

Assessment of copper surface coverage with corrosion inhibitor using AFM-based local electrical measurements

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ABSTRACT

The paper presents a new method of assessment of metal surface coverage with corrosion inhibitor and thus of inhibitor protective performance. It is based on the atomic force microscopy measurement performed in a contact mode. Apart from topography images the proposed approach allows acquisition of local DC maps and local electrical impedance spectra via application of DC bias voltage or AC perturbation signal between the conductive AFM tip and the substrate. Potentialities of this technique in inhibitor performance monitoring were illustrated on the example of copper/benzotriazole system exposed to elevated humidity environment.

KEYWORDS

Copper; corrosion inhibitor; benzotriazole; AFM; interfaces; local measurements

Introduction

Copper is one of the most popular engineering materials, which has been used for ages. From ornaments, jewellery and primitive weapons in prehistoric times, through elements of municipal infrastructure, legal tender in ancient and medieval times to components of numerous current facilities e.g. heat exchanges, electricity wires, connectors and electronic circuitry, it is copper and its alloys like brass and bronze that found wide practical application. Despite its relatively noble character copper requires some protection in order to ensure prolonged service life-time, especially when exposed to aggressive media rendering corrosion. In such situation these are corrosion inhibitors, which are commonly utilised to protect copper. One of the most popular corrosion inhibitors for copper is benzotriazole (BTA). Despite that fact the exact mechanism of benzotriazole action is not fully understood and explained. Accordingly, this topic attracts many scientists who investigate copper/benzotriazole systems.

A comprehensive review on electrochemical corrosion of copper and possibility of its prevention using organic and inorganic inhibitors is provided by Antonijevic and Petrovic [1]. Finsgar and Milosev [2] summarised the state of art in the field of benzotriazole application for inhibition of copper corrosion, putting special emphasis on the surface structure of BTA layer and the mechanisms of its inhibitive action. Qafsaoui et al. [3] used electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy to study susceptibility of copper to pitting corrosion in the presence of different triazole derivative inhibitors. The same measurement techniques were utilised by Kosec and co-workers [4] who proved that benzotriazole was efficient inhibitor not only for copper but also for copper-zinc alloys and zinc metal in aerated 0.5 M NaCl solution. Babic et al. [5] employed polarisation and impedance studies to reveal that benzotriazole forms a multi-layer structure Cu/Cu₂O-Cu(I)BTA on Cu and Cu-10Ni electrodes surface at the concentration of the inhibitor higher than 1 mM and at longer immersion time. The electrochemical methods including potentiodynamic polarisation

measurements and electrochemical impedance spectroscopy were applied to analyse the effect of benzotriazole derivatives on corrosion inhibition of brass [6,7] and bronze [8]. Dynamics of BTA inhibition with respect to brass in artificial seawater was studied by Gerengi et al. [9] using dynamic electrochemical impedance spectroscopy. Benzotriazole was also successfully investigated for corrosion inhibition of the reinforcing bars in ordinary concrete and high performance concrete [10]. BTA was identified as a candidate for corrosion prevention and stabilisation of electrodeposited copper powder intended for sintering [11].

Apart from typical industrial implementations of azole compounds for copper protection, for example in closed water cooling systems [12,13], where the inhibitor is upon continuous circulation and provides barrier film between copper surface and the environment, there are some fields where after deposition of the inhibitor a copper element does not remain in contact with the medium containing the inhibitor any more. An example can be preservation of historical heritage objects in museums, exhibitions and galleries. There are reports on protection of copper artefacts with benzotriazole, which then were exposed to ambient conditions within the museum [14–16]. In such situations there is a need for assessment of efficiency and uniformity of initial surface coverage with the inhibitor, which conditions effective copper protection. Moreover, protected artefacts must be monitored and periodically evaluated for the quality and completeness of inhibitor layer upon exposure. Such attitude allows corrosion risk assessment and undertaking timely decision about renewal of the preventive measures, for instance reapplication of benzotriazole inhibitor.

