Electrochemical and XPS study of 2-mercaptobenzothiazole nanolayers on zinc and copper surface

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Abstract

The electrochemical behavior of copper and zinc in neutral (pH 7.4) borate buffer solution with addition of 0.5 M NaCl and the effect of 2-mercaptobenzothiazole (MBT) on the electrochemical processes and adsorption on these metals has been studied by means of electrochemistry and X-ray photoelectron spectroscopy (XPS). The formation of MBT–metal cation complex films on copper and zinc surface has been shown. The effect of corrosive media composition and time-dependent relations of nanoscale film growth on the surface of the metals investigated have been determined. It was assumed that adsorbed MBT anion forms $M(\text{MBT})_x$, a polymeric complex where $M = \text{Cu}^+$ ($x = 1$) or Zn^{2+} ($x = 2$).

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Introduction

One of the most effective chemical way to protect metals against corrosion is the use of inhibitors, *i.e.*, chemical compounds or their mixtures addition of which to the system slows down and even suppresses metal corrosion without essential losses of the corrosion products into the environment [1, 2]. The most probable way of inhibitor action is based on modification of the surface to a protected state due to adsorption of the inhibitor itself or formation of an insoluble substance with metal cations. They reduce the active surface area of the metal and/or increase the activation energy of the corrosion process which, as a rule, is of electrochemical nature in aqueous media.

Organic inhibitors are most popular. They form almost water-insoluble substances with cations of metals being protected [3, 4]. Due to interaction with a metal surface, these substances frequently form ultrathin (thickness $d \leq 10$ nm) protective films stable against the corrosive environment (humid atmosphere, aqueous solutions of salts, and even some acids). The presence of heteroatoms, such as N and S, in the molecules of organic inhibitors allows them to form chemical bonds with a metal, promoting their adsorption on a surface.

Azoles and thiazoles, especially benzotriazole and its derivatives, are widely used [5, 6]. 2-Mercaptobenzothiazole (MBT) is a less studied but rather effective corrosion inhibitor containing N and S donor atoms. Its structure has been determined in [7] and is

shown in Fig. 1, structure 1. It is also known as an accelerator for rubber vulcanization [8], antioxidant [9] and antiseptic [10].

Figure 1. 2-Mercaptobenzothiazole (structure 1, left), 2,2'-dibenzothiazolyl disulfide (structure 2, right).

Anticorrosive application of MBT and its derivatives was studied for copper and copper alloys [11–21], zinc and silver [19, 22]. According to [23], MBT can be a good inhibitor for mild steel in a wide range of phosphoric acid concentrations. In this paper the electrochemical behavior of copper and zinc in borate buffer (7.4) solution containing 0.5 M NaCl and different concentration of MBT are studied along with determination of the composition and thickness of the layers formed by X-ray photoelectron spectroscopy (XPS).

Experimental

To study MBT adsorption on metals, the electrodes were cut out of zinc (99.9%) and copper (99.9%) rods and fitted in Teflon so that the contact surface was only the cylinder base. The working area of zinc electrodes was 0.50 cm² and that of copper electrodes was 0.78 cm². Before all measurements, the electrodes were smoothed out firstly on rough (P 800), then on fine (P 2500) emery paper (1913 Siawat fc), degreased with acetone and washed with distilled water in an ultrasonic bath. Potentiodynamic curves were obtained in pure borate buffer solution (pH 7.4) containing 0.5 M NaCl, with and without addition of MBT. All substances for solution preparation were of reagent grade, and MBT was recrystallized from an alcohol–water mixture. To prepare the required solutions, MBT powder was firstly dissolved in a small portion of ethanol, then water was added.

Polarization measurements on zinc and copper electrodes were performed at a scan rate of 1 mV/s using an IPC Pro 2000 potentiostat (Russia) in a three-electrode cell with divided electrode compartments. The platinum plate served as a counter electrode and all potentials were measured with respect to a silver chloride electrode (Ag/AgCl). Before each polarization measurement, the electrodes were kept at a negative potential (–1500 mV for zinc and –800 mV for copper) for 15 min to reduce water and air-formed oxide films.

For XPS research zinc and copper samples (1 cm disks) were prepared the same way as for the potentiodynamic studies with polishing to mirror finish with diamond paste

(0.05 μm) on felt tissue. Further the samples were washed two times with distilled water in an ultrasonic bath and immediately introduced in the spectrometer fast entry lock and then transferred to the high vacuum spectrometer chamber.

