Electrochemical Behavior of Cu-Ag Alloys in Perchlorate Solutions Using Cyclic Voltammetric and Current Transients Techniques

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Abstract The electrochemical behavior of Cu-Ag system was studied in 0.5 M NaOH and sodium perchlorate by means of cyclic voltammetry, potentiodynamic anodic polarization and current/ time transients techniques. SEM and EDX microanalysis were used to examine the changes caused by the electrochemical perturbations. In perchlorate free alkali solution the anodic portion of the voltammogram was characterized by the existence of two potential regions I and II. In the first potential region copper dissolves preferentially and exhibits three anodic peaks A_1 , A_2 and A_3 . The anodic peak A_1 was related to the formation of Cu_2O while the anodic peaks A_2 and A_3 are related to the oxidation of Cu and Cu_2O , respectively to CuO and $Cu(OH)_2$. The preferential dissolution of copper was enhanced and the simultaneous dissolution of silver was retarded on increasing the silver content in the alloy. The potential region II was characterized by the appearance of three anodic peaks A_4 , A_5 and A_6 which are related to the formation of mono-layer, and multi-layers of Ag_2O , AgO and Ag_2O_3 , respectively. The addition of increasing amounts of ClO_4^- increases the heights of the anodic peaks and above a limiting value breakdown the anodic passivity and initiate pitting corrosion. The pitting potential decreases linearly with ClO_4^- concentration but increases with increasing scan rate. The potentiostatic current time transients show that the pitting corrosion can be described in terms of an instantaneous three dimensional grows under diffusion control. X-ray diffraction analysis was used to determine the composition of the corrosion products on the electrode surface. Scanning electron microscope was used to monitor pitting corrosion and to elucidate the effect of constituents on the alloy dissolution.

Keywords Cu-Ag alloys, perchlorate, pitting corrosion, cyclic voltammetry, Current-time transients, SEM and x-ray diffraction.

Coatings containing Cu-Ag alloys are highly used in low power circuits used in electronics due to their higher electrical and thermal conductivity compared to those of pure copper or pure silver [1]. Alloying with copper conserves silver and reduces costs [1]. There have been a few studies reported on the dissolution behaviour of metals from copper-silver alloys. The dissolution of silver, copper and silver-copper alloys was studied in acid and cyanide solutions using oxygen or ferric ion as an oxidant [2], in sulphuric acid [3] or in aerated ammoniacal solution [4, 5]. The electrochemical behaviour of Cu-Ag system was studied using different electrochemical techniques such as cyclic voltammetry, potentiodynamic anodic polarization and current time transients in Na_2CO_3 [6], in Na_2CO_3 containing Cl^- ion [7], in NaOH [8] and in NaOH containing sulphide ions [9]. The electrochemical behaviour of these alloys depends on the composition of both, Cu-Ag alloys and the electrolytic solution. In solutions free from additives galvanic coupling played an important role in enhancing the dissolution of the less noble component, copper, and retarded the more noble component, Silver. The addition of chloride [7] or sulphide ions [9] to the electrolytic solution had pronounced effect on alerting the electrochemical behaviour of this system. In this work the susceptibility and mechanism of the Cu-Ag system for pitting corrosion was studied in solutions containing perchlorate ions.

2. Experimental

The working electrodes consisted of Pure Cu and Ag (supplied by Merck 99.99%), and three Cu-Ag alloys, Table 1. The three alloys were prepared by fusion of pure Cu and Ag constituents in a graphite crucible as recommended [6-9]. The constitution of the two alloys was maintained using x-ray fluorescence analysis. All the working electrodes used were rods of an exposed area of 0.5 cm^2 embedded in Teflon so that only the cross sectional area was in contact with the solution. Before each experiment, all the working electrodes

1. Introduction

were polished on emery paper down to grade 1000, and then washed, rinsed with double distilled water and ethanol and dried. A conventional electrochemical cell of 50 ml capacity was used in the present work. It contained three separate compartments of which two were used for fitting the working and the counter electrodes, respectively. The third compartment was used for fitting the reference electrode, which was a Ag/AgCl. The counter electrode was a graphite rod of large surface area (10 cm^2). The solutions used were prepared from AnalaR grade chemicals and used without further purification. All experiments were performed using freshly prepared solutions and freshly polished electrodes. The electrochemical experiments were conducted using an ACM Galvanostat/Potentiostat PC computer. Surface morphology of the alloy I polarized to 600 mV was obtained using scanning electron microscopy (SEM), model JSM-5500LV operated at 10 keV. The composition of the corrosion products formed during anodic polarization over the electrode surface was examined by means of x-ray diffraction analysis using Philips P. W. Model 1730 diffractometer adopted at 40 kV and 25 mA with Cu- α radiation and a Ni filter.