In this paper the authors propose an approach capable of identification of extent of surface coverage with corrosion inhibitor, inhibitor layer uniformity and continuity over the substrate based on analysis of surface topography and its local electrical behaviour. The approach utilises the atomic force microscopy (AFM) technique operating in contact mode regime. Apart from topography these are also local

DC and AC electrical properties of the investigated system that can be measured. This AFM-based method allows performing local impedance imaging [17] and spectroscopy [18]. Details of the technique have been described by the authors elsewhere [19]. The method of AFM-based local electrical measurements employed in these studies takes advantage of the fact that the electrical characteristics are measured between the two electrodes – the conductive AFM tip and the investigated specimen, in this case copper substrate covered with inhibitor layer. The following measurement modes are available: (i) a single-frequency AC voltage perturbation signal is applied between the electrodes and current response signal is registered (impedance imaging mode), (ii) a set of AC voltage perturbation signals from defined frequency range is applied between the electrodes and current response signals are recorded (local impedance spectroscopy), (iii) a DC bias voltage signal is applied between the electrodes and DC response current is measured (DC current mapping or spreading resistance mapping). The tip can be scanned over the surface of the specimen, either in continuous or in quasi-continuous way, or it can be positioned in a stationary manner over the area of interest during the time of measurement and then transferred to another location where the measurement procedure is repeated. In this way it is possible to map AC impedance or DC resistance of the scanned area together with other surface features available via classical AFM measurements such as height profile. The resolution of this method depends on several factors including: the size of the AFM tip, the frequency of the AC perturbation signal, the scan rate and the magnitude of the DC bias voltage. Smaller radius of the AFM tip contributes to higher resolution as then more localised electrical response of the material volume in direct vicinity of the tip/specimen contact point is obtained. The exact volume of material responsible for electrical response is not known, however it seems to be justified assumption that this area remains similar for all successive locations of the tip, especially if the measurements are conducted in dry conditions, without presence of electrolyte. Then there is lower likelihood of signal spreading over larger area in search for better conducting paths. That is why in the case of localised electrical measurements in AFM mode one should speak rather about a map of electrical parameters changes than of their absolute values.

The proposed method was successfully employed in the field of organic coatings where it enabled identification of defected regions [20,21], distinguishing the mode of degradation upon exposure to different types of environmental factors [22] as well as tracing coating behaviour close to glass transition temperature [23]. The methodology was initially implemented by Kalinin et al. for investigation of polycrystalline ZnO [24]. It was also utilised by O'Hayre et al. [25,26] to study solid polymer electrolytes, polycrystalline ZnO varistors and microscale test patterns of different electrical characteristics. Potentialities of this AFM-based approach will be demonstrated on the example of copper treated with benzotriazole as corrosion inhibitor.

Experimental

The investigated sample consisted of circular copper electrode of 1 mm diameter immobilised in epoxy resin as schematically illustrated in Figure 1. Surface of the electrode was mechanically polished with emery paper of gradation

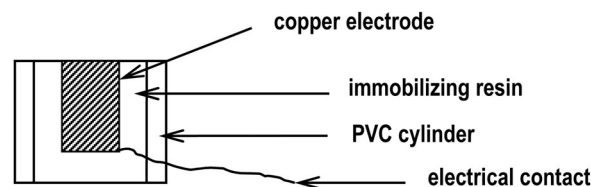


Figure 1. Scheme of the sample subjected to investigation.

increasing up to 4000 and then decreased with ethanol. In order to apply corrosion inhibitor the sample was immersed for 15 min in 1 mM solution of benzotriazole in ethanol.

Effectiveness of the corrosion inhibitor performance was checked upon the sample exposure to elevated relative humidity of 97%. The sample was placed in the headspace of a container filled in half with saturated solution of potassium sulphate. Such system yields defined humidity in the volume above the solution [27]. The total time of exposure was equal 20 days.

