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The Influence of pH on Electrochemical Behavior of Copper in Presence of Chloride Ions

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The electrochemical behavior of copper in borax buffer solutions in pH range 8.0-12.3, with or without chlorides, was investigated. It was found that with increasing pH of the solution the open circuit potential becomes more negative. Analysis of the polarization curves recorded in these experiments leads to a conclusion that anodic polarization behavior of copper includes transition from active to passive region with two anodic current peaks that include formation of Cu_2O film and a film that contains $Cu(OH)_2$ and CuO. It was found that there is a linear relationship between E and log(i) in the active dissolution region, with a Tafel slope of 60mV/dec indicating that the dissolution is not activation controlled and is determined by the diffusion of soluble $CuCl_2^-$.

Keywords: copper, corrosion, borax buffers, chloride ions

1. INTRODUCTION

Copper is metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. It is resistant to the influence of atmosphere and many chemicals, however, it is known that in chloride media it underlies corrosion. The mechanism of copper and copper based alloys electrodissolution in chloride media has been investigated [1], and inhibition of copper dissolution by organic inhibitors was also intensively examined [2]. It is generally accepted that the anodic dissolution of copper is influenced by chloride concentration independently of pH [3,4]. At chloride concentrations lower than 1M, the copper dissolution mechanism can be expressed as [5,6]:

$$Cu + Cl^- \leftrightarrow CuCl + e^-$$

$$CuCl + Cl^- \rightarrow CuCl_2^-$$

Although only some authors clearly noticed formation of $CuCl_2^-$ it is believed to control the kinetics of anodic dissolution of copper in inhibitor free solutions. At chloride concentrations higher than 1M complexes $CuCl_3^{2-}$ and $CuCl_4^{3-}$ are formed [4-6]. However, in the alkaline media containing chloride ions the mechanism can be totally different, so in that case most likely copper oxides are formed [4,7-9].

This paper describes the influence of pH of the solution containing Cl^- ions on electrochemical behavior of copper in borate solutions.

2. EXPERIMENTAL PART

2.1. Preparation of the electrode

The working electrode was made of copper wire obtained by upcasting procedure. It was prepared in the following way. The wire was cut and sealed with cold sealing material based on methyl-metacrylat. The working area was 0.49cm^2. Before each measurement Cu electrode was polished using 1μm grit alumina paste, rinsed with distilled water and dried. The reference electrode was saturated calomel electrode (SCE), and the auxiliary one was made of platinum.

2.2. Reagents

Following reagents were used: 0.1M solution of H_3BO_3; 0.1M solution of $Na_2B_4O_7$; 0.1M solution of NaOH. All solutions were made of a.r. grade chemicals.

The initial solutions, which composition and pH are presented in Table 1, were made by mixing the reagents mentioned in the previous paragraph (H_3BO_3; $Na_2B_4O_7$ and NaOH). pH values of all solutions were determined subsequently using the pH-meter MA 5740 (ISKRA-Slovenia).

Table 1. Composition and pH of the initial solutions

	pH				
Amount of reagents for 100cm^3 of initial solution	8.0	8.7	9.3	10.3	12.3
0.1M H_3BO_3	95 cm^3	75 cm^3	0	0	0
0.1M $Na_2B_4O_7$	5 cm^3	25 cm^3	100 cm^3	12.5 cm^3	12.5 cm^3
0.1M NaOH	0	0	0	24.75cm^3	35 cm^3
H_2O	0	0	0	62.75cm^3	52.5 cm^3

Sodium chloride was added to the initial solutions (0.2924g NaCl in 100 cm^3 of initial solution) in order to obtain 0.05M Cl^- solutions.

2.3. Procedure

The apparatus used for electrochemical tests consists of potentiostat directly connected to a computer via an AD card. Applied methods were: measuring of the open circuit potential and linear voltammetry. The open circuit potential was determined during 5min, afterwards the polarization curves were recorded from the open circuit potential up to approximately 1.0V vs. SCE. Measurements were performed at scan rates of 1 and 10mV/s. All of the measurements where the scan rate is not specified were conducted at the scan rate of 10mV/s. All measurements were conducted at the room temperature. The potential is expressed referring to a saturated calomel electrode.