3. Results and Discussions

3.1. Potentiodynamic Anodic Polarization Measurements

Figure 1. Potentiodynamic anodic polarization of alloy I in 0.5 M NaOH containing different concentrations of NaClO_4 at 25°C and scan rate 50 mV s^{-1} ; (1) 0.0 M, (2) 0.2 M, (3) 0.4 M, (4) 0.006 M, (5) 0.5 M, (6) 0.6 M and (7) 0.7 M.

Figures 1 and 2 illustrate the anodic portion of the voltammograms, (E/i) curves, recorded for the alloys I and III, respectively in 0.5 M NaOH solution in the absence (curve 1) and presence of increasing concentrations. The curves were swept from -1000 mV to 1000 mV (Ag/AgCl) with sweep rate 50 mV s^{-1} . Similar results were recorded for alloy II (not presented). The voltammograms of the alloys I and III, Curve 1, exhibit a complex shape characterized by the contribution of the six anodic peaks prior to oxygen evolution reaction. The first three anodic peaks in the voltammogram are virtually the same as those found in the literature [10-25]. Accordingly, the anodic current peak A_1 was attributed to the electroformation of a Cu_2O layer whereas the anodic peaks A_2 and A_3 are ascribed to the formation of a complex hydrous CuO film resulting in a duplex structure of a passive film. Such a structure represented by an outer CuO/Cu(OH)_2 layer overlaying a barrier Cu_2O .

Table 1. Composition of the materials used

No.	Electrode	Composition wt%	
		Copper	Silver
1	Alloy I	20.0	80.0
2	Alloy II	50.0	50.0
2	Alloy III	80.0	20.0

Figure 2. Potentiodynamic anodic polarization of alloy III in 0.5 M NaOH containing different concentrations of NaClO₄ at 25°C and scan rate 50 mV s⁻¹; (1) 0.0 M, (2) 0.2 M, (3) 0.4 M, (4) 0.006 M, (5) 0.5 M, (6) 0.6 M and (7) 0.7 M.

The second three anodic peaks (A₄, A₅ and A₆) in the voltammogram are virtually the same as those found in the literature [26-29]. The anodic peak (A₄), located at about 175 mV (Ag/AgCl), can be assigned to the anodic oxidation of Ag to [Ag(OH)₂]⁻ by adsorption of OH⁻ and desorption of the products

When the concentration of the complex exceeds the solubility product of Ag₂O, precipitation of the monolayer occurs at the electrode surface. The anodic peak A₅ located at 350 mV, is related to the direct formation and thickening of Ag₂O multilayer

When the thickness of Ag₂O layer reached a certain value the current density drops to small value, indicating the onset of primary passivity. The anodic peak A₆ may ascribed to the conversion of Ag₂O to AgO.

The effect of addition of increasing amounts of NaClO₄ (0.1 to 0.7 M) on the anodic voltammogram of the alloys I and III are shown with curves 2-6 in Figs. 1 and 2, respectively. It seems that the voltammograms depends on ClO₄⁻ concentration. The addition of ClO₄⁻ increases the heights of the six anodic peaks A₁, A₂, A₃, A₄, and A₅ and shifts their peak potentials to less positive values. The

relation between the peak current density of the anodic peaks A₅ (i_p, A₅) and the logarithm of the ClO₄⁻ is given in the Fig. 3. It seems that ClO₄⁻ participates in the elementary act of the anodic dissolution of Cu-Ag alloys. The acceleration influence of ClO₄⁻ in the preferred dissolution potential region of copper (peaks A₁, A₂ and A₃) may ascribe to the formation of soluble ionic Cu species [30]. The influence of ClO₄⁻ on the anodic peak A₅ can be related to the formation of soluble AgClO₄ [31-34]. Therefore, in terms of adsorption model, it can be concluded that both of OH⁻ and ClO₄⁻ are likely adsorbed on the alloy surface [30-34] forming a potentially active dissolution sites. However, the addition of low concentration of ClO₄⁻ (<0.4 M) in 0.5 M NaOH breaks down the passive layer and initiate pitting corrosion at certain pitting potential E_{pit} more negative than the oxygen evolution potential. However, on increasing the concentration of ClO₄⁻ above 0.4 M the value of E_{pit} as well as the peak potential of the anodic peaks was displaced towards less positive values. A plot of E_{pit} vs. the logarithm of ClO₄⁻ is given in Fig. 4 for the three alloys. The SEM images of the three alloys in 0.5 M NaOH containing 0.4 M ClO₄⁻ polarized up to 700 mV confirmed the existence of pits, Fig 5. It is observed the that increasing the silver content in the alloy decreased the intensity of pitting. The x-ray diffraction analysis of alloy I polarized to 700 mV in 0.5 M NaOH containing 0.4 M ClO₄⁻ confirmed the formation of Ag₂O, AgO and Ag₂O₃, Fig. 6.

