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ELECTROCHEMICAL BEHAVIOR OF AgCu50 IN ALKALINE MEDIA IN THE PRESENCE OF CHLORIDES AND 2-MERCAPTOBENZOTHIAZOLE

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Abstract

Electrochemical behavior of an alloy AgCu50, pure copper, and pure silver, respectively, was investigated by measuring the open circuit potentials using anodic potentiodynamic polarization and potentiostatic method in 0.1 moldm^{-3} NaOH + 0.02 moldm^{-3} NaCl solution, without and with adding 2-mercaptobenzothiazole in various concentrations (0.00001 – 0.001 moldm^{-3}). Anodic polarization curves for AgCu50 alloy, showed four current peaks. Potentiostatic curves showed that values of the stationary current densities drop down with the increase of 2-mercaptobenzothiazole concentration in the electrolyte. The electrode surface was analyzed by optical microscopy after the potentiostatic oxidation. Micrographs confirmed that 2-mercaptobenzothiazole has got the inhibitory effect by forming the film of CuMBT and AgMBT which protect the electrode surface from corrosion.

Keywords: *Silver; Copper; Alloy AgCu50; Potentiodynamic polarization; 2-mercaptobenzothiazole.*

1. Introduction

Electrochemical techniques are widely used for characterization of metalic materials. In the available literature it can be found a great number of papers describing the use of electrochemical measurements in that purpose, especially from the point of view of corrosion stability of metals in different media [1-5].

Although copper and its alloys belong to the group of semi-noble metals, they are not resistant to corrosion, especially in the presence of halogen ions. One of the efficient protection methods involves the application of corrosion inhibitors. The protection mechanism by using the inhibitors is based on forming the passive layer which protects the surface of metal or alloy from penetration of the corrosion agent [6-9]. The compounds that can be used as corrosion inhibitors for copper and its alloys are numerous and a possibility for their application depends on various factors.

The inhibitors from the group of azoles [10-15] are proved in protecting copper and copper alloys from corrosion. One of the inhibitors from the azole group is 2-mercaptobenzothiazole (MBT). The inhibition MBT efficiency is strongly dependent on the structure and chemical properties of the species formed under the specific experimental conditions. Subramanian R. and Lakshminarayanan V. [11], investigated the adsorption characteristics and the influence of benzotriazole (BTA), mercaptobenzothiazole (MBT), benzimidazole (BIMD), mercaptobenzimidazole (MBIMD), imidazole (IMD) and tetrazole on the growth of the oxide film on copper surface in 0.1 moldm^{-3} NaOH by cyclic voltammetry method and electrochemical impedance spectroscopy.

MBT has got three atoms available for the coordination, nitrogen and sulfur ring atoms and a sulfur atom as a part of thiocarbonyl group. Sulfur atom of thiocarbonyl group (C=S), which has been ionized in the alkaline media, can react with copper and form thick polymer film. The efficiency of the various azole inhibitors for copper in 0.1 moldm^{-3} solution of NaOH was presented in following order:

MBT>BIMD≈MBIMD>BTA≈IMD

The research of Subramanian R. and Lakshminarayanan V. [11] showed that water insoluble polymer film of Cu(I)-mercaptobenzothiazolate, which is formed on the surface by the reaction of copper(I) ions with the adsorbed MBT, represents the barrier towards corrosion media.

Forming surface films on copper for two structurally similar inhibitors, 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzimidazole (MBIA) was investigated by Chadwick D. and Hashemi T. [12]. The results showed that both of these inhibitors

Dedicated to the memory of Professor Dragana Živković

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exhibited good efficiency in different conditions. X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger spectroscopy were used for the investigation. It was proved that these inhibitors form surface films with copper in the forms of Cu(MBT) and Cu_2(MBIA) which protect copper from corrosion.

Finšgar M. and Merl D. [13] investigated 2-mercaptobenzothiazole as a corrosion inhibitor of copper in 3% solution of NaCl. They used EIS, potentiodynamic curves, 3D profilometers and XPS measurements for the investigations. Electrochemical measurements showed that copper corrosion in the solution which contained MBT was diffusion-controlled process. MBT acts as mixed type of inhibitor when copper was immersed into MBT solution for 100 hours. It was also shown that nitrogen atom and exocyclic sulfur atom of MBT were included into molecular adsorption. The thickness of the surface layer was estimated to 1.5 ± 0.5 nm.