3. RESULTS AND DISCUSSION

3.1. The anodic polarization behavior of copper in solutions of various pH

The copper electrode was polarized in solutions of various pH (8.0, 8.7, 9.3, 10.3, and 12.3) which compositions are listed in Table 1. The results of these tests are shown in Figs. 1-3 and Table 2.

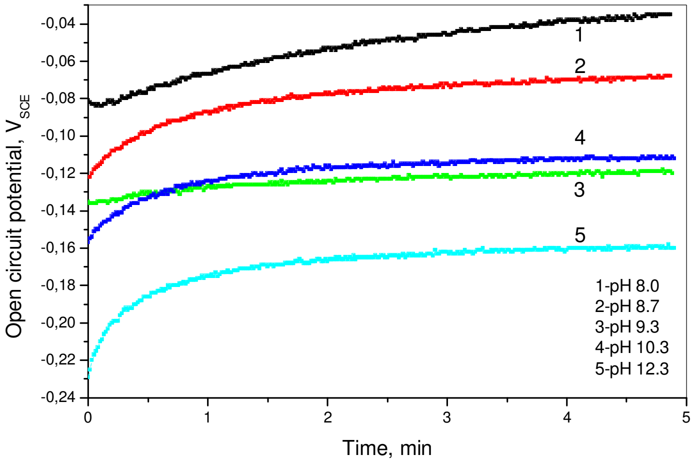

Figure 1. The open circuit potential of Cu electrode in borax buffers

It was found that, at all tested pH, the open circuit potential increases with time until it reaches constant value. The same is observed in literature [10,11]. It is shown (Table 2) that with increasing pH of the solution the open circuit potential becomes more negative. There is no strictly linear relationship between the open circuit potential and pH of the solution.

Anodic behavior of Cu in alkaline solutions was a subject of numerous electrochemical researches. Those were mainly focused on formation and structure of passive anodic films [12,13], including those formed at the lower potentials where oxide film contains Cu(I) oxidation state and at the higher potentials where Cu(II) oxidation state is present. With an increase of potential it is believed that the final step in passivation of copper is formation of Cu(II) film [8,9].

Analysis of the polarization curves recorded in these experiments, shown in Fig. 2, leads to a conclusion that anodic polarization behavior of copper includes transition from active to passive region with two anodic current peaks that include formation of Cu_2O film and a film that contains $Cu(OH)_2$ and CuO. Similar findings were reported by other authors [3,8,14-22]. It can be seen, from the polarization curves, the peaks are clearly observed at pH 8.0, 8.7 and 9.3, and for that pH interval, peaks potentials (E_p) move in negative direction, while at the same time peaks current densities (j_p) become higher. [8] At pH 10.3 and 12.3 peaks are not distinct. Besides, at higher pH, current densities are lower, and also, the second peaks become broader. The same observations are noted by other researchers [8]. There is a linear dependence between the potential of the first anodic peak potential and pH with the slope -0.070V/pH. Tromans and Sun [8] and Abd El Haleem and Abd El Aal [17] observed similar dependance with the slope -0.059V/pH and 0.059V/pOH, respectively.

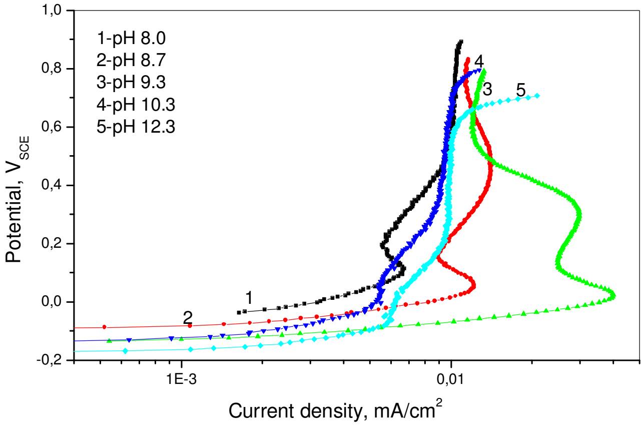

Figure 2. The polarization curves recorded in borax buffers of different pH at scan rate of 1mV/s

