POTENTIOSTATIC INVESTIGATION OF AgCu ALLOY IN ALKALINE MEDIUM IN PRESENCE OF CHLORIDE IONS

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ABSTRACT

Electrochemical behaviour of AgCu alloy (50 mass.% Ag + 50 mass.% Cu) has been investigated by potentiostatic method. Investigations were conducted in 0.1 mol dm^{-3} NaOH with the absence and presence of NaCl (0.001-0.5 mol dm^{-3}). Previous investigations using cyclic voltammetry showed that, beside six anodic current peaks which appear in pure sodium hydroxide, in presence of chloride ions with concentration higher than 0.001 mol dm^{-3} another additional current peak appears ascribed to the formation of silver chloride, while current waves of formed copper chlorides are very similar to the ones of copper oxides and can only be noticed by the change in the altitude of peaks. Potentiostatic measurements were conducted on all potentials of anodic current peaks during 100s. According to potentiostatic curves it has been concluded that with the increase of Cl^- ion concentration in solution the value of stationary curve density is growing unequally and results with the appearance of three regions with different slopes on the curve log j = f (log C_{Cl}). In the first area (with Cl^- ion concentration up to 0.005 mol dm^{-3}) chloride ions do not have significant influence on the process of corrosion. In the second area, with Cl^- ion concentration from 0.01 mol dm^{-3} to 0.1 mol dm^{-3}, chloride ions have activation effect which leads to the formation of silver and copper chloride on alloy surface. In the third area, with Cl^- ion concentration higher than 0.1 mol dm^{-3}, increase of chloride concentration does not lead to the suitable increase in the chloride formation rate, i.e. curve enters the saturation.
Keywords: Silver, Copper, AgCu alloy, Chloride, Anodic oxidation

1. Introduction

The AgCu binary system belongs to the eutectic type of alloy. The alloy with 50mass.% Cu and 50 mass.% Ag is used for solders in industry [1]. The goal of this work was to investigate the behaviour of this alloy in 0.1 mol dm^{-3} NaOH with the presence and absence of chloride ions using electrochemical methods, particularly potentiostatic measurements.

Mechanism of anodic oxidation of Cu an Ag in alkaline solution has been described in our previous works [2-5]. In presence of chloride ions the following reactions may take place on copper:
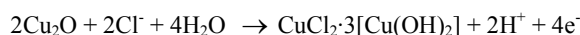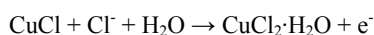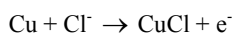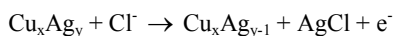
$$Cu + Cl^- = CuCl + e^-$$

$$CuCl + Cl^- = CuCl_2^-$$
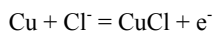
In alkaline medium formation of Cu_2O is favoured in comparison to the formation of CuCl layer [6,7]. The same is concluded from E-pH diagram for Cu-Cl- H_2O system presented by Tromans and Sun [8], so electrochemical behaviour of copper in a solution containing chloride ions is seen as a competition between the formation of Cu_2O film which leads to passivity, and nucleation and growth of CuCl layer resulting with pitting. Kunze et al. [9] concluded that the effect of chlorides on the initial stages of anodic oxidation of Cu(111) in alkaline solutions depends mainly on the $[Cl^-]/[OH^-]$ ratio, i.e. on chloride concentration when concentration of hydroxyl ions is constant.

Oxidation of silver in solution containing chlorides leads to formation of AgCl [10,11]:

$$Ag + Cl^- \rightarrow AgCl + e^-$$
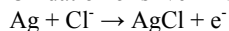
The formation of the monolayer AgCl follows an adsorption of Cl^- ions [10,12,13]; afterwards there is three-dimensional growth of AgCl which leads to formation of compact layer.

Hazzazi et al. [14] investigated AgCu alloy in borate buffer solution and concluded that addition of Cl^- ions results with formation of $CuCl_2 \cdot H_2O$ and AgCl on electrode surface. Zaky [15] investigated CuAg alloy (Ag 80 mass. % + Cu 20 mass. % and Ag 20 mass. % + Cu 80 mass. %) using cyclic voltammetry method in carbonate solution and concluded that increase of Cl^- ion concentration in solution results with formation of $CuCl_2 \cdot H_2O$, $CuCl_2 \cdot 3[Cu(OH)_2]$ and AgCl alloys on the surface due to following reactions:

$$Cu_xAg_y + Cl^- \rightarrow Cu_xAg_{y-1} + AgCl + e^-$$

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

$$CuCl + Cl^- + H_2O \rightarrow CuCl_2 \cdot H_2O + e^-$$

$$2Cu_2O + 2Cl^- + 4H_2O \rightarrow CuCl_2 \cdot 3[Cu(OH)_2] + 2H^+ + 4e^-$$

2. RESULTS

Cyclic voltammogram presented in Figure 1 indicates potentials at what current peaks appear, i.e. potentials at what electrochemical reactions occur in investigated system. The voltammogram is recorded in 0.1 mol/dm^3 NaOH + 0.05 mol/dm^3 NaCl at scan rate of 20 mV/s.