Hope H. A. et.al. [14] investigated the behavior of silver in cyanide solution in the presence of 2-mercaptobenzothiazole, where AgMBT complex was observed.

J.C. Marconato et al. [15] investigated the effect of 2-mercaptobenzothiazole on copper corrosion in 10^{-2} moldm^{-3} $HClO_4$ solution in ethanol. When MBT is added, the inhibition of anodic copper dissolution and cathodic reaction of hydrogen evolution is observed. The concentration of MBT of 0.001 moldm^{-3} leads to four times reduction of current density, as a consequence of complex formation between metal ions and the inhibitor.

2. Experimental

The experimental research within this paper included following investigations:

- measuring the open circuit potentials for the alloy AgCu50 and pure metals Ag and Cu in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl during 120 s;
- recording the anodic polarization curves for Ag, Cu and alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl;
- recording the anodic polarization curves for Ag, Cu and alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl with addition of MBT in different concentrations (0.00001 moldm^{-3} – 0.001 moldm^{-3}); NaOH and NaCl manufactured by "Zorka Pharma" Sabac, Serbia;
- recording the potentiostatic curves at -0.1 V vs. SCE and 0.2 V vs. SCE for the AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl under different concentrations of MBT (0.00005 moldm^{-3} – 0.001 moldm^{-3}); the manufacturer of 2-mercaptobenzothiazole ($C_7H_5NS_2$) is "SIGMA-ALDRICH CHEMIE GmbH " Switzerland;
- surface analysis of the alloy AgCu50 using optical metallographic microscope (EPY TIP 2) after potentiostatic treatment.

The solutions were prepared in amounts of 500 ml each with the chemicals of p.a. purity and distilled water, in order to use always fresh solution.

The working electrodes were formed from pure refined metals (99.99% purity Ag and Cu), and their mixtures in the appropriate proportion, by smelting in a quartz furnace at a temperature of 1250°C, casting and subsequent cooling. The obtained castings were treated further with an aqueous solution of nitric acid (HNO_3, 1:1) to remove the oxides formed during cooling, after which they were subjected to the processes of rolling and drawing to obtain wires of dimensions Ø = 1 mm and h = 150 mm. Further annealing of these samples at 600°C for 30 min led to recrystallization. The working electrode surface represents a vertical intersection of the 1 cm long and 1 mm wide wire [16]. The working surface of the electrode was 0.1 cm^2. Saturated calomel electrode (SCE) was used as a reference electrode and platinum electrode was used as a counter electrode (platinum sheet of 2 cm^2). The electrochemical system used for the experimental procedure was fully developed at Technical Faculty in Bor, University of Belgrade [17]. The experiments described in this paper were performed at the temperature of 25 ± 0.5°C.

3. Results and discussion

3.1. Measuring the open circuit potentials for silver, copper and alloy AgCu50 in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl

The open circuit potential in some media indicates stability of the investigated metals in the given environment. The change of the open circuit potential with time, from the moment of electrode immersion in an electrolyte to its stabilization, indicates that the processes are occurring spontaneously at the contact surface until the achieving of stable equilibrium in the system electrode - electrolyte. The results of measuring the open circuit potentials for copper, silver and alloy AgCu50, presented in Figure 1, show that measured potential for copper stabilizes very fast at -0.2256 V vs. SCE. The open circuit potential for silver also stabilizes quickly at -0.1591V vs. SCE, while the value of open circuit potential for the alloy AgCu50 after the stabilization is -0.2145V vs. SCE.

Measuring the open circuit potential shows that the measured potential for silver is the most positive, and therefore, the electrode made of pure silver is most stable. Also, the measured potential for pure copper is, in this case, the most negative, whereas the value of the potential measured for the alloy, as expected for the eutectic alloy to which AgCu50 belongs, lies at the potential value between silver and copper.

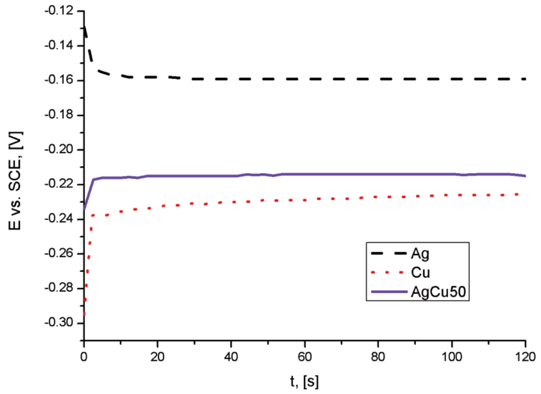

Figure 1. *Open circuit potentials for pure copper, pure silver and alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl during 120 s*

3.2. Anodic polarization curves for pure silver, copper and alloy AgCu50 in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl

Potentiodynamic method is based on the change of the working electrode potential with time and measuring the corresponding current that occurs as a result of oxidation-reduction processes. By using this method, the electrochemical parameters specific to a particular process can be obtained.