Surface examination after electrochemical treatment was performed using an HB-100 Auger-microscope (Vacuum Generators, GB) supplied with a CLAM1 XPS chamber furnished with an Al anode ($h\nu$ –1486.6 eV, radiation power 200 W). Pass energy of the analyzer was set at 50 eV, in some experiments it was set to 20 eV to increase resolution. Spectrometer was calibrated by the lines $\text{Au}4f_{7/2}$ and $\text{Cu}2p_{3/2}$ the energies of which were accepted as 84.0 and 932.6 eV, accordingly. To account for the sample charging, the peak of C1s electrons of carbonaceous contamination was used, whose energy E_b was taken equal to 285.0 eV. Analyzer chamber pressure was below 10^{-8} Torr. Accuracy in position of peak maxima was better than 0.3 eV.

Deconvolution of spectra into components was performed after the Shirley background subtraction [24]. Concentrations of elements were calculated using integrated intensity under peaks taking into account photoionization cross-sections σ of the corresponding electronic shells [25], with some corrections obtained in the analysis of substances with known stoichiometry. Using integrated intensity of all principal peaks in MultiQuant program [26], thickness of the layers formed on a surface was calculated with account for mean free path of electrons λ [27]. In all cases, the layers were accepted as laminar with the following sequence: metal/oxide/inhibitor/topmost layer consisting of OH^- and carbon contamination.

To deconvolute XPS spectra the Gaussian curves were used (sometimes with up to 50% of Lorentz contribution). To examine the quantitative and qualitative composition of the films formed on a surface of metal samples in the test solution in the presence of MBT, the spectra of C1s, O1s, N1s, S2p, $\text{Cu}2p_{3/2}$, and $\text{Zn}2p_{3/2}$ electrons were analyzed. In case of zinc and copper, the peak positions of $\text{Zn}2p_{3/2}$ and $\text{Cu}2p_{3/2}$ oxide (2+ and 1+ accordingly) and metal state are practically indistinguishable, and on the contrary, the Auger spectra ZnLMM and CuLMM of these states are quite discernible and they may be approximated by a combination of individual characteristic spectra as offered in [28].

Results and discussion

Electrochemical studies. Potentiodynamic curves of zinc were recorded in water–alcohol borate buffer (pH 7.4) with 0.5M NaCl with and without addition of MBT. Figure 2a shows that increasing the MBT concentration noticeably reduces the anodic current and moves its peak towards more positive potentials. Electrode passivity is observed already at MBT concentration of 0.5 mmol/l. Increasing the MBT concentration also shifts pitting to more positive potentials.

Potentiodynamic measurements of copper in 0.5 M NaCl solution without and with addition of various MBT concentrations gave the following results. In the blank solution,

Figure 2. Potentiodynamic curves for zinc (a) and copper electrodes (b) in MBT solution.

the maximum current density is observed at the first dissolution maximum corresponding to oxidation of copper to Cu^+ and at the second maximum which corresponds to oxidation to Cu^{2+} (Fig. 2b). Upon addition of 0.25 mmol/l MBT (curve 2), a small decrease in the first maximum occurs, but there is no noticeable effect on the second peak. One can observe during an increase in potential that at some positive potential, namely, about +200 mV, the solution in the vicinity to the electrode becomes non-transparent. With injection of 0.5 mmol/l MBT (curve 3), a considerable suppression of the first anodic peak and a sharp increase in the second one is observed. It may be related to electrochemical activity of MBT [13]. In some range of potentials (200–400 mV, depending on pH), MBT is oxidized to give 2,2'-dibenzothiazolyl disulfide (see structure 2). The resulting substance “blocks” the electrode surface, and after a certain time the current decreases. Due to possible removal of some parts of product from the electrode, a characteristic “current jump” can be observed on the potentiodynamic curve.

XPS analysis. Besides carbon and hydrogen, the MBT molecule contains nitrogen ($E_b = 401.1$ eV for N1s electrons) and two sulfur atoms of *endo*-S1 and *exo*-S2 types (structure 1). The latter atoms differing in charge appear in XPS spectra as two doublets of S2p electrons with E_b 164.8 eV and 162.3 eV, shifted from each other by 2.5 eV, while S2 is observed at smaller E_b because of a greater negative charge built on the *exo* atom. The presence of MBT in the surface film can be proved by the N1s and S2p peaks, and their chemical shifts change in an opposite way when the substance is adsorbed (Fig. 3b) in comparison with MBT powder (Fig. 3a). After interaction of MBT with the surface, the N1s peak shifts to lower energies ($\Delta E = 0.8$ eV) and is observed at 400.5 eV, indicating both deprotonation of the nitrogen atom and its interaction with metal cations. Two doublets of S2p electrons differing by 2.5 eV for MBT powder are shifted towards greater energies, especially the peak of the *exo* sulfur atom that shows its participation in

interaction with the metal surface. Similar changes were observed when MBT was adsorbed on copper from phosphate solutions [29].

