Universal Journal of Chemistry 1(1): 1-6, 2013
DOI: 10.13189/ujc.2013.010101 http://www.hrpub.org

Electrochemical Dissolution and Passivation of Cu-Ni Alloys in Sodium Sulphate Aqueous Solution

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Abstract The electrochemical behaviour of two copper-nickel alloys is studied in 0.1 M Na_2SO_4 using cyclic voltammetry, potentiodynamic and current time transient techniques. The microstructure of the compounds formed during anodic sweep is characterized using x-ray diffraction analysis. The forward sweep is characterized by the existence of two well-defined potential regions; the selective dissolution and the simultaneous dissolution potential regions. The first potential region consisted in two anodic peaks A_1 and A_2 corresponding to the formation of $Ni(OH)_2$ and NiO, and Cu_2O, respectively. The second potential region consisted in two anodic peaks A_3 and A_4 corresponding to the formation of CuO and Ni_2O_3, respectively. It is found that the Cu-Ni system in sulphate solution follows the dissolution-redeposition mechanism of the dissolution of metals from the alloys. The X-ray diffraction analysis confirmed the existence Ni_2O_3 and CuO on the electrode surface of nickel rich alloy polarized to potential more noble than the potential of A_4 and the existence of Cu_2O and NiO on the surface of copper-rich alloy polarized to a potential in the A_2 region. Atomic Force microscope images show surface enlargement beyond the critical potential E_{crit}.

Keywords Copper-nickel, sulphate, cyclic voltyammetry, potentiodynamic, current transient, SEM

1. Introduction

The copper–nickel system is an isomorphous one in which only a single type of crystal structure is observed for all ratios of the components [1].Many studies have been conducted of the dealloying of copper-based alloys. The electrochemical behavior of Cu–Ni alloys has been studied by numerous authors in alkaline solutions [2-7].It was established that the passivity of arrange of Cu–Ni alloys in 0·1MKOH solution was due to oxide film growth by migration under a high electric field. The rate-controlling parameters were a function of the copper content of the alloy, but largely followed the kinetics of film growth of pure nickel. Analysis by Auger electron spectroscopy of the formed anodic films indicates that the oxide film is predominantly nickel oxide even when the Cu content in the alloy is 70%, suggesting that Cu in the alloy does not affect the film growth process to any significant extent.

The passive layer formed potentio-statically in 1·0 M NaOH on Cu–50 wt-%Ni has also been investigated, using X-ray photoelectron spectroscopy(XPS)and ion scattering spectroscopy(ISS) [6].The thickness and the composition of the sublayers of the passive film, as well as the composition of the underlying metal surface, were found to depend on electrochemical parameters such as potential and time of passivation.

Copper-nickel alloy [1] is an amorphous system where copper and nickel forms one single phase all over the range of composition. Two mechanisms of dissolution are generally proposed for the dissolution of metals from isomorphous alloys: simultaneous dissolution of both components of the alloy followed by redeposition of one component on the surface and selective dissolution of one element from the crystal lattice. Three mechanisms are proposed for the dissolution of metals from alloys below their critical potential Ecrit. For a binary alloy AB, below its critical potential, removal of the less noble component B occurs where the more noble component A is present as a layer that covers the alloy surface, which is then ceased any further removal of the less noble component and the current decays to a very low value and is termed the passivation current denisity ipass. As soon as the critical potential of the alloy is reached, the surface losses its planarity and the current rises sharply to a very high value where both components dissolve simultaneously. The ionization - redepositoin mechanism assumes an initial simultaneous ionization of both components A and B. This step may involve intermediate formation of ad-atoms of the less noble component, B. Alternatively; direct transfer of B ions from kink sites to the electrolyte solution must be considered [9, 10]. Irrespective of these details of the initial charge transfer step, the electropositive component A is thought to redeposit on the alloy surface in a consecutive step. It is assumed that an ions may be dissolved from the alloy at underpotentials that are cathodic with respect to the reversible potential EA'

that agglomerates on the electrode surface. They have, therefore, the character of an unstable intermediate species and will be plated out on the surface of A' crystals at the same electrode potential.