The anodic polarization curves for pure silver, copper and alloy AgCu50 in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl under scan rate of 20 mVs^{-1}, obtained by the potentiodynamic method, are given in Figure 2.

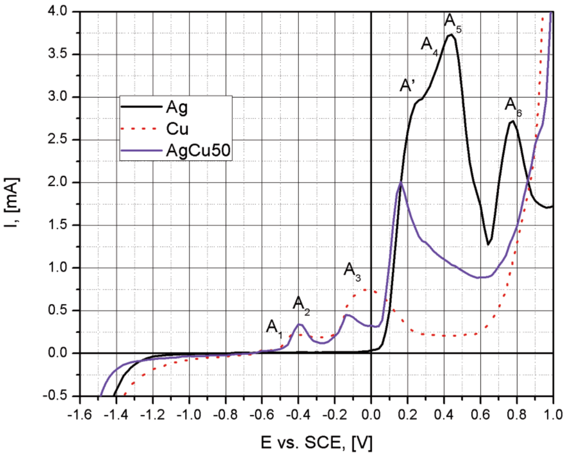

Figure 2. *Anodic polarization curves for pure silver, copper and alloy AgCu50 in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl; scan rate 20 mVs^{-1}; electrode surface area 0.1 cm^2*

According to polarization curve for pure copper three current peaks can be observed, marked as A$_1$, A$_2$ i A$_3$. During the oxidation of pure copper and pure silver adsorption of the OH$^-$ particles occurs on the surfaces of these metals in alkaline solutions [16, 18-25]. The addition of NaCl in that area leads to the adsorption of Cl$^-$ particles. The current peak A$_1$ is attributed to reactions of the parallel competitive adsorption of both these types of anions.

The current peaks A$_2$ and A$_3$ correspond to forming of copper oxides, Cu$_2$O and CuO, which is confirmed by extensive research of many authors [16, 19-31] and performes by reactions:

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \quad (1)$$

$$Cu_2O + H_2O = 2CuO + 2H^+ + 2e^- \quad (2)$$

The investigations also shown that in the same potential range copper chlorides are formed according to following mechanism [25, 32-35]:

$$Cu + Cl^- = CuCl_{ads} + e^- \quad (3)$$

$$CuCl_{ads} + Cl^- = CuCl_2^- \quad (4)$$

$$Cu + CuCl_2^- = 2CuCl + e^- \quad (5)$$

Based on the number of results available in the relevant scientific literature, it can be stated that the current peaks A$_4$, A$_5$ and A$_6$ correspond to the formation of silver oxides. At first, the forming of oxide Ag$_2$O-type I happens, then oxide Ag$_2$O-type II, which correspond to the current peaks A$_4$ and A$_5$, and finally occurs oxide AgO, corresponding to the current peak A$_6$, by the reactions [16, 21-25, 36-39]:

$$2Ag + H_2O = Ag_2O + 2H^+ + 2e^- \quad (6)$$

$$Ag_2O + H_2O = 2AgO + 2H^+ + 2e^- \quad (7)$$

The current peak A' is attributed to forming the silver chloride, AgCl, according to reaction [16, 34, 40,41]:

$$Ag + Cl^- \rightarrow AgCl + e^- \quad (8)$$

Starting from +0.1 V vs. SCE three current waves, A', A$_4$ and A$_6$ overlap until about 0.65 V vs. SCE. It means that in that potential area oxides and chloride of silver form simultaneously.

3.3 The influence of mercaptobenzothiazole on electrochemical behavior of silver, copper and the alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl

The possibility of using mercaptobenzothiazole as the corrosion inhibitor of silver, copper and alloy AgCu50 was tested by recording the anodic polarization curves in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl with the addition of different concentrations of MBT in the range 0.00001 - 0.001 moldm^{-3}. Anodic polarization curves were recorded in the potential range of -1.6 V vs. SCE to 0.8 V vs. SCE at scan rate of 20 mVs^{-1} at 25 °C.