Initial state of the copper/benzotriazole system before the exposure and its subsequent changes were evaluated with the following measurements.

AFM topographical and electrical measurements

The SPM Ntegra Aura system by NT-MDT Co. was employed in AFM measurements. The maximum scan area was $8100 \mu\text{m}^2$ ($90 \mu\text{m} \times 90 \mu\text{m}$). Measurement resolution equalled $0.35 \mu\text{m}$ (scanned distance $90 \mu\text{m}$ divided by a number of pixels in a line – 256). A diamond coated conductive AFM probe was used in scanning by the tip mode. Scanning frequency was equal to 0.7 Hz. The Nova software by NT-MDT Co. was utilised for recording, processing and analysis of the images.

Apart from the height profile these were also local DC current maps that were collected. They were determined for the bias voltage of 20 mV applied between the AFM tip and the copper substrate. Scanning frequency was equal to 0.7 Hz.

Local impedance spectroscopy measurements were carried out in the stationary regime with the AFM tip placed at selected localisation. The measurement set-up consisted of the Parstat 2236 workstation operating in two-terminal measurement mode. One terminal was connected to the copper substrate, the second one was in contact with the conductive layer of the AFM probe by means of a dedicated holder. Local impedance spectra were recorded in the frequency range between 0.1 MHz and 1 Hz with 30 points per frequency decade. The amplitude of perturbation voltage was 100 mV RMS.

The magnitude of AC perturbation and DC bias signals were selected and adjusted experimentally prior to the main measurements in order to ensure linear current-voltage dependence of the tip as well as reliable current response signal, clearly distinguished from the noise level.

All AFM-based measurements were performed in dry conditions, without immersion in electrolyte. The sample was dried in laboratory conditions for 12 h before every AFM examination. It means these measurements were not electrochemical in character since no faradaic processes were determined. They provided only electrical characteristics reflecting the local properties of the examined surface.

Global electrochemical impedance spectroscopy measurements

Global electrochemical impedance spectroscopy measurements were executed in a two-electrode system where the copper substrate was a working electrode and platinum mesh was a counter electrode. The measurements were performed upon immersion in 1% potassium sulphate solution. Accordingly, they were electrochemical in character as opposed to the aforementioned AFM-based investigations. Surface area of the sample subjected to investigation was 0.8 mm^2 . The experimental set-up consisted of the Schlumberger 1255 frequency response analyser. Impedance spectra were collected in the frequency range from 1 to 1 MHz. Ten points per each frequency decade were recorded. The amplitude of the perturbation signal was equal 10 mV.

Results and discussion

Figure 2 shows exemplary, representative topography image of the copper surface covered with benzotriazole acquired with the use of AFM. It reflects the state of the surface following inhibitor application via immersion of the copper specimen in the solution of benzotriazole in ethanol, however prior to the exposure to elevated humidity of 97%. The maximum difference in height profile over the investigated region does not exceed 600 nm, which can be regarded relatively smooth surface. Certain waviness of topography visible on the image probably originates from the state of copper surface after the polishing operation. This observation suggests that the layer of benzotriazole inhibitor covered copper with uniform, thin layer, which did not contribute to significant and abrupt changes of the topography profile.

Uniform, complete coverage of the copper surface with the inhibitor is evidenced by a local DC current map recorded with the AFM-based approach (Figure 3). The current map corresponds to the region, the topography of which is presented in Figure 2. It can be seen that on predominant part of the surface the magnitude of DC current recorded is of single pA order. There are only few randomly distributed spots where the current magnitude reaches 30–40 pA. Such results show that commanding part of the surface constitutes a barrier for a flow of DC current between the AFM tip and the copper substrate. It is due to presence of the compact, uniform, protective layer of benzotriazole inhibitor.