The volume diffusion mechanism, which was introduced by Pickering and Wagner [11], does not consider an "under potential dissolution" of the electropositive component. Instead, the atoms of the latter are assumed to accumulate as mobile ad-atoms on the electrode surface. It may be expected, therefore, that these ad-atoms will have an increasing tendency to move back to the kink sites and steps and to block any further removal of the less noble component from these positions by the usual mechanism of the metal dissolution. Provided that the anodic over potential is high enough, there is, however, an alternative possibility that the preferential dissolution will proceed from terrace sites (which may be in the vicinity of the kink sites [12]. This process results in the formation of surface vacancies. The major concept of the volume diffusion mechanism is that by the injection of these surface vacancies into the bulk of the alloy, a large vacancy super saturation is developed adjacent to the alloy /electrolyte interface which enhances the diffusivity beyond its thermal value. Repopulating of the electrode surface with Cu atoms via volume diffusion is therefore considered to be possible even at room temperature.

The surface diffusion mechanism considers the nucleation and growth of the crystals of the pure, or almost pure, noble component via a surface diffusion process. Following earlier suggestions by Gerischer [13], this mechanism may be described in detail by a model which, for a binary AB, includes:

1. Removal of both components from steps kink sites and formation of ad-atoms of the more noble component A at electrode potentials $E < E_C$. The ad-atoms may subsequently (a) crystallize via surface diffusion or (b) accumulate at the steps and kink positions, where they are thought to block the removal of the less noble species. However, in contrast to the assumptions that were made with the volume diffusion process, a small but finite steady-state dissolution rate of B atoms is now considered to be possible by exchange of places between A and B atoms.

2. Removal of B atoms from terrace sites in order to account for the increased dissolution rate at $E > E_C$. Since the remaining an atom is expected to form a porous layer of small individual crystallites, this process is thought to operate without transport of B atoms to the electrode surface via volume diffusion.

This present work has used two alloys of different compositions, one being copper rich and the other nickel rich, to elucidate the mechanism of dissolution and the composition of the passive films formed in the Cu–Ni system in $0{\cdot}1M Na_2SO_4$ solution. The voltammetric profiles of pure copper and pure nickel were included for comparison. The microstructure and composition of the passive film formed during the anodic sweep was characterized by X-ray diffraction analysis. Atomic force microscopy(AFM) was used to examine the alloy surface for surface enlargement associated with the electric field beyond the critical potential E_{crit}.

Table 1. Composition of the studied alloys

No.	Name	Composition %	
		Cu	Ni
1	Alloy I	80	20
2	Alloy II	20	80

2. Experimental

Pure copper and nickel (supplied by Merck 99.99%) and two copper-nickel alloys of the composition Cu-20 wt% Ni and Cu-80 wt% Ni were used in studying the voltammetric behaviour copper-nickel alloys in aerated Na_2SO_4 solution. The alloys were made by fusion of pure two metals in a graphite crucible at a desired temperature, air cooled and scraped into the desired thickness area. The electrodes were then mounted in a Teflon mount so as only their cross sectional areas were exposed to solution. Before each experiment, the electrodes were mechanically polished starting with fine grained emery papers and followed with alumina paste to obtain a mirror-like electrode surface, then rinsed with acetone and doubly distilled water. Measurements were performed in Na_2SO_4 solutions prepared from Analar grade chemicals and used without further purification. A conventional electrochemical cell of 100 cm capacity was used for the present work. It was contained three separated compartments two of them were used for fitting both the working and the platinum counter electrodes. The third compartment was used for fitting the reference electrode, which is saturated calomel electrode (SCE).

Cyclic voltammetric, potentiodynamic anodic polarization and potentiostatic current/time measurements were carried out with the help of an EG&G potentiostate\Galvanostate Model 237A controlled by a PC computer using 352 corrosion software.

Morphology of the alloy surface in the potential range beyond the critical potential E_{crit} was maintained by scanning electron micrographs SEM), model XL-200 Philips operated at 15 k eV. The composition of the corrosion products formed during anodic polarization over the alloys surfaces was studied using x-ray diffraction analysis using Philips P. W. Model 1730 diffractometer adopted at 40 kV and 25 mA with Cu-k_α radiation and a Ni filter.