3.3.1. The influence of mercaptobenzothiazole on electrochemical behavior of silver in 0.1 moldm^{-3}

NaOH + 0.2 moldm^{-3} NaCl

The anodic polarization curves for pure silver at scan rate of 20 mVs^{-1} in a solution of 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl with and without the addition of mercaptobenzothiazole are shown in Figure 3.

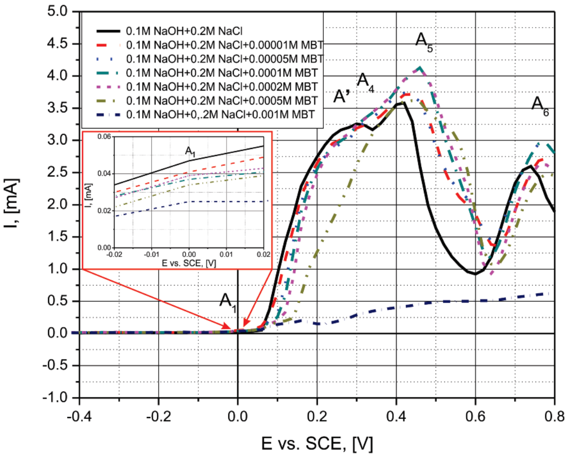

Figure 3. *Anodic polarization curves for pure silver in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl, without and with MBT; scan rate 20 mVs^{-1}; electrode surface area 0.1 cm^{2}*

During the oxidation of pure silver in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl, the adsorption of OH^{-} particles on the silver surface occurs in parallel with the adsorption of Cl^{-} ions, which corresponds to current peak A$_{1}$.

The current peak A$^{'}$, which corresponds to forming of silver chloride AgCl, is located at lower potential values and the current densities are lower compared to current peaks A$_{4}$ and A$_{5}$. The interaction of MBT with silver can be displayed by following reactions [14]:

$$MBT^{-} \rightarrow (MBT)_{ads} + e^{-} \quad (9)$$

$$Ag + MBT^{-} \rightarrow AgMBT + e^{-} \quad (10)$$

In the presence of MBT, peak potentials shift to more positive values, wherein the shift is being increased with the increase of MBT concentration. Up to the concentration of 0.001 moldm^{-3}, it can not be spoken about the inhibitory activity of MBT on the processes of the silver oxidation in the analyzed solution. The significant inhibitory effect can be only achieved at concentration of 0.001 moldm^{-3} MBT.

3.3.2. The influence of mercaptobenzothiazole on electrochemical behavior of copper in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl

In Figure 4 are presented the anodic polarization curves for pure copper in 0.1moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl without and with MBT, under the scan rate of 20 mVs^{-1}.

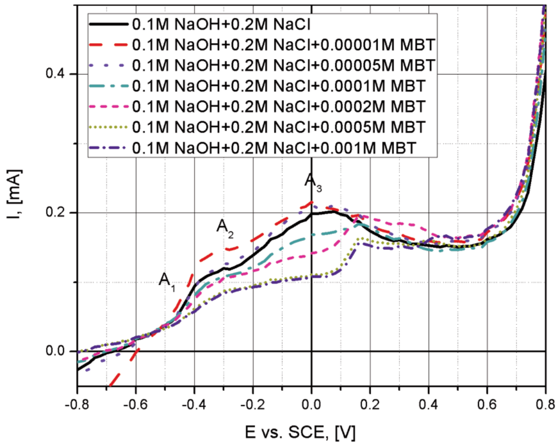

Figure 4. *Anodic polarization curves for pure copper in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl, without and with MBT; scan rate 20 mVs^{-1}; electrode surface area 0.1 cm^{2}*

On the anodic polarization curves three current peaks, A$_{1}$, A$_{2}$ and A$_{3}$, were observed. The Figure 4 shows that MBT has an inhibiting effect at concentrations greater than 0.00005 moldm^{-3}. This effect occurs due to forming of protective Cu(I)-MBT and Cu(II)-MBT films [15]. It can be also seen that the anodic current peaks occur at more positive potentials with increasing the concentrations of mercaptobenzothiazole. Analogously to the processes proven on silver, it can be assumed that the formation of the films proceeded by the reactions:

$$MBT^{-} \rightarrow (MBT)_{ads} + e^{-} \quad (11)$$

$$Cu + MBT^{-} \rightarrow Cu(I)MBT + 2e^{-} \quad (12)$$

$$Cu + MBT^{-} \rightarrow Cu(II)MBT + 3e^{-} \quad (13)$$

3.3.3. The influence of mercaptobenzothiazole on electrochemical behavior of alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl

In Figure 5 are presented the anodic polarization curves for alloy AgCu50 in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl without and with MBT under scan rate of 20 mVs^{-1}.