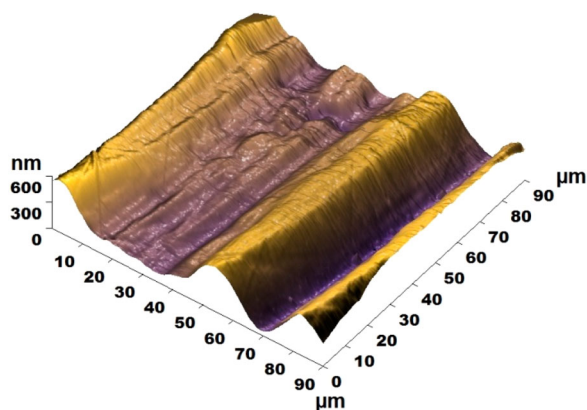


Figure 2. AFM topography image of copper surface covered with benzotriazole collected prior to elevated humidity exposure.

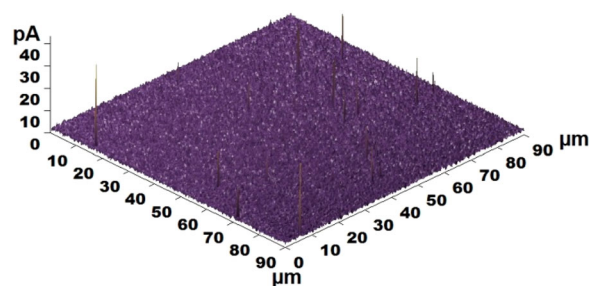


Figure 3. AFM DC current map of copper surface covered with benzotriazole collected prior to elevated humidity exposure.

Electrochemical characteristics of benzotriazole covered copper surface prior to the elevated humidity exposure were provided also by global electrochemical impedance spectroscopy measurements. Figure 4 illustrates a global electrochemical impedance spectrum in the Nyquist format recorded for the investigated copper/benzotriazole sample. The spectrum takes a form of depressed semicircle revealing impedance of a few hundred-k Ω magnitude. Similar spectra are reported in literature as characteristic of copper/benzotriazole systems [4]. The global spectrum is consistent with the AFM findings, but unlike the proposed AFM-based approach the global spectrum, due to its averaging character, does not provide local insight into copper surface coverage with benzotriazole inhibitor.

Ability of the AFM-based approach to reflect local variations in copper surface coverage with benzotriazole proved to be crucial when it came to the sample assessment upon exposure to the elevated humidity environment. Figure 5 presents exemplary, representative topography image of the copper surface covered with benzotriazole following 10 days of

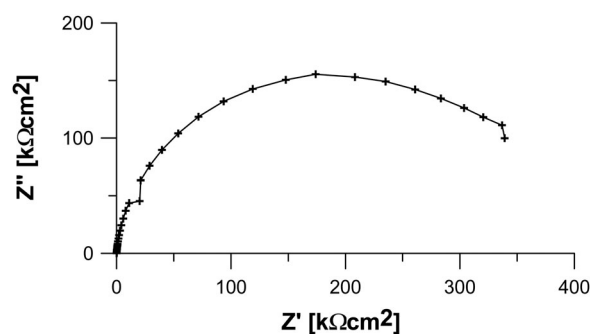


Figure 4. Global electrochemical impedance spectrum of copper surface covered with benzotriazole recorded prior to elevated humidity exposure.

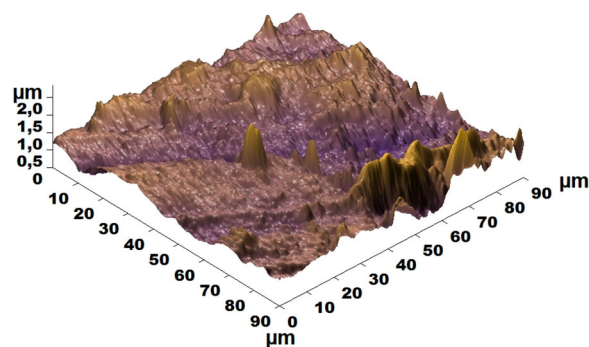


Figure 5. AFM topography image of copper surface covered with benzotriazole collected after 10 days of elevated humidity exposure.

the exposure to 97% relative humidity. As compared to the initial state the surface profile is more corrugated with some height peaks reaching 2 μm . This picture suggests certain damage done to the inhibitor layer, which creates a potential corrosion risk for the underlying copper substrate.

