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Influence of pH and Chloride Ions on Electrochemical Behavior of Brass in Alkaline Solution

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This paper describes an investigation of the corrosion behavior of Cu37Zn brass in borate buffer solutions at various pH, with and without the addition of chloride ions. The results lead to the conclusion that the anodic current densities depend on pH and chloride ions. The current density increased in pH interval from 8.0 to 9.3 in borate buffer solutions without chloride ions. In a sodium tetraborate solution with the addition of Cl^- ions, current density decreased in pH interval from 8.0 to 10.3

Keywords: Brass, Chloride ions, Polarization, Corrosion

1. INTRODUCTION

Copper and its alloys are widely used in industry because of their good resistance to corrosion, and are often used in cooling water systems, for shipboard condensers, power plant condensers and petrochemical heat exchangers. Brass is very interesting for many scientists, because of its great industrial importance. Behavior of brass was studied in seawater [1,2], NaCl [3-8], H_2SO_4 [9], HNO_3 [10,11], borate buffer [12, 13], sodium tetraborate [14]. The mechanism of copper and copper based alloys electrodissolution in chloride media has been investigated [15], and inhibition of copper dissolution by organic inhibitors was also intensively examined [16]. Brass is liable to dezincification in aggressive media. Two theories explain mechanism of dezincification. The first theory assumes selective dissolution of Zn, which goes in solution, and porous rest, rich with Cu, remains on brass surface. The second theory assumes simultaneous dissolution of Cu and Zn with redeposition of Cu from solution on brass surface. The rate of this process is often determined by the diffusion rate of disolved oxygen to the metal surface and the reaction is said to be under mass transport control [17]. Passive film can be formed during electrochemical measurements on the metal surface, and composition of film depends on potential. Passive film formed on copper surface consists of inner

Cu_2O and outer CuO [12,18]. Passive film formed on the brass surface is more complex and contain $ZnO{\cdot}xH_2O$ at more negative potential or Cu_2O and CuO at more positive potential [12,19]. ZnO becomes more dominant in the protective layer with increasing Zn content in the alloy [12].

This study presents the results of research of electrochemical behavior of Cu37Zn brass in borate buffer solutions, with and without chloride ions, at various pH values.

2. EXPERIMENTAL PART

The working electrode was made of Cu37Zn brass with an area of 0.49cm^2. The electrode was prepared from a brass wire (ø=0.79cm), it was cut and sealed with epoxy resin. Before each measurement, the working 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**.** The apparatus used for electrochemical measurements holds potentiostat directly connected to a computer via an AD card.

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.

Composition and pH of initial solutions are presented in Table 1. The initial solutions were made by mixing the solutions mentioned above (0.1M H_3BO_3, 0.1M $Na_2B_4O_7$ and 0.1M NaOH). pH values of solutions were measured using pH-meter MA5740 ISKRA-Slovenia.

Table 1. Composition and pH of 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

NaCl (0.2924g NaCl in 100cm^3) was added in initial solution. Concentration of chloride ions was 0.05M.

The following methods were used: measuring of the open circuit potential (OCP) and linear voltammetry. The linear voltammograms were recorded starting from the corrosion potential to 1.0V vs. SCE. Measurements were conducted at a scan rate of 1 and 10mVs^{-1}. All measurements were done at the room temperature.

The electrochemical behavior of Cu37Zn brass in borate buffer solutions with and without chloride ions was investigated in the following way:

a) The electrode was immersed in the borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3) in which polarization was performed.

b) The electrode was immersed in the borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3) with the addition of NaCl solution (C_{NaCl}=0.05moldm^{-3}) in which polarization was immediately performed.

3. RESULTS AND DISCUSSION

3.1. Effect of pH on behavior of Cu37Zn brass in a borate buffer solution

Open circuit potential of Cu37Zn brass was recorded over the period of 5min in borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3). It was found that open circuit potential becomes more positive with time at all tested pH (Fig.1.). Milosev et al. [20] came to the same result in their investigation. Also, it was observed that OCP becomes more negative when pH increases [21] and measurements showed that OCP was in the range of -0.088 to -0.195V vs. SCE (Fig.2.). The potential change was greater at lower pH values (pH 8.0 – 8.7) and slower at pH>9.3 (Fig.2.).