From Figure 5 it can be observed that up to MBT concentration in the solution of 0.0002 moldm^{-3} all current peaks occur at approximately the same potential values on the anodic polarization curves with the addition of MBT and the anodic polarization curves without the addition of MBT. At concentrations from 0.0005 moldm^{-3} to 0.001 moldm^{-3} MBT in the potential range from 0.3 V to 0.65 V vs. SCE, values of the current density are lower than values without the addition of MBT. Given that new current peaks do not appear in the presence of MBT on the anodic polarization curves, it can be assumed that there are no new electrochemical reactions, but MBT, by its adsorbing on the alloy surface, blocks part of the active electrode surface. It can be assumed that with

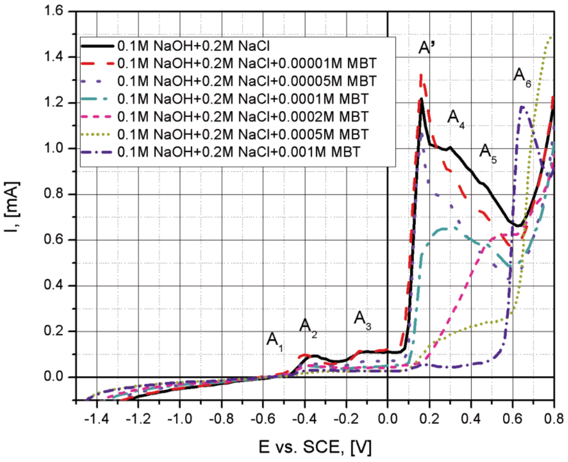

Figure 5. *Anodic polarization curves for alloy AgCu50 in 0.1 moldm^{-3} NaOH with the addition of 0.2 moldm^{-3} NaCl without and with MBT; scan rate 20 mVs^{-1}; electrode surface area 0.1 cm^{2}*

the addition of MBT, the film CuMBT on copper in the alloy AgCu50 is formed according to the following reactions:

$$Cu_{(Ag\text{-}Cu)}+MBT^{-}_{aq}\rightarrow(Cu_{(Ag\text{-}Cu)}\text{-}MBT)_{ads}+e^{-} \quad (14)$$

or

$$(Cu_{(Ag\text{-}Cu)}\text{-}H_2O)_{ads} + MBT^{-} \rightarrow$$
$$(Cu_{(Ag\text{-}Cu)}\text{-}MBT)_{ads} + H_2O_{aq} + e^{-} \quad (15)$$

At the same time in the uncovered area oxides and chlorides of copper and silver are being formed.

Analogously, forming of film of AgMBT on silver in the alloy AgCu50 can be expected according to following reactions:

$$Ag_{(Ag\text{-}Cu)}+MBT^{-}_{aq}\rightarrow(Ag_{(Ag\text{-}Cu)}\text{-}MBT)_{ads}+e^{-} \quad (16)$$

or

$$(Ag_{(Ag\text{-}Cu)}\text{-}H_2O)_{ads} + MBT^{-} \rightarrow$$
$$(Ag_{(Ag\text{-}Cu)}\text{-}MBT)_{ads} + H_2O_{aq} + e^{-} \quad (17)$$

Next to the formed complex AgMBT, the formation of the oxides Ag_2O and AgO occurs, whilst the formation mechanism of oxide Ag_2O is being changed in relation to the oxide that was formed without the addition of mercaptobenzothiazole. Chlorides and oxides of copper and silver are formed on the alloy surface until the entire surface is being covered with the complexes CuMBT and AgMBT.

3.4. Potentiostatic measurments

Potentiostatic investigations were carried out at -100 mV vs. SCE and at 200 mV vs. SCE during 100 s. These potentials correspond to current peaks A_3 and A' on the polarization curves. The obtained potential curves are shown in Figures 6 and 7.

In Figure 6 are shown potentiostatic curves after potentiostatic treating the alloy for 100 s in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3}, with and without various concentrations of MBT on the potential -0.1 V vs. SCE, which corresponds to the current peak A_3.