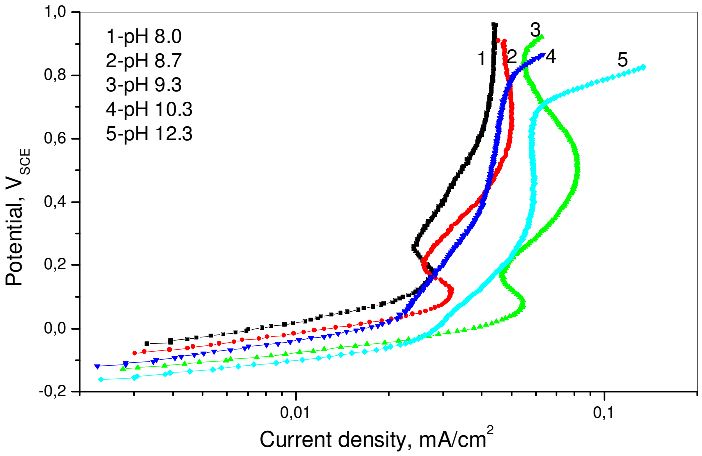

Figure 3. The polarization curves recorded in borax buffers of different pH at scan rate of 10mV/s

The parameters presented in Table 2 are obtained by the analysis of the polarization curves shown in Fig 2. It can be seen that b_a has a value of 120mV vs. SCE at all pH accept 9.3 indicating that in the active region copper dissolves by releasing one electron. Based on this conclusion, equations describing copper dissolution at the first and the second peak can be expressed as:

$$Cu \rightarrow Cu^{+} + e^{-} \quad (\text{ I peak })$$
$$Cu^{+} \rightarrow Cu^{2+} + e^{-} \; (\text{ II peak })$$

The current density increases at the potentials higher than the second peak potential. According to the literature it can be attributed to the formation of poorly protective CuO film that allows further interaction between Cu and the electrolyte [3], transpassive dissolution of Cu^{2+} from the oxide surface [22], a breakdown of the passive film connected with local decrease of pH due to the copper oxidation reaction at the electrode surface and the formation of soluble complexes [8] or the evolution of oxygen on the electrode surface [8,22] at the corresponding potential ($E_{O2/H2O}$=1.229-0.0591 pH , V_{SHE}; V_{SHE}=V_{SCE} + 0.242 V).

Table 2. Influence of pH on E_{OCP}, j_{corr}, b_a, E_p and j_p (Data are obtained using the polarization curves shown in Fig 2.).

pH	E_{ocp}, V_{SCE}	j_{corr}, mA/cm^2	b_a	I peak		II peak	
				E_p,V_{SCE}	j_p,mA/cm^2	E_p,V_{SCE}	j_p,mA/cm^2
8.0	-0.035	0.0018	0.124	0.114	0.0067		
8.7	-0.068	0.0023	0.113	0.049	0.0122	0.479	0.01418
9.3	-0.120	0.0024	0.088	0.023	0.03944	0.295	0.02988
10.3	-0.112	0.0016	0.123				
12.3	-0.160	0.0016	0.118				

Comparison of Figures 2 and 3, where scan rates are 1mV/s and 10mV/s, respectively, shows that at higher scan rate current densities increase, while the anodic peaks are broader and shifted to more positive potentials. The increase of current density with the scan rate is noticed by Walton et al. [23] and Tromans and Sun [8] as well.

3.2. The influence of chloride ions

The anodic polarization of copper electrode was conducted in the solutions of various pH, like in the previous section, with the addition of 0.05M NaCl in order to examine the influence of chloride ions.

It is found that, in the presence of 0.05M NaCl, the open circuit potentials of Cu electrode increase with time as well as in the solutions without chlorides, except at pH 8.0 and 8.7. The same is observed in literature [10,11]. Comparison of the open circuit potential values obtained in the solutions with (Fig. 4) and without (Fig. 1) presence of chlorides indicates that the presence of chloride ions renders the open circuit potentials more negative. The same is observed by Milic and Antonijevic [11]. In the pH range 8.0-10.3 there is a linear increase of the open circuit potential with pH (Fig. 5), with the slope of 0.032V/pH, and at pH=12.3 there is a discrepancy and the open circuit potential decreases.