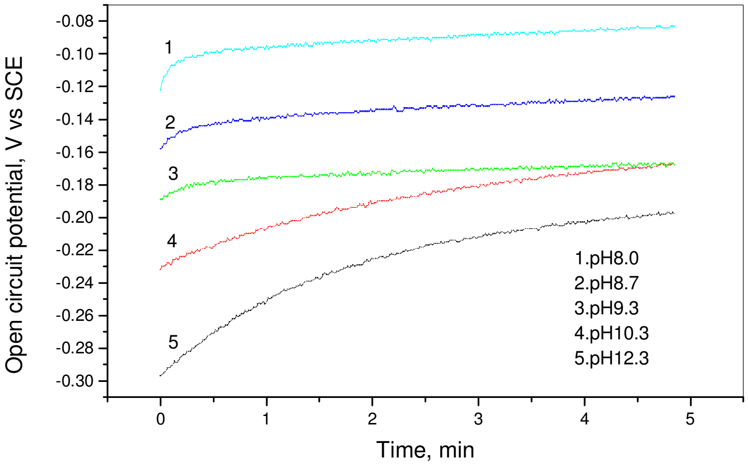

Figure 1. Open circuit potential as a function of time of immersion for Cu37Zn in borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3)

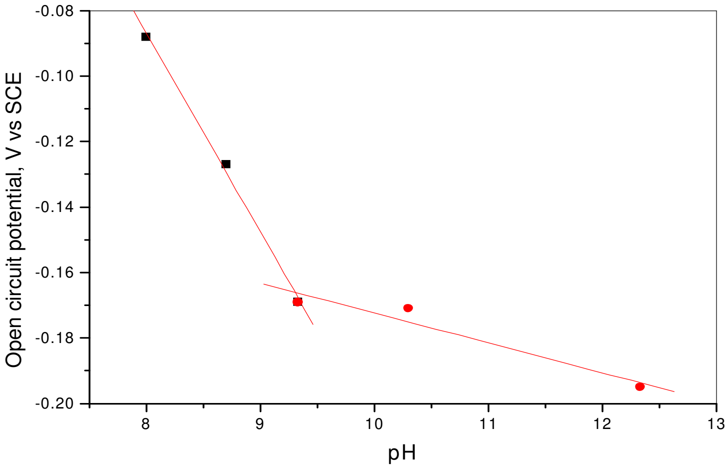

Figure 2. Open circuit potential as a function of pH in borate buffer solutions

Anodic polarization curves recorded in the borate buffer solutions of various pH are presented in Fig. 3. and 4. Polarization was performed at a scan rate of $1 mVs^{-1}$ (Fig.3.) and $10 mVs^{-1}$ (Fig.4.).

Analysis of polarization curves recorded in these experiments leads to conclusion that current density depends on pH in the both cases (Fig. 3. and 4.). It is also observed that current density increased in pH interval from 8.0 to 9.3 but at the pH 10.3 current density considerably decreased. At pH 12.3 current density increased which leads to conclusion that dissolution of brass is intensive in more alkaline solution. Three peaks (A_1, A_2 and A_3) were observed at pH 8.0, 8.7 and 9.3 (Fig.3.) and these peaks correspond to the Cu(I)-oxide formation. Also, formation of Cu_2O was observed by other authors [17,19,22-24]. Cuprous oxide (Cu_2O) [25] is the primary oxidation product in alkaline solution, and that was confirmed by the following equation:

$$2Cu + 2OH^- = Cu_2O + H_2O + 2e^-$$

It is observed from Fig. 3. and 4. that breakdown potential depends on pH, solution pH increase causing drop of breakdown potential values.

It is very difficult to determine an exact composition of brass surface in alkaline solution and some authors claim that on the brass surface in alkaline solution the layer exists, which is predominantly ZnO at lower potentials [20,26,27]. Also, it is very important to mention that composition of formed surface layer depends on potential. ZnO and $Zn(OH)_2$ were formed at more negative potentials while Cu_2O, CuO and $Cu(OH)_2$ formation takes place at higher potentials [17].

The parameters presented in Table 2 are obtained by the analysis of the polarization curves shown in Fig 3. It can be seen that Tafel slopes are very similar (83.8-$87.9 mVdecade^{-1}$) in pH interval from 8.0 to 12.3. (Tab.2.), indicating that mechanism of reaction didn't change [11,28] when pH values were changed.