Figure 3. XPS spectra of S2p and N1s electrons: (a) MBT powder; (b) MBT after adsorption on zinc.

In the case of chloride solutions, traces of Cl ions can be observed as a weak peak of Cl2p electrons showing physical adsorption of chloride ions on the surface from which they are washed off upon an intense ultrasonic wash.

As mentioned above, the XPS Zn2p_{3/2} peak for metallic state is undistinguishable from that of Zn²⁺ [30–38]. In such cases, ZnLMM Auger transitions induced by X-ray radiation (Fig. 3a) are used. For zinc, in the case of Zn(MBT)₂ complex formation, the main peak energy E_{ZnLMM} has an intermediate value between 499.5 and 498.0 eV which are characteristic of Zn(OH)₂ and ZnO, respectively [30]. It is important to note that as the ZnO layer thickness increases, the difference between the E_{ZnLMM} values for ZnO and Zn(m) grows and this is to be taken into account in deconvolution of spectra.

To study the formation of oxide films and surface layers created by the inhibitor, zinc samples were exposed for a predetermined time in MBT solutions and then the spectra were recorded. Analysis of the Auger spectra (see Fig. 4a) allows one to distinguish the presence of the metal (arrow 1), oxide (arrow 2) and MBT complex (arrow 3) characteristic

spectra and to calculate their ratio. It is obvious from Fig. 4a that when a zinc sample is exposed in an MBT solution, firstly a film of zinc oxide-hydroxide is formed, and after a longer time, the $\text{Zn}(\text{MBT})_2$ complex prevails.

To find the metal-to-ligand ratio in the complex, we have analyzed the element intensities with the relative sensitivities σ and mean escape depth λ taken into account. During the longest possible exposure, the thickest film was formed, and the ratio of zinc, sulfur and nitrogen was found to be 1:4:2, respectively. This information is used in modeling the surface layers when calculating their thickness by MultiQuant program. As shown in Fig. 4b, during exposure in 0.05 mmol/l MBT solution the thickness of the complex film grows, and oxide thickness decreases. It may mean that oxide layer reacts with MBT, and a $\text{Zn}(\text{MBT})_2$ complex film is formed on the surface.

Characteristic peaks of the copper–MBT complex, Cu_2O and metallic copper are presented in the corresponding CuLMM Auger spectra. The CuLMM peak of the Cu–MBT complex formed during exposure of a copper electrode in 0.1 mmol/l MBT solution is observed at $E_{\text{CuLMM}} = 571.4$ eV [13] that considerably differs from Cu_2O and Cu(m), 570.0 eV and 568.0 eV, accordingly, and it is rather easy to distinguish their spectral pattern in the observed CuLMM spectra. This E_{CuLMM} value is close to E_{CuLMM} of CuSCN powder [29] in which sulfur and nitrogen atoms are ligand atoms to Cu(I). It should be noted that the $\text{Cu}2p_{3/2}$ peak of the Cu-BTA complex is observed at 933.1 eV, though if of Cu_2O and Cu(m) are present simultaneously, it is obviously impossible to distinguish it.

In many studies [28, 31–38] it has been shown that the $\text{Cu}2p_{3/2}$ peak positions of metallic copper (932.6 eV) and Cu_2O (932.8 eV) almost coincide. These values differ considerably from those reported in [38] in which an attempt to separate the two states is done. However, the low spectrometer resolution makes this deconvolution highly doubtful. On the other hand, copper(2+) gives a characteristic spectrum in which, along with the main $\text{Cu}2p_{3/2}$ peak (~ 935 eV), an intense satellite is observed at ~ 943 eV. Thus, data of XPS and Auger spectra allow us to determine quite accurately the copper oxidation states on the surface of the samples. [28, 31]

The time-dependent evolution of the CuLMM spectrum profile of the sample in a solution containing MBT is presented in Fig. 5a. The bottom spectrum is for copper etched with Ar^+ ions, with the position of the maximum observed at 568 eV (line 1). In the course of exposure, the oxide component (which is observed at 570 eV, line 2) first increases, then the main signal corresponding to Cu(MBT) complex emerges at 571.4 eV (line 3). For clarity, the lines on the diagrams show positions of the maxima for individual components: metal, oxide and complex.

Exposing copper samples in distilled water or buffer solution gives an Auger spectrum that consists of two states, Cu^0 and Cu^{1+} (Fig. 7a).

Figure 4. Evolution of ZnLMM Auger spectra (a) and variation of the thicknesses of the complex film and oxide layer (b) depending on exposure time of zinc in 0.05 mmol/l MBT solution.

