂O₃ particles the surfaces were rinsed thoroughly with deionized

water and cleaned in an ultrasonic bath. Afterwards several corrosion protocols were used to obtain the different corrosion products mentioned above.

Cuprite (Cu_2O) was formed through the anodic polarization of the copper samples at -0.360 V/MSE for 16 h in a 0.1 M Na₂SO₄ solution (Beldjoudi 1999). Copper covered with nantokite (CuCl) was obtained by immersing pure copper coupons for 1 h in a saturated CuCl₂.2H₂O solution. After rinsing with deionized water, they were exposed to the air for a night (Lamy 1997). For atacamite (Cu₂(OH)₃Cl), a solution of 15.07 g (NH₄)₂CO₃.NH₃ and 10.02 g NH₄Cl in 100 ml deionized water was first prepared. The copper samples were wetted twice a day with this solution. This procedure was repeated for five days. Between each application the samples were left to dry in the air. The samples were left in the air another five days without any treatment (Lamy 1997). The protocol used to obtain a mixture of atacamite and paratacamite (both isomers of Cu₂(OH)₂Cl) was almost the same; only the solution was different: 10.02 g Cu(NO₃), 3H₂O and 10.01 g NaCl in 100 ml deionized water was prepared (Lamy 1997). Finally the protocol to form chalcocite (Cu₂S) included placing the samples in a closed box for 30 min together with a mixture of 4 ml 20 per cent NH₄S and 20 ml deionized water (Lamy 1997).

Stabilization treatments

Various concentrations of sodium sesquicarbonate solutions are used by conservators to stabilize bronze artifacts. Lower concentrations are favoured though to limit rinsing steps. For this study a 1 per cent (by mass) sodium sesquicarbonate solution was prepared by dissolving 11.89 g/l of Na₂CO₃.NaHCO₃.2H₂O (Sigma) in deionized water (pH = 10).

Corrosion measurements

Corrosion potential measurements as well as voltammetric curves were recorded in a 1 per cent (by mass) sodium sesquicarbonate solution. The instrumentation was a PC-controlled potentiostat and software package type GPES4.9 (Autolab PGSTAT10, ECO Chemie). A mercury sulphate electrode (MSE, Hg/Hg₂SO₄,K₂SO₄(sat)) electrode was used as reference electrode (=0.640 V vs. normal hydrogen electrode, NHE). Copper coupon disc electrodes of 6 mm diameter in 150 ml of the electrolyte solution were considered. The solution was not stirred during the measurement. The voltammograms were recorded with scan rates of 1 mV/s.

Results

A set of artificially corroded copper coupons was prepared according to the description in subsection 'Sample preparation'. The samples were immersed in a 1 per cent (by mass) sodium sesquicarbonate solution while corrosion potential measurements were made. Figure 1 shows the corrosion potential measurements during the first 12 days for each of the coupons immersed separately in the sodium sesquicarbonate solution. In what follows, the curves will be discussed one by one.

Pure copper

The corrosion potential of pure copper reaches a relatively good equilibrium after one day. There are still small variations, but there is no overall increase or decrease of the corrosion potential with time.

The voltammograms measured immediately after immersion and after three days of immersion in the 1 per cent (by mass) sodium sesquicarbonate are given in Figure 2. The curve immediately after immersion (full line) shows a low peak starting at -0.675 V/MSE and a second one starting at -0.85 V/MSE. The second peak seems to be caused by the reduction of carbonate species present in the electrolyte (Osetrova 1998) although our experiments with both platinum and copper indicate reduction processes not occurring at the same potential. After



Figure 1. Corrosion potential vs. time measurements for pure copper and copper covered with different corrosion products immersed in 1 per cent (by mass) sodium sesquicarbonate



Figure 2. Voltammogram of pure copper measured after immersion for 3 days in 1 per cent (by mass) sodium sesquicarbonate (dotted line) compared with measurements made immediately after immersion time in the solution (full line) (electrolyte: 1 per cent (by mass) sodium sesquicarbonate, scan rate: 1 mV/s)

three days of immersion in the 1 per cent (by mass) sodium sesquicarbonate solution the peak at -0.7 mV/MSE disappears in comparison with the curve measured immediately after immersion. The peak at -0.85 mV/MSE is still present though. A new peak starts around -1.1 V/MSE. This last peak could indicate the formation of cuprite (for which the reduction potential should be -1.25 V/MSE, see below). Note that the values of the currents corresponding to the maximum of the peaks are very small compared with the values measured in presence of corrosion products. Cuprite covers the metal and slows down the corrosion process, which can be seen in the constant to slightly increasing corrosion potential.