Conformation of this supposition is a local DC current map recorded for the corresponding region using the proposed AFM-based approach (Figure 6). It shows that the investigated surface is no longer electrically uniform as it used to be at the beginning of the test. There are clearly resolved regions, which do not constitute a barrier for the DC current flowing between the AFM tip and the copper substrate. The magnitude of current in these places is ca. 40 pA, which distinguishes them from the rest of the surface. In this way it was possible to identify and spatially localise the spots where benzotriazole was depleted from the surface due to the exposure to elevated humidity.

Additional confirmation of differentiated behaviour of the copper/benzotriazole system depending on spatial localisation on the surface is provided by the local impedance spectra acquired with the AFM-based approach. The local spectrum presented in Figure 7 was collected in the place marked as N in Figure 6. It corresponds to a non-conductive region of the investigated surface, which is due to presence of protective layer of benzotriazole. Recorded impedance is of tenth of G Ω order. On the contrary the local impedance spectrum shown in Figure 8 was recorded at the conductive spot indicated as C in Figure 6. In this case impedance is of a few M Ω order suggesting depletion of the inhibitor layer and potential corrosion risk to copper in this place.

Table 1 presents the electrical parameters obtained via modelling of the local impedance spectra collected on the

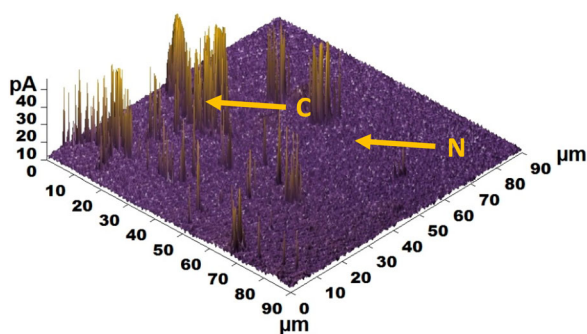


Figure 6. AFM DC current map of copper surface covered with benzotriazole collected after 10 days of elevated humidity exposure.

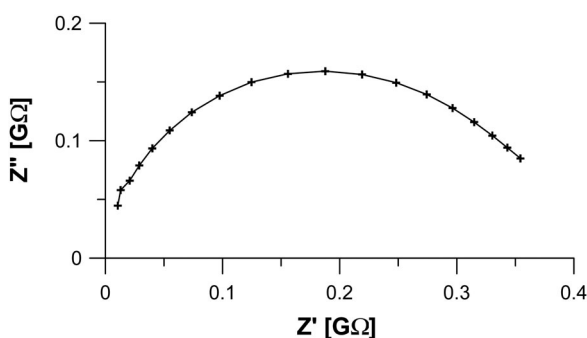


Figure 7. Local impedance spectrum of copper surface covered with benzotriazole recorded using the AFM set-up after 10 days of elevated humidity exposure. The spectrum corresponds to the non-conductive region indicated as N in the DC current map in Figure 6.

