Journal of Cultural Heritage 15 (2014) 99–103

Available online at
SciVerse ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Original article

Corrosion monitoring in archives by the electrical resistance technique

Milan Kouril [a,*], Tomas Prosek [b], Bert Scheffel [c], Yves Degres [d]

[a] Institute of Chemical Technology, Technicka 5, 16628 Prague, Czech Republic
[b] Institut de la Corrosion/French Corrosion Institute, 220, rue Pierre-Rivoalon, 29200 Brest, France
[c] Fraunhofer Institute for Electron Beam and Plasma Technology, Winterbergstrasse 28, 01277 Dresden, Germany
[d] NKE electronics, rue Gutenberg, 56700 Hennebont, France

ARTICLE INFO

Article history:
Received 22 August 2012
Accepted 8 April 2013
Available online 13 May 2013

Keywords:
Electrical resistance
Corrosion monitoring
Indoor air quality
Archive
Corrosivity classification

ABSTRACT

It is essential that corrosion monitoring of indoor atmospheres should be highly sensitive, especially, when corrosion rates corresponding to the lowest standard corrosivity categories are supposed to be identified within one or a few days. The electrical resistance technique in combination with high-sensitivity electrical resistance sensors enabled detection of a corrosion loss on an atomic scale. Case studies have demonstrated the sensors' ability to timely inform the users about changes in the atmosphere quality. In confrontation with quartz crystal microbalance technique, resistometric sensors provided better explainable data.

1. Introduction

A team of European researchers, museum experts and industry representatives developed the transportable real-time measuring device AirCorr within a project supported by the European Commission (MUSECORR: Protection of cultural heritage by real-time corrosion monitoring, Collaborative Project, 7th Framework Programme, Contract N° 226539, 06/2009–07/2012) in order to control the impact of corrosive atmospheres, especially on objects of importance to cultural heritage [1–3]. The plug-in sensor units can be exchanged easily and hence can be used to monitor and protect various metallic objects. Being a method used for corrosion monitoring, the electrical resistance (ER) technique was selected to measure the corrosion rate. It records corrosion loss in metal thickness with the slope of the curve corresponding to the corrosion rate. Deviations from the curve slope indicate the changes in corrosion conditions, which information is effectively used to identify the causes of corrosion aggressiveness elevation and to verify the effectiveness of the respective corrosion measure – it acts as an early warning. The method is especially recommendable for detection of the onset of corrosion [4]. In contrast to other methods [5–12] used for monitoring of atmospheric corrosion, the resistometric method provides direct information about the metal corrosion loss.

The indoor atmosphere corrosivity category is determined on the grounds of the corrosion rate of steel, zinc, copper and silver [13]. Corrosion rates ranging within the order of hundreds $mg\,m^{-2}\,a^{-1}$ correspond to the second lowest corrosion category IC2. Expressed by the loss in metal thickness in time, corrosion rates in IC2 atmosphere correspond to the order of tens $nm\,a^{-1}$. Monitoring of the corrosion rate corresponding to the lowest categories of indoor atmosphere corrosivity is inevitable to make sure that, for instance, sensitive electronic equipment is protected and that metallic artefacts are duly and safely preserved when exhibited, transported or stored in depositories [12].

2. Research aims

This paper presents two on-site studies, during which the AirCorr monitoring system (AirCorr I Plus, NKE) was tested in two archives with diverse conditions. The main goal was to check sensitivity of corrosion sensors when exposed to specific real conditions.

3. Materials and methods

The concept of the measuring device is simple, yet highly effective: the electronic unit measures and registers the change of the electrical resistance of a thin metal track applied on an insulating substrate (Fig. 1) over time. If the metal corrodes, the track's cross-sectional area decreases and the electrical resistance increases. However, the sensitivity and service life of sensors mainly depend on the thickness of the metallic track: the lower the thickness, the higher the sensitivity. On the other hand, low thickness leads to a

* Corresponding author. Tel.: +420220443750; fax: +420220444400.
E-mail addresses: kourilm@vscht.cz (M. Kouril), tomas.prosek@institut-corrosion.fr (T. Prosek), bert.scheffel@fep.fraunhofer.de (B. Scheffel), ydegres@nke.fr (Y. Degres).

1296-2074/$ – see front matter
http://dx.doi.org/10.1016/j.culher.2013.04.002

Fig. 1. AirCorr corrosion monitoring system equipped with Ag-50 nm and Cu-50 nm sensors.