Cuprite

The corrosion potential of cuprite (Figure 1) shows a quick increase in the first few hours, after which it seems to reach a sort of equilibrium. The potentials are quite stable and lay around the same value as the potentials of pure copper immersed in sodium sesquicarbonate. Voltammetric experiments made after one day and after immersion for one week in the sodium sesquicarbonate solution (Figure 3) show only the presence of cuprite.

The areas under the peaks give information on the thickness of the cuprite layer present on the surface. As indicated in Figure 3, the measurement made after one day is quite similar to the one measured immediately after immersion in the solution, but after longer immersion times (3 days) the reduction peak of cuprite tends to decrease and remains then more or less stable. When looking at



Figure 3. Voltammogram of copper covered with cuprite, measured after immersion for some time in 1 per cent (by mass) sodium sesquicarbonate (electrolyte: 1 per cent (by mass) sodium sesquicarbonate, scan rate: 1 mV/s)

Figure 1 we indeed observe slight changes in measurements of $E_{\rm corr}$. Clearly, the thickness of the cuprite layer varies as a function of immersion time but more investigation is needed to confirm this preliminary result.

Nantokite

The pattern of nantokite shows a fast decrease of $E_{\rm corr}$ with time (Figure 1). This trend indicates a transformation of corrosion products. The duration varies from one to two hours to almost a day depending on the amount of corrosion product. Then $E_{\rm corr}$ shows again an increase. The slope is at first rather steep (20–50 mV in 2–5 h), but decreases later and gets stable after 2–4 days, indicating a passivation behaviour. Most of the time it indicates the formation of a more protective film. The slow increase that follows reinforces this hypothesis. Voltammograms have been recorded at several stages of the corrosion potential vs. time plot. The voltammograms measured immediately after immersion in 1 per cent (by mass) sodium sesquicarbonate (Figure 4) reveal the presence of nantokite (peak starting at –0.5 V/MSE) and cuprite (peak starting at –1.25 V/MSE).

The voltammograms recorded at the end of the first $E_{\rm corr}$ decrease show a nantokite peak much smaller than in the voltammograms of the just immersed



Figure 4. Voltammograms of copper covered with nantokite after different immersion times in 1 per cent (by mass) sodium sesquicarbonate (electrolyte: 1 per cent (by mass) sodium sesquicarbonate, scan rate: 1 mV/s)

samples, indicating nantokite is disappearing. According to the literature, nantokite is said to be converted into paratacamite or cuprite (Oddy et al. 1970, Leyssens et al. 2004). The reductions of nantokite and paratacamite both start between -0.5 and -0.53 V/MSE (Lamy 1997), which makes it difficult to assign a peak to one of them. It is possible that part of the nantokite is converted to paratacamite. But more obvious the cuprite peak has grown, so nantokite is certainly converted to cuprite (Leyssens et al. 2004).

New voltammograms were recorded later, during the rise of the corrosion potential. The peak at -0.5 V/MSE rises again. It appears that dissolved products precipitate or, otherwise, that chloride ions from the solution are reacting with the corrosion layer to form nantokite or paratacamite. X-ray diffraction (XRD) measurements recorded around that time indicate that less nantokite can be found (Leyssens et al. 2004). The presence of cuprite and paratacamite is more pronounced in the XRD diffractograms, which indicates that the voltammogrammic peak at -0.5 V/MSE will be mostly due to paratacamite. The peak at -1.2 V/MSE indicates that cuprite is still present. But the shoulder starting at -1.3 V/MSE shows that a new corrosion product is forming. The last voltammogram, recorded after a month, confirms this trend. Taking into account the XRD measurements performed after two weeks immersion (Leyssens et al. 2004) this peak is assigned to the reduction of malachite.