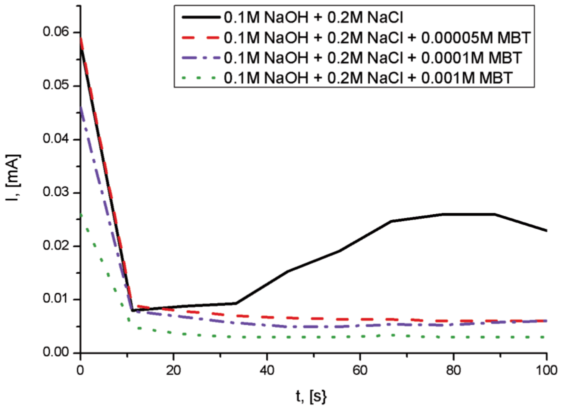

Figure 6. *Potentiostatic curves for alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl without and with MBT in various concentrations, on the potential of -0.1V vs. SCE during 100 s; electrode surface area 0.1 cm^{2}*

From Figure 6, it can be observed that the current density obtained for a solution of 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl, after the initial sharp drop increases slowly up to 90 s, reaches a maximum and then slightly decreases. Based on the E-pH diagram for the Cu-Cl-H_2O, showed by Tromans D. and Sun R. [42, 43], this happens at potentiostatic curve most likely due to competition between the formation of Cu_2O film which leads to passivity, and CuCl nucleation and growth condition which results in pitting. Modestov A. D. et.al. [44] came to conclusion that in the alkaline medium in the presence of chloride ions initially Cu_2O is formed, followed by CuCl and CuO forming.

With the addition of MBT current densities monotonically decrease until they reach a value of the stationary current density. With the addition of mercaptobenzothiazole Cu(I)MBT film is formed, which protects the alloy against oxidation that is more intense if the concentration of MBT is greater.

In Figure 7 potentiostatic curves for the alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl are shown, with and without the addition of different concentrations of MBT at the potential of 0.2 V vs. SCE during 100 s.

From Figure 7 it can be observed that the current density monotonically decreases with time until it reaches a steady state. The current density in a solution containing 0.00005 moldm^{-3} MBT has a greater value than the current density without mercaptobenzothiazole on the entire potential.

At MBT concentrations of 0.0001 moldm^{-3} and 0.001 moldm^{-3} on the whole potentiostatic curves the values of current density are lower than the value of the current density in the absence of MBT.

The approximate values of the stationary current density on the potentials -0.1 V vs. SCE and 0.2 V vs. SCE are shown in Table 1. By comparing the results obtained on two different potentials, it can be stated that the investigated inhibitor provided better oxidation resistance of the investigated alloy at lower potential. Current densities, with values given in Table 1, are the lowest in both cases at MBT concentration of 0.001 moldm^{-3}.

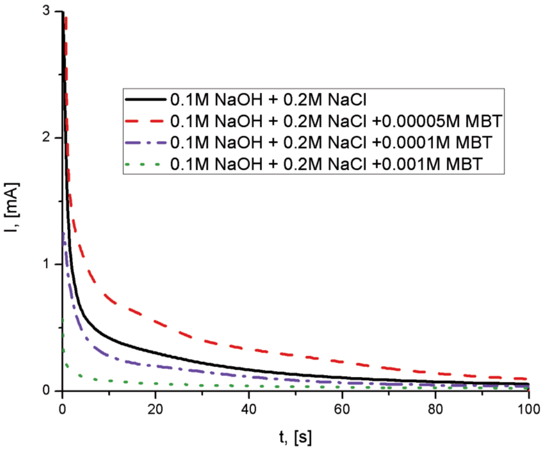

Figure 7. *Potentiostatic curves for alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl without and with various concentrations of MBT on the potential of 0.2 V vs. SCE during 100 s; electrode surface area 0.1 cm^2*

Table 1. *The approximate values of the stationary current density*

Electrolyte	-0.1 V vs. SCE	0.2 V vs. SCE
	j, [mAcm^{-2}]	
0.01M NaOH + 0.2M NaCl	0.26	0.55
0.01M NaOH + 0.2M NaCl+0.00005M MBT	0.06	0.96
0.01M NaOH+0.2M NaCl+0.0001M MBT	0.06	0.37
0.01M NaOH+0.2M NaCl+0.001M MBT	0.03	0.23

3.5. Surface characterization of the alloy AgCu50 by optical microscopy after potentiostatic treatment

Characterization of the alloy surface was carried out by optical microscopy after potentiostatic treating the alloy in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl, with and without the addition of different concentrations of MBT at the potential of -0.1 V vs. SCE during 100s.