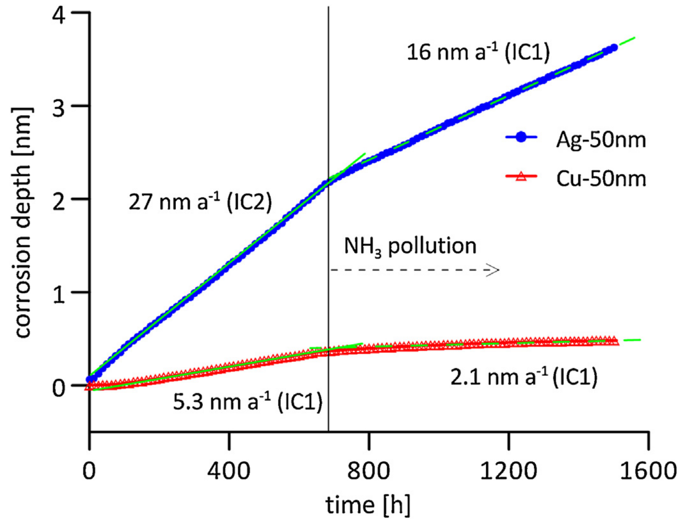

Fig. 2. Corrosion depth record of silver and copper by means of the resistometric technique.

shorter service life. Therefore, sensors with different track thicknesses are available for applications in different environments.

It measures corrosion loss in metal thickness and the slope of the curve corresponds to the corrosion rate. Deviations from the curve slope indicate changes in corrosion conditions. The method is especially recommendable for detection of the corrosion onset [4]. Despite other methods [5–13] used for monitoring of atmospheric corrosion, the resistometric technique provides information directly about the metal corrosion loss.

The AirCorr logger is equipped with digital temperature and relative humidity sensors with 3.5% precision in the case of relative humidity and 0.5 °C precision of temperature reading.

Corrosion response of the electrical resistance probes was compared to other two independent techniques. The quartz crystal microbalance (OnGuard 3000, Purafil) indicates the silver/copper sensor mass change vs. time curve, therefore it could be used for corrosion monitoring in terms of corrosion product layer build-up.

The overall corrosion loss and the average corrosion rate can be determined either by means of mass gain/loss or galvanostatic reduction of corrosion products formed on silver or copper coupons as specified in the ISO 11844-2 standard. The latter technique was used in duplicate in order to verify the results obtained by the resistometric and the quartz crystal microbalance technique. Preparation of the specimens and the exposure arrangement complied with the ISO 11844-2 standard requirements. Since the exposure period was much shorter than that required by the ISO standard, the corrosion category cannot be determined by any of the three techniques. For the same reason, the corrosion layer formed on the surface of the coupons was very thin, almost invisible, thus the electrical current density applicable for the galvanostatic reduction was half of the current density specified in the ISO standard (62.5 $\mu A\,cm^{-2}$) with the intention to prolong the time to complete the reduction and to improve reliability of the time to reduction reading.

4. Results and discussion

4.1. A modern archive building

Corrosivity of atmosphere was determined in a multi-story reinforced-concrete building of the archive using silver and copper sensors. The building is located in a city with traffic air pollution. Concreting was done in winter and the upper floors were concreted when it was freezing. An antifreeze admixture was used for concrete mixture. Such admixture (urea) decomposes in concrete slowly, releasing ammonium to the surrounding environment. Thus the air in the top floors has a typical ammonium odour. It is said that ammonium in the air is not harmful to the documents but might be dangerous for metallic parts made of copper or brass especially. A stable temperature of 15 ± 2 °C and relative humidity of 55 ± 5% is maintained in the archive in summer and 50 ± 5% in winter.

The AirCorr logger (Fig. 1) equipped with a highly sensitive silver sensor (Ag-50 nm) and copper sensor (Cu-50 nm) was installed in the archive. Firstly (27 days), the logger was placed on a floor, which was built from concrete that was not mixed with urea. No ammonium can be smelled there. After that the logger was moved onto the floor with a very strong ammonium odour. The aim was to test the response of the AirCorr system to the change of the air composition–the presence of ammonium. The silver corrosion depth of 2.05 nm within the 647 hours (Fig. 2) corresponds to the corrosion rate of 27 $nm\,a^{-1}$. The testing period was not sufficient enough to classify the corrosivity according to the ISO 11844 standard but if it was possible such corrosion rate would correspond to the IC2 corrosivity category. The corrosion rate identified within the same period for copper was 5.3 $nm\,a^{-1}$ (corrosion depth after 647 hours was 0.35 nm). After moving the AirCorr logger onto the upper floor (ammonium pollution) the corrosion rate of silver surprisingly dropped to 16 $nm\,a^{-1}$. The corrosion rate of silver remained constant during the second exposure period on the upper floor. In the case of copper, the corrosion rate was 2.1 $nm\,a^{-1}$ and it decreased slowly during the second period (Fig. 2). The significance of corrosion monitoring rests mainly on its ability to detect changes in the corrosivity of the environment. In the case of the modern archive building, the corrosivity towards both the copper and silver sensors is lower on the upper floor with ammonium pollution.

The surface of copper was analysed by XPS after the exposure. The film of corrosion products contained a significant amount (app. 50%) of copper (II) and nitrogen bounded in an organic compound. Since urea is known for its corrosion inhibitive action to copper, adsorption of urea on the metallic surface from the atmosphere might be the reason for reducing the corrosion rate of copper and silver after exposing them on the upper floor.

A quartz crystal microbalance logger (OnGuard 3000, Purafil) was exposed along with the AirCorr I Plus logger. The OnGuard logger records a mass gain of the copper and silver coated crystals