Atacamite

The recording of E_{corr} with time for copper covered with atacamite shows at first a quick decrease in the first few hours followed by a new increase, after which it decreases again but much more slower (Figure 1). The decrease of the corrosion potential with time indicates the transformation of corrosion products.

The voltammogram immediately measured after immersion (Figure 5) shows several peaks. The peak starting around -0.5 V/MSE can be attributed to atacamite. The peaks at lower potentials correspond to the reduction of soluble by products. The voltammogram recorded after one day immersion in 1 per cent (by mass) sesquicarbonate shows that the atacamite peak (-0.5 V/MSE) is decreased. Instead cuprite (-1.2 V/MSE) and malachite (-1.3 V/MSE) are formed.



Figure 5. Voltammogram of copper covered with atacamite after immersion for 1 day in a 1 per cent (by mass) sodium sesquicarbonate solution, compared with the voltammogram of a sample measured immediately after immersion

Mixture of atacamite and paratacamite

The corrosion potential of the mixture of atacamite and paratacamite first increases to then decrease more than 40 mV in the first three days (Figure 1). After which the decrease with time is much slower. Once again, this trend indicates the transformation of the corrosion products.

A representative voltammogram recorded immediately after immersion in the sodium sesquicarbonate solution is given in Figure 6 and shows one big peak



Figure 6. Voltammogram of copper covered with a mixture of atacamite and paratacamite after several immersion times in a 1 per cent (by mass) sodium sesquicarbonate solution

starting around -0.5 V/MSE, indicating the presence of either paratacamite or atacamite. Nevertheless nantokite (-0.5 to -0.53 V/MSE) can also be present hidden under this peak as suggested by previous XRD spectra (Leyssens 2004).

After immersion for one day in the 1 per cent (by mass) sodium sesquicarbonate solution, two layers could be seen: a red layer adjacent to the metal surface with a green layer above (Leyssens 2004). In the voltammograms (Figure 6) two peaks are recorded. The peak starting at -0.62 V/MSE could be caused by paratacamite (Cu₂Cl(OH)₃), which is a green corrosion product. The other peak starting around -1.19 V/MSE can be attributed to cuprite, which explains the red colour. The identification of the layers is conformed to the XRD data (Leyssens 2004).

The voltammogram recorded after 14 days immersion (Figure 6) still shows the presence of paratacamite (-0.62 V/MSE). The peak starting around -1.3 V/MSE can be attributed to malachite.

Chalcocite

The $E_{\rm corr}$ measurement of chalcocite shows an increase of the corrosion potential in the first week (Figure 1). After approximately eight days the potential reaches a plateau around -0.455 V/MSE.

The voltammogram immediately measured after immersion is presented in Figure 7. A big peak starts at -1.45 V/MSE, which can be attributed to the presence of chalcocite. The voltammogram recorded after one day still shows the peak starting at -1.45 V/MSE. Furthermore, a small peak can be seen at -1.2 V/MSE, indicating that cuprite may be forming by longer immersion.



Figure 7. Voltammogram of copper covered with chalcocite after different immersion times in 1 per cent (by mass) sodium sesquicarbonate

Further investigation is required to study the corrosion product formed after eight days which corresponds to the plateau obtained in Figure 1.

Discussion

Chemical and electrochemical transformation of the artificially prepared corrosion products occurring during immersion in a sodium sesquicarbonate solution were monitored for two weeks.

The corrosion potential of cuprite quickly reaches a steady state in the solution. This is in agreement with previous XRD measurements that showed that cuprite is stable in sodium sesquicarbonate (Leyssens 2004). Nevertheless, the voltammograms indicate that the thickness of cuprite changes during the immersion. Further investigation is needed though to confirm this preliminary hypothesis.