During the potentiostatic treating of the alloy at the potential of -0.1 V vs. SCE in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl conditions for reactions (1-5) exist, whose products are copper oxides and chlorides. These products are clearly visible in Figure 8a. The addition of MBT leads to adsorption of MBT on the alloy surface and formation of CuMBT and AgMBT complexes which protect the alloy against corrosion. This effect is noticeable already at the lowest investigated concentration of MBT in the solution

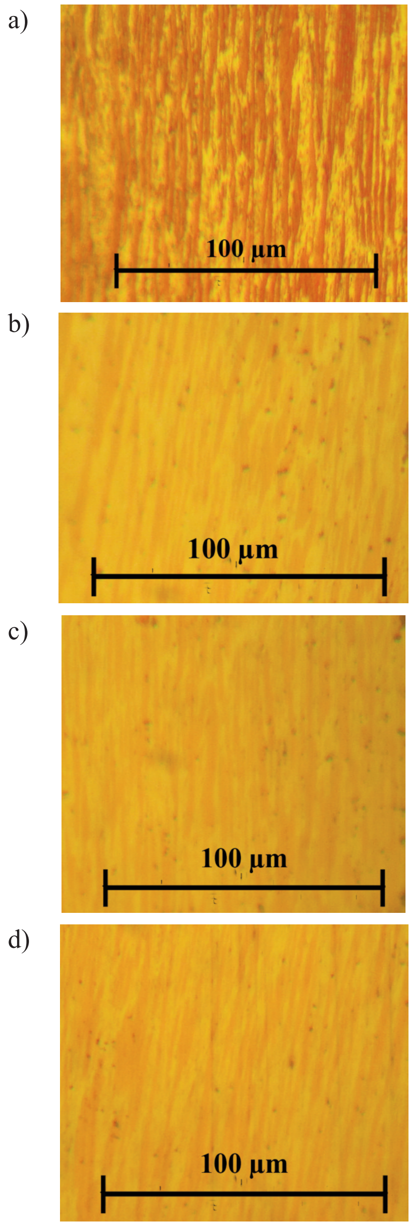

Figure 8. *Micrographs of the AgCu50 surface after potentiostatic treatment on the potential of -0.1 V vs. SCE during 100 s; electrode surface area 0.1 cm^2 : a) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl; b) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl + 0.00005 moldm^{-3} MBT; c) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl + 0.0001 moldm^{-3} MBT;d) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl + 0.001 moldm^{-3} MBT.*

(Figure 8b). With the increase of MBT concentration, the presence of copper oxide and chloride is decreasing (Figures 8c and 8d). Accordingly, it can be stated that MBT at a concentration of 0.0001 moldm^{-3} gives good surface protection from corrosion.

Figures 9 (a), (b), (c), (d) show the micrographs of the alloy AgCu50 surface after the potentiostatic treating the alloy at the potential of 0.2 V vs. SCE during 100 s in a solution of 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl without the addition of MBT and in the same solution supplemented with MBT at a concentration from 0.00005 moldm^{-3} to 0.001 moldm^{-3}. The micrographs obtained in the solution 0.1 moldm^{-3} NaOH + 0.2moldm^{-3} NaCl indicate following phases: black phase which corresponds to copper and silver oxides, green, which is derived from copper chloride and the white phase, which comes from the silver chloride. Namely, on the potential of 0.2 V vs. SCE, conditions for reactions (1-8) exist, whose products are silver and copper oxides and chlorides. Micrograph 9a shows that the surface is almost completely covered with the products, wherein the oxides (black phase) are predominant. Figures 9b and 9c indicate changes in the structure of the precipitate, already at the lowest inhibitor concentration (0.00005 moldm^{-3}, Fig. 9b), that is more intense with the concentration increase. At the highest investigated concentration of MBT in a solution of 0.001 moldm^{-3}, corrosion products on the alloy surface are almost completely absent (Figure 9 d).

The addition of MBT leads to adsorption of MBT on the alloy surface and formation of complexes CuMBT and AgMBT which protects the alloy against corrosion. With the increase of MBT concentration in the solution, the micrographs show the declining of black, green and white phase, which points to lower quantities of formed silver and copper oxides and chlorides. Consequently, MBT in higher concentration better protects the surface from the oxidation.