3. Results and Discussion

The electrochemical behaviour of the alloys I and II was studied in 0.1 M Na_2SO_4 between E_c = -1600 mV up to E_a = 200 mV and 1000 mV, respectively with sweep rate of 50 mV s^{-1} and the data is represented graphically in Figure 1. The curves of pure copper and pure nickel were introduced

for comparison. The electrochemical behaviour of pure copper, Fig. 1 (curve 1), studied between E_c = -1600 mV and E_a = 200 mV and was characterized by the appearance of two anodic peaks A_2 and A_3, and two cathodic peaks C_2 and C_3. The anodic peaks A_2 and A_3 are related to the formation of Cu_2O and CuO, respectively [14].

$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-$ E= -0.19 V (SCE) A_2 [1]

$Cu_2O + H_2O \rightarrow 2CuO + 2H^+ + 2e^-$ E = -0.01 V (SCE) A_3[2]

At the same time, the existence of the cathodic peaks C_2 and C_3 was ascribed to the reduction of Cu_2O to Cu and CuO to Cu_2O, respectively.

Figure 1, curve 2, represents the cyclic voltammetric behaviour of pure nickel [14] studied between E_c = -1600 mV and E_a = 1000 mV. Two anodic peaks, A_1 and A_4, appear on sweeping the potential in the anodic direction. These peaks are related to the formation of NiO and Ni_2O_3, respectively.

$Ni + H_2O \rightarrow NiO + 2H^+ + 2e^-$ E = -0.515 V (SCE) A_1[3]

On sweeping the potential in the cathodic direction only one cathodic peak C_4 appears due to the reduction of Ni_2O_3 to NiO. The cathodic C_1, which is mainly ascribed to the reduction of NiO to Ni, does not appear due to the transformation (on switching the potential at E_a of more noble values) of NiO to species, which are reduced at more negative potential [15].

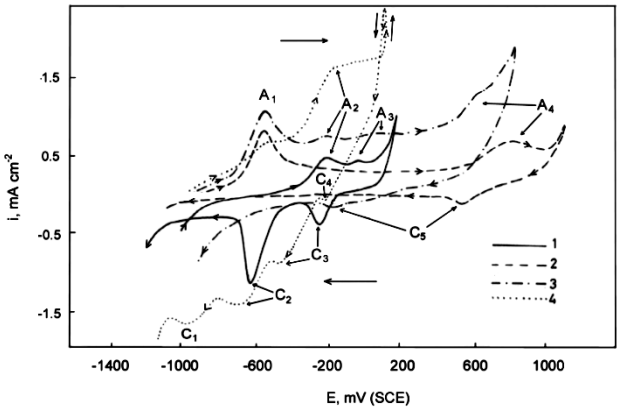

Figure 1. Cyclic voltammograms of (1) copper, (2) nickel, (3) alloy I, and (4) alloy II in 0.1 M Na_2SO_4 at 25°C and scan rate 50 mV s^{-1}

Figure 1, curves 3 and 4 represent the cyclic voltammetric behaviour of the alloys I and II, respectively. The cyclic voltammograms were characterized by the existence of well-defined potential regions (separated by a certain critical potential E_{crit}); the subcritical or selective dissolution potential region and the simultaneous dissolution potential region. The zero current potential of the two alloys are situated at potentials more negative than those of pure copper and pure nickel.

3.1. The Subcritical Potential Region

It seems that the dissolution of the alloys in this region follow the dissolution – redeposition mechanism where both copper and nickel dissolves initially followed by the redeposition of the more noble component, copper. This region was characterized by the appearance of the anodic peaks A_1 and A_2. The anodic peak A_1 represent the situation where both of copper and nickel dissolves followed by copper redeposition on the alloy surface and the oxidation of nickel to NiO and/ or $Ni(OH)_2$. It is seems that, taking into consideration the molar ratio of nickel in the alloy, the peak current density i_p of the peak A_1 was increased on alloying nickel with copper. These results indicate the enhancement of the selective dissolution of nickel from the alloy with increasing the copper content. These results indicate that the dissolution of copper with nickel initially assists the diffusion of the nickel from the bulk of the alloy towards its surface and hence increases the peak current density of the anodic peak A_1.By thermodynamic reasoning, it can be shown that this process is impossible unless, in accordance with the principles of irreversible thermodynamics, a coupling between the anodic partial reactions occurs, which may reflect an average activity of adsorbed ad-atoms of the electropositive component Cuthat exceeds unity [13]. If this situation prevails, Cu^+ ions may be dissolved from the alloy at underpotentials that are cathodic with respect to the reversible potential E_{Cu}' that agglomerates on the electrode surface. They have, therefore, the character of an unstable intermediate species and will be plated out on the surface of Cu crystals at the same electrode potential, which leads to the appearance of the anodic peak $A_2$and formation of CuO.