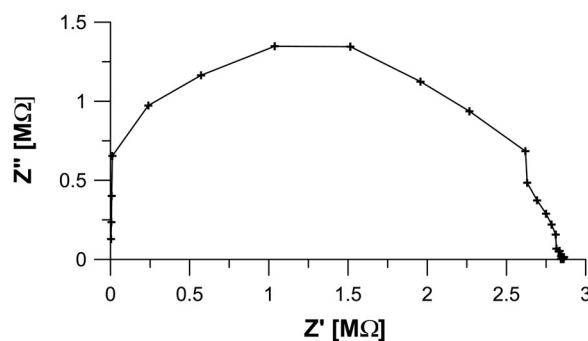


Figure 8. Local impedance spectrum of copper surface covered with benzotriazole recorded using the AFM set-up after 10 days of elevated humidity exposure. The spectrum corresponds to the conductive region indicated as C in the DC current map in Figure 6.

non-conductive region (Figure 7) and the conductive region (Figure 8) of the investigated surface. The modelling was performed using the electrical equivalent circuit consisting of a resistor and a capacitor connected in parallel (RC circuit). It can be seen that resistance drops by two orders of magnitude upon a transition from the non-conductive region to the conductive one, which could be an evidence of deteriorated protective effect in the latter region. At the same time capacitance increases by three orders of magnitude that can be associated with depletion of thickness of the inhibitive layer present on copper surface.

Topography (Figure 9) and DC current map (Figure 10) images illustrate that 20 days of exposure to elevated 97% humidity resulted in serious, if not complete, destruction of the benzotriazole layer on copper substrate. The height profile shows very uneven surface with a multitude of sharp peaks and valleys. The maximum difference in height over the investigated region amounts ca. 2 μm , which is similar to the situation following 10 days of exposure. However, local electrical characteristics of the surface are entirely different than after 10 days of exposure. The local DC current map

Table 1. Electrical parameters obtained via modelling of the local impedance spectra collected on non-conductive region (Figure 7) and conductive region (Figure 8) of the investigated surface (simple parallel RC equivalent circuit applied).

Location on sample surface	Resistance (M Ω)	Capacitance (fF)
Non-conductive region	341.2	3.9
Conductive region	2.8	8432

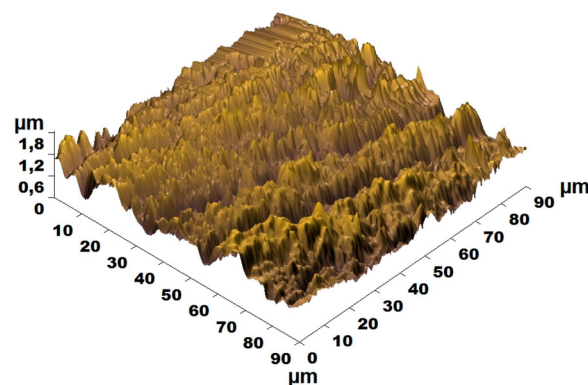


Figure 9. AFM topography image of copper surface covered with benzotriazole collected after 20 days of elevated humidity exposure.

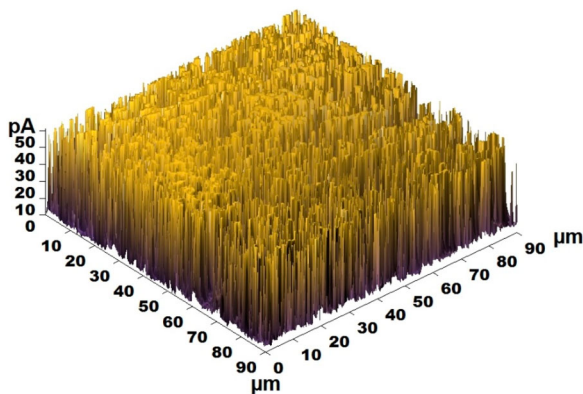


Figure 10. AFM DC current map of copper surface covered with benzotriazole collected after 20 days of elevated humidity exposure.

reveals that all the surface does not constitute a barrier for the current flow, the magnitude of which attains 50 pA. Thus, it can be concluded that the copper surface is no longer protected by the benzotriazole inhibitor layer.

A global electrochemical impedance spectrum recorded at the end of exposure is presented in Figure 11. It reveals more than one time constant and can be regarded characteristic for bare copper spectrum [4]. In this way the local findings revealing complete destruction of the benzotriazole inhibitor layer on copper are consistent with the global results.