Comparing the micrographs obtained at different potentials at the same other conditions, it is evident that on more negative potential a better protection from corrosion can be achieved by using MBT as an inhibitor.

4. Conclusions

Based on the experimental investigations of the electrochemical behavior of alloy AgCu50, as well as pure metals silver and copper in a sodium hydroxide solution with the presence of chloride ions and mercaptobenzothiazole, the following can be concluded:

Measurement of open circuit potentials in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCI indicate that potential for silver is the most positive, potential for pure copper is the most negative, while as expected for Ag-Cu system, which belongs to the group of eutectic alloys, potential for the alloy AgCu50 lies between the potentials of silver and copper.

The investigation of the electrochemical behavior of pure silver, pure copper and alloy AgCu50 in 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl with the addition MBT, reveals the same current peaks as on anodic polarization curves without MBT. Analysis of the resulting anodic polarization curves shows that at low

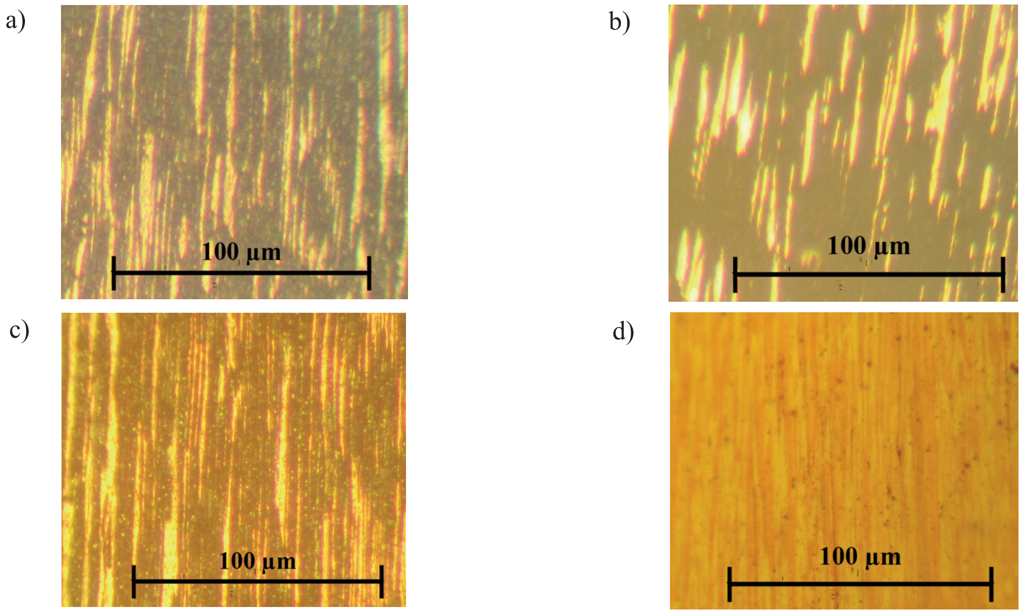

Figure 9. *Micrographs of AgCu50 surface after potentiostatic treatment on the potential of 0.2 V vs. SCE during 100 s; electrode surface area 0.1 cm^2: a) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl; b) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl + 0.00005 moldm^{-3} MBT; c) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl + 0.0001 moldm^{-3} MBT; d) 0.1 moldm^{-3} NaOH + 0.2 moldm^{-3} NaCl + 0.001 moldm^{-3} MBT.*

concentrations, in some cases, MBT may have an activating effect, especially in the cases of pure copper and copper alloys. On the contrary, with increasing the concentration above 0.0001 moldm^{-3}, MBT provides good protection of the pure metal surface as well as the alloy AgCu50. At higher MBT concentrations anodic current peaks are shifted to more positive values of the potential, and at MBT concentration of 0.001 moldm^{-3} the current densities abruptly fall, reaching values close to zero.

Potentiostatic measurements on the alloy AgCu50 confirm that the mechanism of MBT action depends on its concentration extent in the electrolyte. On the basis of optical micrographs obtained after the potentiostatic treatment, it can be concluded that in the presence of MBT in a concentration greater than 0.0001 moldm^{-3} oxides and chlorides of copper and silver are formed to a negligible extent. Comparing the micrographs obtained at different potentials in the same other conditions, it can be concluded that more negative potential enables better protection from corrosion.

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