$Cu_x\text{-}Ni_y + H_2O \rightarrow Cu_{x-1}\text{-}Ni_{y-1}.Cu_{redep} + NiO + 2H^+ + 2e^-$ A_1 [5]

$2Cu_{x-1}\text{-}Ni_{y-1}.Cu_{redep} + H_2O \rightarrow 2Cu_{x-1}\text{-}Ni_{y-1} + Cu^+ + e^-$ A_2 [6]

3.2. Simultaneous Dissolution Potential Region

This region lies at potential nobler than the critical potential E_{crit} of the alloys, where simultaneous dissolution of both nickel and copper occur. The following observations can be made: (i) in alloy I (low nickel content) the surface losses its planarity and acquires the porous structure as shown by the hysteresis loop of the voltammogram on switching the potential in the cathodic direction and as seen from the SEMmicrograph in Fig. 2.The formation of surface porous structure was reported [16] for an active Ni dissolution in H_2SO_4 at potentials - 0.25 VAg/AgCl by a step-flow mechanism, followed by the rapid formation of large three-dimensional etch pits, leading to considerable surface roughening.(ii) in alloy II (high nickel content) this region was characterized by the appearance of three anodic peaks A_3 and A_4 corresponding to the formation of CuO and Ni_2O_3, respectively. Figure 3 represent x-ray diffraction analysis of the layer formed on the surface of alloy I polarized to -100 mV showed that this layer composes of NiO, $Ni(OH)_2$ and Cu_2O. The X-ray diffraction analysis of the layer formed on the surface of alloy II polarized to 1000 mV showed that this layer composes of Ni_2O_3 and CuO, Fig. 4

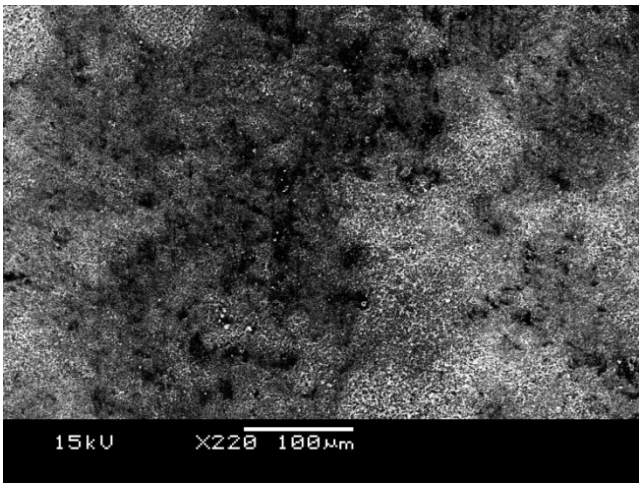

Figure 2. SEM micrograph of the alloy I surface after anodic polarization to 200 mV in0.1 M Na_2SO_4 at 25°C and scan rate 50 mV s^{-1}(x220)

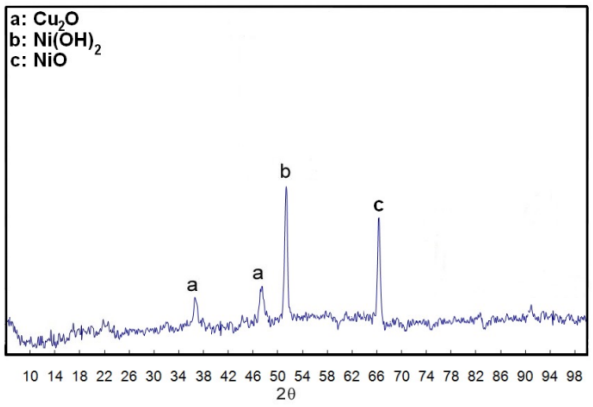

Figure 3. X-ray diffraction analyses of the surface of alloy I after anodic polarization to -100 mV in 0.1 M Na_2SO_4 at 25°C