Figure 3. Relation between $\log i_p$ of the anodic peak and $\log c_{\text{NaClO}_4}$ for the anodic peak A_5 : (1) alloy I, (2) alloy II and (3) alloy III.

Figure 4. Relation between E_{pit} of the anodic peaks and $\log c_{\text{NaClO}_4}$ for : (1) alloy I, (2) alloy II and (3) alloy III.

Figure 5. SEM micrographs of alloys surfaces in 0.5 M NaOH containing 0.4 M NaClO₄ anodically polarized to 700 mV (x4000): (1) alloy I, (2) alloy II and (3) alloy III.

Figure 6. X-ray diffraction pattern of alloy I surface after anodic polarization to 700 mV in 0.5 M NaOH that contains 0.4 M NaClO₄.

Figure 7. Cyclic voltammograms of alloy I in 0.5 M NaOH containing 0.4 M NaClO₄ at 25°C and different scan rate; (1) 25 mV s⁻¹, (2) 50 mV s⁻¹, (3) 75 mV s⁻¹, (4) 100 mV s⁻¹ and (5) 125 mV s⁻¹.

Figure 7 illustrates the influence of the scan rate on the anodic behavior of Alloy I in 0.5 M NaOH containing 0.4 M NaClO₄. Under the prevailing conditions, the increase in the scan rate (v) results in a marked increase of the height of the anodic peaks A₁ and A₂ and the current densities in the primary passive region. When v is high, an initiation of passivity breakdown can be noticed only at more positive potentials, corresponding to a sufficiently short pit incubation time [35]. The incubation time for initiation of passivity breakdown, i.e. for a first pit nucleation, is caused by the time required for ClO₄⁻ penetration into the passive layer.

3.2. Current / Time Transient Measurements

In order to get more information about the breakdown of

the passivation by ClO₄⁻ ions, potentiostatic current/time transients at constant step potentials $E_{s,a}$ were recorded for Alloys I, II and III. Figure 8, 9 and 10 shows the effect of the anodic step potential $E_{s,a}$ on the transients at a given concentration of ClO₄⁻ (0.4 M) in 0.5 M NaOH, whereas Fig. 11 demonstrates the effect of ClO₄⁻ concentration on the transients for alloy III at a given $E_{s,a}$ 600 mV. The data of Figs. 8, 9 and 10 infer that for $E_{s,a} < E_{pit}$ the current density decreases monotonically to a steady state value. If the contribution of the double layer charging process is neglected, the overall transient current density (i) can be assigned to two main processes: the passive layer growth (i_{gr}) and silver electrodisolution through the passive layer (i_{dis}):

$$i = i_{gr} + i_{dis} \quad (4)$$

Figure 8. Current transients vs. time recorded for alloy III in 0.5 M NaOH containing 0.4 M NaClO₄ at 25°C at constant anodic step potentials, $E_{s,a}$: (1) 300 mV, (2) 400 mV, (3) 500 mV, (4) 600 mV, (5) 700 mV, (6) 800 mV, (7) 900 mV and (8) 950 mV.

Figure 9. Current transients vs. time recorded for alloy II in 0.5 M NaOH containing 0.4 M NaClO₄ at 25°C at constant anodic step potentials, $E_{s,a}$: (1) 300 mV, (2) 400 mV, (3) 500 mV, (4) 600 mV, (5) 700 mV, (6) 800 mV, (7) 850 mV and (8) 900 mV.

Figure 10. Current transients vs. time recorded for alloy I in 0.5 M NaOH containing 0.4 M NaClO₄ at 25°C at constant anodic step potentials, $E_{s,a}$: (1) 200 mV, (2) 300 mV, (3) 400 mV, (4) 500 mV, (5) 600 mV, (6) 700 mV and (7) 800 mV.

Figure 11. Current transients vs. time recorded for alloy I in 0.5 M NaOH containing different concentrations of NaClO₄ at 25°C at 640 mV: (1) 0.4 M, (2) 0.45 M, (3) 0.5 M, (4) 0.55 M, (5) 0.6 M, (6) 0.65 M, (7) 0.7 M and (8) 0.75 M.