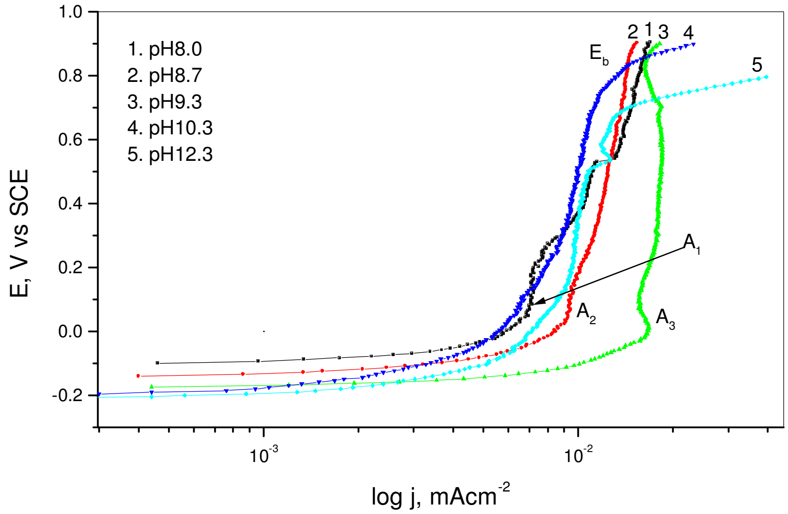

Figure 3. Polarization curves of Cu37Zn brass in the borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3). Polarization was performed immediately after the immersion of the electrode in the borate buffer solutions, $1 mVs^{-1}$

Table 2. Electrochemical parameters of Cu37Zn brass in borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3)

pH	E_{corr} [V vs. SCE]	I_{corr} [μAcm^{-2}]	b_a [$mVdec^{-1}$]
8.0	-0.088	1.1	83.81
8.7	-0.127	1.7	85.34
9.3	-0.169	6.4	86.09
10.3	-0.171	1.1	87.74
12.3	-0.195	1.8	87.86

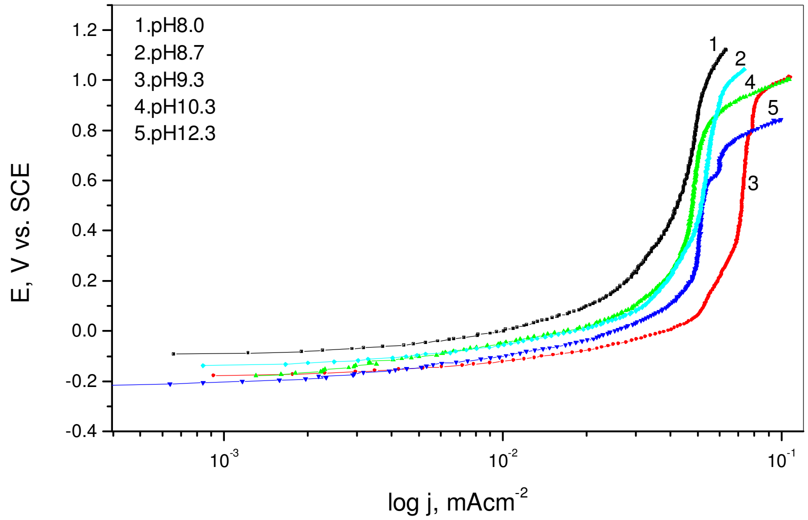

Figure 4. Polarization curves of Cu37Zn brass in borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3). Polarization was performed immediately after the immersion of the electrode in the borate buffer solutions, 10mVs^{-1}

3.2. Effect of chloride ion concentration on behavior of Cu37Zn brass in a borate buffer solution

The anodic polarization of brass electrode was conducted in the solutions of various pH, like in the previous part, with the addition of 0.05moldm^{-3} NaCl in order to examine the influence of chloride ions.

It is found that open circuit potential depends on pH values, and becomes more negative with increasing pH (Fig. 5.). It is also observed that open circuit potential has more negative values in the solution with NaCl then in the solution without NaCl at the same pH. The same is observed by Milic and Antonijevic [29].

Polarization curves of Cu37Zn brass in the borate buffer solutions of various pH with addition of NaCl (C_{NaCl}=0.05moldm^{-3}) are showen in Fig.6. It is observed that current density decreased with pH increase in pH interval from 8.0 to 10.3 at potential more negative then 0.4V vs. SCE. Also, is observed that current density had a similar values at a large region of potential (from 0.1 to 0.85V vs. SCE) at pH 9.3, and this indicate that passive layer formed on the electrode surface is the most stable at that pH (Fig6, curve 3). Brass passivation is attributed to the complex passive layer, consisting of $ZnO·xH_2O/Cu_2O-CuO$, formation, which is less resistant to Cl^- ion attack than protective layer formed on Cu electrode, however, localized corrosion occurred no sooner than $E>E_b$ [13]. The peaks A_1 and A_2 are observed at pH=8.0 and 9.3. These peaks affirm building Cu_2O on brass surface. Formation of Cu_2O onto brass surface in chloride containing media was observed by Procaccini et al. [23], Mamaş et al. [30] and El-Sherif et al. [31].