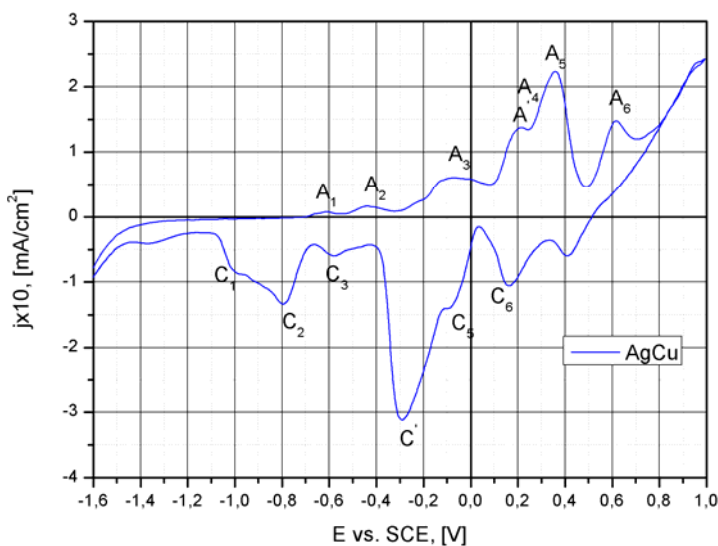*Figure 1. Cyclic voltammogram for the AgCu (50 mass.% Ag) alloy in 0.1 mol dm^{-3} NaOH + 0.05 mol/dm^3 NaCl at scan rate of 20 mV/s*

Potentiostatic measurements were conducted on all potentials of anodic current peaks (A_1, A_2, A_3, A_4, A_5, A' and A_6) during 100s. In the paper only potentiostatic curves obtained for alloy in 0.1 mol dm^{-3} NaOH with different concentrations of NaCl at 620 mV vs. SCE, which is attributed to the peak A_6, are presented (Figure 2). It is obvious that with time current density is decreasing monotonously until it reaches stationary state.
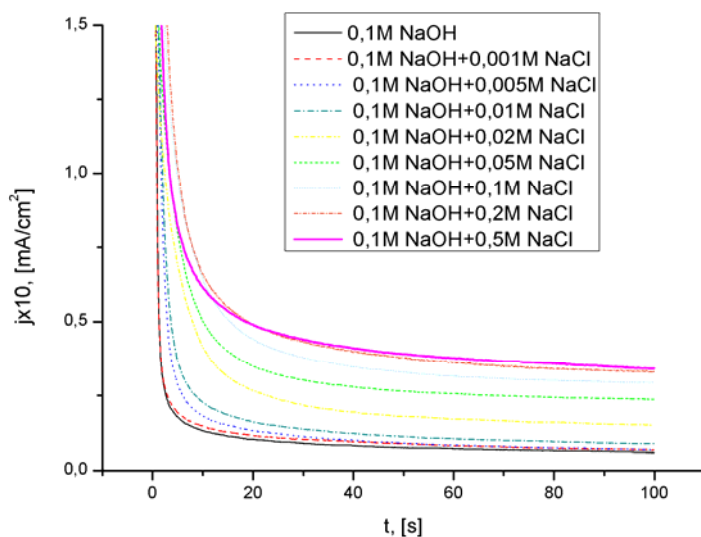
Figure 2. Potentiostatic curves of the AgCu (50 mass.% Ag) alloy in 0.1 mol dm^{-3} NaOH at E = 620 mV vs. SCE and different concentrations of chloride ions

According to data obtained from Fig. 2, Figure 3 represents current density reached after 100s in dependence on the NaCl concentration in log j = f (log C_{Cl^-}) coordinate system. There are three clearly distinct regions observed. In first region where Cl$^-$ ion concentration is up to 0.005 mol dm^{-3}, presence of these ions has no significant influence on oxidation process of the investigated alloy. In second region where concentration is from 0.01 mol dm^{-3} to 0.1 mol dm^{-3}, chloride ions have obvious activation effect, while increase of current density is almost linear in log j = f (log C_{Cl^-}) system. In that area more intensive formation of chlorides of both present metals occurs.
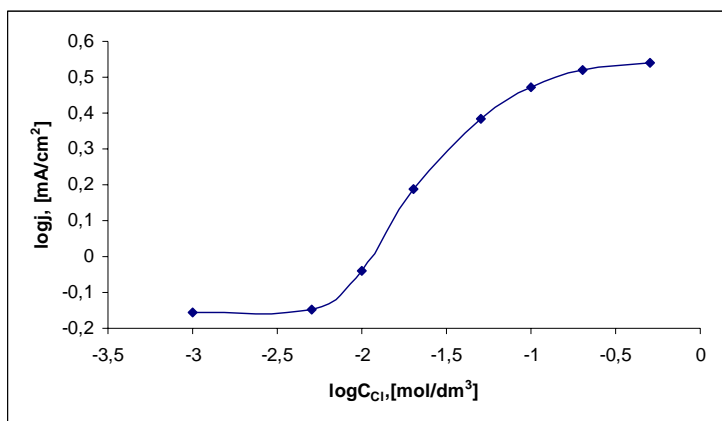

Figure 3. The dependence of stationary current density (after 100 s) on concentration of chloride ions

With Cl$^-$ ion concentration higher than 0.1 mol dm^{-3} curve gradually becomes saturated, i.e. chloride concentration increase does not lead to suitable chloride formation rate. It could be assumed that at that point all active sites on alloy surface were occupied by adsorbed ions, followed by reaction product, and that further increase of Cl$^-$ ion concentration in solution can not reflect on the number of adsorbed particles nor on quantity of formed product in the unit of time.

3. CONCLUSION

Based on potentiostatic measurements, there are three areas observed on dependency curve log j = f(log C_{Cl^-}). In the first area (with Cl^- ion concentration up to 0.005 mol dm^{-3}) chloride ions do not have significant influence on the process of corrosion. In the second area, with Cl^- ion concentration from 0.01 mol dm^{-3} to 0.1 mol dm^{-3}, chloride ions have activation effect which leads to the formation of silver and copper chloride on alloy surface. In the third area, with Cl^- ion concentration higher than 0.1 mol dm^{-3}, increase of chloride concentration does not lead to the suitable increase in the chloride formation rate, i.e. curve enters the saturation.

4. ACKNOWLEDGMENT

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