Figure 5. Evolution of CuLMM Auger spectra (a) and variation in the layer thickness of the MBT–Cu complex and Cu₂O depending on copper electrode exposure time in 0.1 mmol/l MBT solution. The lines in (a) show: pure metal etched with Ar⁺ ions (1), oxide (2), complex (3).

Exposure of copper in 0.1 mmol/l MBT solutions results in appearance of peaks of S2p and N1s electrons that indicates strong adsorption of MBT even after thorough ultrasonic wash. Besides, the third component is present in the CuLMM Auger spectra, with a maximum at 571.4 eV that indicates Cu–MBT complex formation. This fact and the changes in the S2p and N1s spectra can confirm the formation of a complex of copper with MBT upon adsorption of the latter on a surface. Figure 5b shows cuprite formation with a thickness of no more than 2 nm on the surfaces of metal copper. It is noteworthy that the spectrum characteristic of Cu²⁺ is not observed.

Figure 6. Modeling the CuLMM Auger spectra with components (example). Treatment of copper electrode in buffer solution (a) without MBT and (b) with MBT.

Analysis of the surface of copper samples exposed in 0.5 M NaCl with and without addition of MBT has shown that after three hours of immersion in 0.5 M NaCl solution, the copper Auger spectrum is completely approximated by a spectrum of Cu_2O . After 2 hours of immersion in 0.5 M NaCl with addition of 0.1 mmol/l MBT, the surface contains almost 70% of a Cu–MBT complex (Fig. 6b). After the longest exposure, the position of the peak at ~ 571.4 eV in the Auger spectrum may correspond to the Cu–MBT complex. The ratio of copper, sulphur and nitrogen is approximately 1:2:1, which corresponds to a Cu(MBT) complex composition, *i.e.*, 1:1.

The result of thickness calculation of Cu_2O and inhibitor layers is presented in the diagram (Fig. 5b). It should be outlined that in solution without the inhibitor, the oxide thickness increases up to ~ 9 nm in 960 min, but in the presence of MBT (similarly to zinc) the oxide layer growth ceases at about 1–2 nm. This allows us to conclude that MBT reacts with oxide to form a metal–MBT complex. Some error in calculations of the film thickness may be explained by imperfect surface preparation: even after polishing of the samples with diamond powder to mirror finish, there is some roughness on the surface, which affects the film density and smoothness. In these regions, a sponge-like film may form, and the oxide or metal substrate (bulk) can “shine through”. In the “thickness – time” diagrams for both oxide and MBT, it is possible to approximate the points obtained with a linear function in semi-logarithmic coordinates $d = f(\lg t)$. It means that film growth obeys the logarithmic law. It has been established experimentally that exactly the same dependence is observed for oxide films growth during copper oxidation below 100°C [39].

It is known that processes which take place on copper surface in slightly acidic media include the following reactions [40]:

and in this case copper can be in form of $\text{Cu}(\text{OH})_{\text{ad}}$ or $\text{Cu}_2\text{O}_{\text{ad}}$. In the presence of chloride ions CuCl_{ad} is formed on the surface and its solubility is extremely low ($K_{\text{sp}}[\text{CuCl}] = 1.72 \cdot 10^{-7}$) [41]. However, it turns to a soluble complex with an increase in NaCl concentration:

The same process takes place for zinc [42]:

and in the presence of chloride ions zinc is transformed into a soluble salt or complex:

Conclusions

Analysis of the data obtained during electrochemical tests of individual copper and zinc has shown that as little as 1 mmole of MBT can completely suppress the first peak of dissolution of copper or zinc. In neutral borate buffer solution (pH 7.4) this concentration exceeds MBT solubility and can be obtained by adding ethyl alcohol to solution. For zinc, an increase in MBT concentration also shifts the pitting potential to more positive values.

Analysis of XPS spectra gives evidence of the formation of oxide layers on copper and zinc when exposed in pure borate buffer or with addition of 0.5 M NaCl; the oxide layer continuously grows in time. When MBT is added to corrosive media, the oxide layer thickness remains constant (1–2 nm), but at the same time $\text{Zn}(\text{MBT})_2$ or $\text{Cu}(\text{MBT})$ complexes grow. Taking into account the character of interaction of MBT solutions with copper and zinc surface, it is possible to draw the conclusion that interaction does not terminate as a monolayer has formed, but continues with formation of a polymeric film consisting of Zn^{2+} and Cu^+ cations and MBT anions. This film is characterized by an after-effect and is not removed ultrasonically. This opens some perspectives in practical use of MBT for protection of copper and zinc from corrosion. Moreover, the results obtained will help in analysis of processes that proceed in adsorption of MBT on a brass surface.

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