The preliminary decrease of the corrosion potential for nantokite in sodium sesquicarbonate occurs as well in water and corresponds to the following reactions (Oddy et al. 1970):

$$2CuCl (nantokite) + H_2O \rightarrow Cu_2O (cuprite) + 2Cl^- + 2H^+$$
(1)

2CuCl (nantokite) + 2H₂O + O₂ \rightarrow Cu₂(OH)₃Cl (paratacamite) + HCl. (2)

The voltammograms indicate though that reaction (1) is more pronounced than reaction (2).

These transformations are followed by the formation of malachite, which can be explained by the reactions suggested by MacLeod (1987a, b):

$$4CuCl + O_2 + 8HCO_3^{-} \rightarrow 4Cu(CO_3)_2^{2-} + 4H^+ + 4Cl^- + 2H_2O$$
(3)

$$Cu_2(OH)_3Cl \text{ (paratacamite)} + 4CO_3^{2-} \rightarrow 2Cu(CO_3)_2^{2-} + 3OH^- + Cl^-.$$
 (4)

The ion $\text{Cu}(\text{CO}_3)_2^{2-}$ is supposed to be stable in the presence of bicarbonate ions but Oddy and Hughes (1970) already indicated the precipitation of this compound. In this way a layer of malachite (CuCO_3 . $\text{Cu}(\text{OH})_2$) can be formed on the bronze (Oddy and Hughes 1970). It is probably the formation of the stable malachite that causes the corrosion potential to rise after six days. However, more experiments are needed to clarify how the formation of malachite is reflected in the change of the corrosion potential.

Similar results were obtained with the samples covered with either atacamite or a mixture of atacamite and paratacamite. The red-brown cuprite layer underneath the blue-green atacamite/paratacamite/nantokite layer developed in the solution. The decrease of the corrosion potential during the first days of the immersion process can be caused by the decomposition of the copper chloride species. This decrease is later slowed down by the formation of a stable malachite (as mentioned in the discussion of nantokite) and cuprite layer.

The voltammograms indicate no significant changes in the chalcocite layer when immersed in the sodium sesquicarbonate solution. Only small amounts of cuprite are found. On the other hand, the corrosion potential vs. time shows a long steady rise to reach a plateau after eight days, indicating the formation of a protective film on the surface. Nevertheless, neither the voltammograms nor the XRD data show the formation of new corrosion products. Further measurements are required to explain the behaviour of the corrosion potential in full detail.

Conclusion

Artificially formed patinas on copper are certainly affected during the immersion in 1 per cent (by mass) sodium sesquicarbonate as is shown both by $E_{\rm corr}$ and voltammetric measurements. Cuprite does not transform in other corrosion products but the thickness of the cuprite layer changes with time. Nantokite on the other hand is converted to cuprite and paratacamite. Later on malachite forms. Similar results were obtained with the samples covered with atacamite and

with a mixture of atacamite and paratacamite. Monitoring of the corrosion potential with time appears as a very promising and simple technique to record these transformations, particularly when the corrosion layers are made of a single corrosion product.

Further research is required in the case of real artifacts that are commonly covered with a stratigraphy of different corrosion products, which are all affected separately by the solution used.

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Materials

Ammonium carbonate, cupric nitrate trihydrate, sodium chloride, sodium sulfate Fluka Industriestrasse 25 CH-9471 Buchs SG Switzerland E-mail: Fluka@sial.com Tel.: +41 (0)81 755 25 11 Fax: +41 (0)81 755 28 15 Sodium sesquicarbonate Sigma Aldrick DW/CA

Sigma-Aldrich NV/SA Kardinaal Cardijnplein 8 2880 Bornem Belgium Tel.:+32 (0)3 899 13 01 Fax: +32 (0)3 899 13 11

Ammonium chloride, ammonium sulfide about 20 per cent solution, copper(II)chloride dihydate Merck Eurolab nv Geldenaaksebaan 464 B-3001 Leuven Belgium Tel.: +32 (0)16 38 50 11 Fax: +32 (0)16 38 53 85 Web site: www.merckeurolab.be