The growth of the passive layer can be regarded as the formation of a new solid phase (Ag₂O) on the metal surface. The silver electrodisolution through the passive layer can be explained in terms of Ag⁺ diffusion from the metal/film interface to the film/solution interface [36]. These two processes can occur independently on the entire electrode surface. For $E_{s,a} > E_{pit}$ the transition current density initially decreases to a minimum value at time t_i (incubation time), i.e. when the ClO₄⁻ ions penetrate the passive layer and reach the metal surface, pits start to grow, and the current rises steeply. In this case the overall transient current density is given by three contributions:

$$i = i_{gr} + i_{dis} + i_{pit} \quad (5)$$

i_{pit} is related to the pit growth current density, i.e. the rate of pitting corrosion, and follows a relationship with the square root of time as shown in Figs. 12, 13 and 14

Figure 12. Dependence of i_{pit} on $t^{1/2}$ for alloy II in 0.5 M NaOH containing 0.4 M NaClO₄ at different step potentials $E_{s,a}$: (1) 800 mV, (2) 900 mV and (3) 950 mV.

Figure 13. Dependence of i_{pit} on $t^{1/2}$ for alloy II i in 0.5 M NaOH containing 0.4 M NaClO₄ at different step potentials $E_{s,a}$: (1) 700 mV, (2) 800 mV, (3) 850 mV and (4) 900 mV.

Figure 14. Dependence of i_{pit} on $t^{1/2}$ for alloy I i in 0.5 M NaOH containing 0.4 M NaClO₄ at different step potentials $E_{s,a}$: (1) 600 mV, (2) 700 mV and (3) 800 mV.

These results agree well with Hills model [36] which can be described by the equation.

$$i_{\text{pit}} = 23/2 \cdot P \cdot t^{1/2} \quad (6)$$

where $P = zF\pi N^0 D^{3/2} C^{3/2} M^{1/2} \rho^{1/2}$, N^0 is the number of sites available for pitting corrosion, D , C , M , and ρ are the diffusion coefficient, the concentration, the molecular weight, and the density of the dissolved materials, and the other terms have their usual meaning. The current relationship with $t^{1/2}$ suggests that the pit growth is an instantaneous three-dimensional nucleation followed by growth controlled by diffusion. The dependence of the pitting growth current on the potential value indicates that there is a distribution of nucleation sites of different

energies which nucleate at distinct potential [35]; in other words, the more positive the applied potential, the more activated sites will be present.

From the data of Figs. 8, 9 and 10 it can be concluded that an incubation time is necessary before the pit nucleation and growth process to occur. The incubation time decreases with increasing potential step $E_{s,a}$. This observation can be confirmed by plotting the rate of ClO₄⁻ penetration defined as $(1/t_i)$ vs. $E_{s,a}$ [36]. The result is given in Fig. 15 where a straight line relationship is observed, indicating that the rate of penetration increases steadily with E_s . In addition, the data of Fig. 15 show that the rate of penetration increases (and, consequently, the incubation time decreases) with increasing ClO₄⁻ concentration at a given $E_{s,a}$.

Figure 15. Dependence of $1/t_i$ on $E_{s,a}$ in 0.5 M NaOH containing 0.4 M NaClO₄ for (1) alloy III, (2) alloy II and (3) alloy I.

4. Conclusions

1. The pitting corrosion susceptibility of three Cu-Ag alloys in 0.5 M NaOH solutions free from and containing various concentrations of perchlorate ions was examined using potentiodynamic polarization, cyclic voltammetry and chronoamperometric techniques.

2. In perchlorate-free sulphate solution for all samples, the potentiodynamic anodic polarization curves exhibit a well-defined anodic peaks A₁, A₂ and A₃, A₄, A₅ and A₆, corresponding to the formation of Cu₂O, CuO, Cu(OH)₂, Ag₂O, AgO and Ag₂O₃, passive films, respectively.

3. The addition of perchlorate ions to the NaOH solution tends to stimulate metal dissolution and induce pitting attack at the pitting potential, E_{pit} , for the three alloys.

4. In presence of ClO₄⁻ ions, SEM examinations confirmed the existence of pits on the electrode surface and the density of pits decreases with increasing %Cu in the alloys.

5. The pitting corrosion of all samples increases with increasing ClO₄⁻ concentration, while it decreases with increasing Cu content in the sample.

6. Chronoamperometric studies revealed that an incubation time, t_i , is necessary before pit nucleation and growth to occur.

7. The dependence of anodic current densities on potential scan rate shows that the dissolution of the alloy is controlled by mass transfer in the solution.

8. The perchlorate pitting corrosion resistance of the three samples decreases in the order: alloy I > alloy II > alloy III.

9. The pit growth of the three alloys can be described in terms of an instantaneous three-dimensional growth under diffusion control.

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