Copper behavior in chloride solutions authors most commonly explain by the formation of compounds consisting of copper and chloride, whether it is a deposition of CuCl or formation of soluble complex $CuCl_2^-$, and the dissolution occurring at more active negative potentials without formation of copper oxides [3,8,24].

There is a linear relationship between E and log(i) in the active dissolution region, with a Tafel slope of 60mV/dec, and the analysis of that area indicate that the dissolution is not an activation controlled and is determined by the diffusion of soluble $CuCl_2^-$ [3,8,25]. The current of the peak that corresponds to the end of Tafel region is attributed to the formation of CuCl film [3,24]. This is in accordance with the mechanism that is given in the introduction.

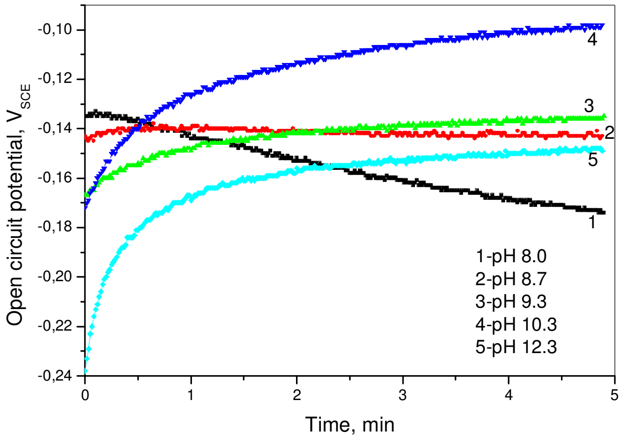

Figure 4. The open circuit potential of Cu electrode in borax buffers of different pH containing 0.05M NaCl

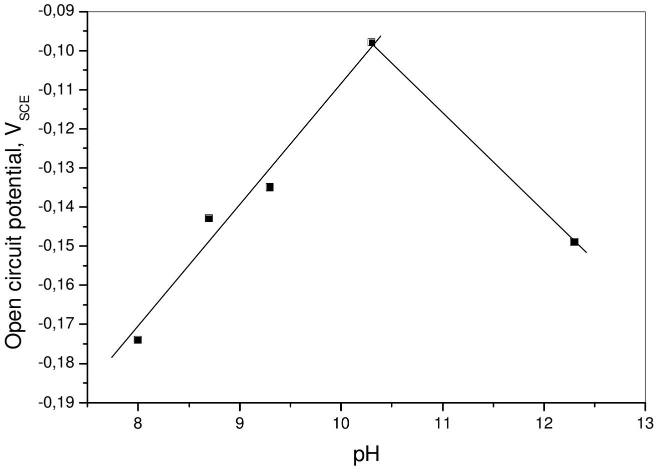

Figure 5. The correlation between the open circuit potential of Cu electrode in 0.05M NaCl borax buffers and solution pH

Nevertheless, in alkaline media formation of Cu_2O film can be favored over the formation of CuCl as some authors observed [4,7]. The same conclusion can be drawn from the E-pH diagrams for discussed system that are presented by Tromans [9]. So, in the solution containing chloride ions, the electrochemical behavior of copper should be observed through two parallel reactions leading to either the formation of Cu_2O film, that leads to the passivity, or nucleation and growth of CuCl layer [15,26]. The polarization curves recorded for copper in borax buffers containing 0.05M NaCl, shown in Fig. 6, are similar to those recorded in pure borax buffer solutions (Figs. 2 and 3) but with higher current densities indicating the activating effect of chloride ions. This is in agreement with the data obtained by other authors [8,10,11,15,27]. It is also observed that chloride ions have smaller effect at higher pH. This result is confirmed by Modestov et al. [27]. Two anodic current peaks occur (Table 3). Azzaroni et al. [7] investigated the anodic dissolution of copper in borax solution containing 0.1M KCl, whereby they assumed that Cu transforms to Cu_2O film at I peak while combined electroformation $Cu_2O/CuO/Cu(OH)_2$ takes place on Cu_2O film at II peak. They consider that, in this potential region, copper dissolution as Cu(I) and Cu(II) through this complex oxide film also contributes the anodic current involved in the peaks. These processes can be schematically presented by: Cu → $Cu_2O/CuO/Cu(OH)_2$.