Polarization of brass alloys in chloride containing media results in the formation of various oxide, oxychloride and/or chloride corrosion products differing in the Cu and Zn contents [20]. Cu_2O, CuO and $Cu(OH)_2$ compounds are the most often bare compounds on the brass surface in chloride containing media [32]. In the presence of chloride ions in borate buffer solution the ZnO layer formed on the brass surface is mixed with a Cu-rich layer which is developed in the process of dezincification [20]. In the chloride solution, formation of the soluble complex $CuCl_2^-$ was observed [30,31], as well as insoluble CuCl on the electrode surface [30,32] which was recognized as main corrosion product in that kind of solution [33]. Formation of products in the chloride containing solution is restricted by concentration of chloride ions. In the solutions which contain Cl^- ions up to $0.3 moldm^{-3}$ $CuCl_2^-$ was produced, while in the presence of higher concentration of chloride ions $CuCl_2^-$ hydrolyse and form passive Cu_2O layer [31].

The kinetics and mechanism of brass anodic dissolution and surface film formation in the chloride solution can be explained by the following reactions [5,6]:

$$Zn^{2+} + H_2O = ZnO + 2H^+ \text{ or}$$

$$Zn + H_2O = ZnO + 2H^+ + 2e^-$$

$$2Cu^+ + H_2O = Cu_2O + 2H^+ \text{ or}$$

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^-$$

After the surface has become covered with ZnO and Cu_2O, CuCl is formed on the surface by the reaction:

$$Cu^+ + Cl^- = CuCl$$

$$2CuCl = Cu + CuCl_2$$

and $CuCl_2^-$ is formed by the dissolution of CuCl:

$$CuCl + Cl^- = CuCl^-_2$$

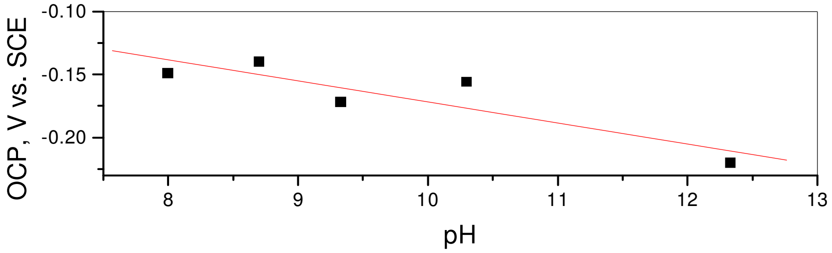

Figure 5. Open circuit potential as a function of pH in borate buffer containing 0.05moldm^{-3} NaCl

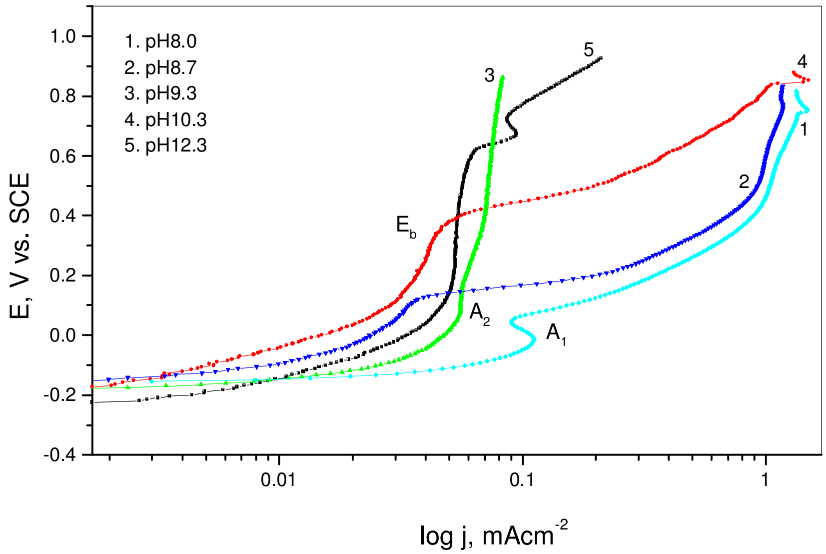

Figure 6. Polarization curves of Cu37Zn brass in borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3) containing 0.05moldm^{-3} NaCl. Polarization was performed immediately after the immersion of the electrode in the solution, 10mVs^{-1}

4. CONCLUSIONS

The open circuit potential of brass Cu37Zn in borate buffer solutions ranges from -0.088V to -0.195V vs. SCE. The anodic polarization curves recorded at pH 8.0, 8.7 and 9.3 show three peaks A_1, A_2 and A_3 corresponding to Cu_2O formation. The breakdown potential becomes more negative with the increase of pH values.

In borate buffer solutions containing chlorides (0.05moldm^{-3}) the open circuit potential have more negative values than in borate buffer solutions without chlorides, at the same pH values. Two peaks are observed from the polarization curves, which point to Cu_2O formation on brass surface. The protective layer on brass surface was the most resistant at pH 9.3.

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