Summarising, the proposed AFM-based approach allowed following the changes of copper surface coverage with benzotriazole as the corrosion inhibitor. Both local topography and electrical images provided information on the evolution of protective action offered by the inhibitor at particular stages of the exposure to elevated humidity. These are local DC current maps, which are especially useful for identification and spatial localisation of the regions, which are depleted in the inhibitor layer and constitute the potential spots of corrosion onset. There is an on-going discussion about the detailed mechanism of BTA, but also other corrosion inhibitors, action. Actually, it is not exclusively molecular adsorption of the inhibitor layer but also other factors, such as inhibitor addition-caused local change of pH in direct vicinity of the substrate, change of structure of electrical double layer, formation of oxide or salt film on the substrate, which contribute to inhibitive action. At this stage of the experiment it is not possible to discriminate, which other factor(s) could have been responsible for the observed local electrical characteristic as the proposed method does not allow identification of particular compounds present on the investigated surface. Nevertheless, the regions of enhanced and impaired inhibitive action have been identified as well as their distribution and

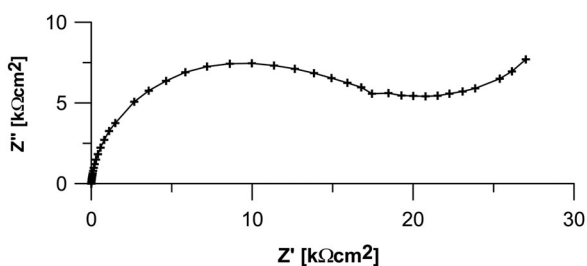


Figure 11. Global electrochemical impedance spectrum of copper surface covered with benzotriazole recorded after 20 days of elevated humidity exposure.

evolution upon exposure to elevated humidity have been presented, regardless of the additional compounds contributing to this inhibition phenomenon.

The results obtained with the AFM-based approach are consistent with the global electrochemical impedance results, hence they can be treated as supplementary ones in providing local information about inhibitor performance, overcoming the averaging shortages of the global techniques. The proposed AFM-based technique, considering the fact that the local measurements are performed in electrolyte-less conditions, can be used as a tool for monitoring and periodical inspection of the state of the inhibitor protected objects, which are not subjected to electrolyte immersion, for instance some museum artefacts.

Summary

The investigations carried out on the copper/benzotriazole system allow stating the following conclusions:

- the proposed AFM-based approach enables local assessment of copper surface coverage with benzotriazole as the corrosion inhibitor and tracing changes in the coverage upon exposure to elevated relative humidity environment,
- initially, after application of the inhibitor copper surface was uniformly covered with continuous benzotriazole layer – uniformity of the layer was revealed by the AFM topography images; its tightness was confirmed by collected local DC current maps,
- exposure to 97% relative humidity resulted in gradual depletion of the inhibitor layer, which could be traced with the proposed AFM-based approach – higher magnitude of DC current recorded on the maps as well as lower magnitude of local impedance measured made it possible to identify and spatially resolve of the fraction of copper surface without benzotriazole layer,
- progress and extent of the inhibitor layer degradation could be followed by collecting successive local topography and electrical images as well as local impedance spectra,
- the proposed AFM-based approach provides additional information, supplementary with respect to the global impedance measurements yielding only the results averaged over large area, which allows spatially resolved assessment of evolution of the corrosion inhibitor removal from copper surface on a local scale,
- the suggested approach can be implemented for periodical evaluation of inhibitor layer condition, especially in the case when protected object is not in contact with the medium providing continuous supply of the inhibitor, for instance in case of exhibited historical and museum artefacts. Then it would be helpful in evaluation of the inhibitor durability and deciding whether the inhibitor layer calls for refurbishment in order to provide effective protection of the precious element.

Disclosure statement

No potential conflict of interest was reported by the author.

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