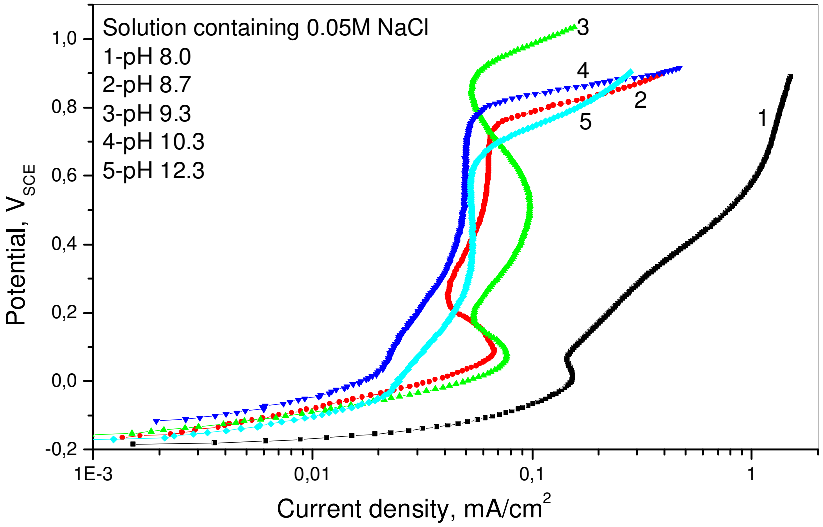

Figure 6. The anodic polarization curves recorded for copper in borax buffers of different pH containing chloride ions of concentration of 0.05M at scan rate of 10mV/s

Table 3. The influence of solution pH on E_p and j_p (Data are obtained using the polarization curves shown in Fig. 6.).

	I peak		II peak	
pH	E_p,V_{SCE}	j_p,mA/cm^2	E_p,V_{SCE}	j_p,mA/cm^2
8.0	0.015	0.15312		
8.7	0.087	0.06736		
9.3	0.079	0.07666	0.513	0.09784

It is observed, in this research, that at more positive potentials, than corresponding to the II peak, at pH 8.7, 10.3 and 12.3 an almost constant current occurs. It can be related to the copper oxide growth and the generalized copper dissolution through the complex oxide film. The beginning of current increase and the rapid increase of current density in the passive region indicate pits growth at the copper electrode, which is also observed in the works of other authors [7,27,28]. The pitting corrosion of copper in chloride is explained by Cu_2O film formation on the copper surface and trapped CuCl [29] or the damage of the protective layer [30]. Other authors [8] explain the current increase by the formation of soluble complexes influencing oxide films solubility that is pH dependant. If the oxides solubility increases once the diffusion flux of buffer species is not enough to maintain constant pH at the electrode surface the film easily brakes down. E-pH diagram [3,8,9] shows that $CuCl_2^-$ complex becomes more stable at the lower anodic potentials in weakly alkaline solutions and more stable with decreasing pH, while at higher pH it does not form at all, instead copper oxides and ions are present.

4. CONCLUSIONS

The open circuit potential measured in borax buffer solutions with increasing pH becomes more negative and has values from -35 to -160mV. The anodic polarization curves for copper in borax buffers indicate the surface passivation. Two anodic current peaks related to the formation of Cu_2O and CuO appear. The peaks are clearly observed at pH 8.0, 8.7 and 9.3, while at higher pH they are less distinct. In borax buffers containing chloride ions (0.05M) the open circuit potential has more negative values, than in buffers without those ions. The polarization curves indicate similar behavior to the pure buffer solutions, whereby the higher current densities occur.

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