The complementary relationship between the anodic and cathodic peaks was studied by sweeping the potential from E_c = -1600 mV and reversing it at different E_a values. Inspection of the data in the voltammogram of alloy I, Figs. 5 and 6 showed that on reversing E_a at value more noble than the potential of the anodic peak A_1 two cathodic peaks C_1 and C_2 appear as a result of reduction of $Ni(OH)_2$ and NiO to Ni respectively. Reversing E_a at value more noble than the potential of the anodic peak A_2 three cathodic peaks C_1, C_2 and C_3 appear. The cathodic peak C_3 is related to the reduction of Cu_2O to Cu. On reversing E_a at value more noble than the potential of the anodic peak A_3 four anodic peaks C_1, C_2, C_3 and C_4 appear. The cathodic peak C_4 represents the reduction of CuO to Cu_2O. On reversion the potential beyond the potential value of the anodic peak A_4an new cathodic peak, C_5, appears as a result of the reduction of Ni_2O_3 to Ni^{+2} compounds.

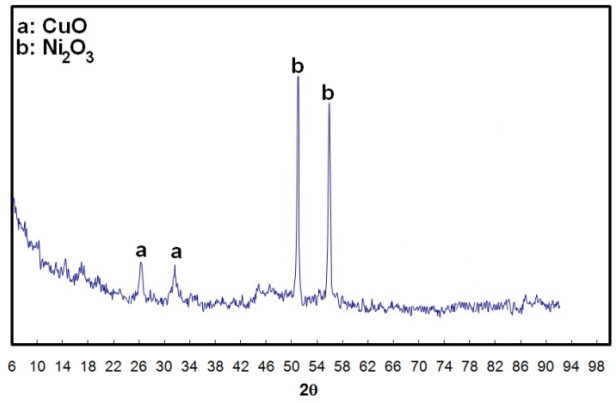

Figure 4. X-ray diffraction analyses of the surface of alloy II after anodic polarization to 700 mV in 0.1 M Na_2SO_4 at 25°C

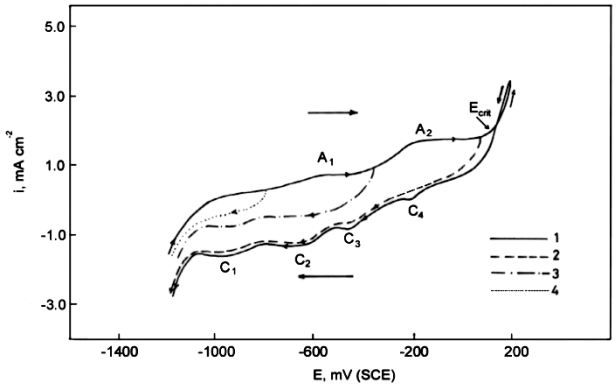

Figure 5. Cyclic voltammograms of alloy I in 0.1 M Na_2SO_4 at 25°C, scan rate 50 mV s^{-1} and various reversing anodic potentials: (1) -750 mV, (2) -400 mV, (3) 0.0 mV and (6) 200 mV

Figures. 7 and 8 show the influence of the sweep rate on the electrochemical behaviour of the alloys I and II, respectively. The general shapes of the volammograms remained unchanged with increasing the sweep rate. It seems that, incrasing the scan rate increases the peak current densities i_p of the anodic peaks and shifts their peak potentials E_p as well as the critical potential E_{crit} to more noble potentials. The voltammograms were used to analyze the dependence of peak current density i_p and peak potential E_p on the sweep rate. Figure 9 represents the linear dependence of the peak current density i_p of the anodic peaks on the root of the scan rate, where lines passing by origin was obtained for the anodic peaks A_2, A_3 and A_3 (alloy II) or slightly different than zero for the peaks A_1 and A_2 (alloy I) and A_1 (alloy II). The intercepts different than zero indicate that the induction rate is required before the electrode reactions become limited by diffusion. The linear dependence of the peak potential E_p of the anodic peaks A_1, A_2, A_3 and A_4 of alloy II and A_1 of alloy I vs. log vis given in Fig 10.

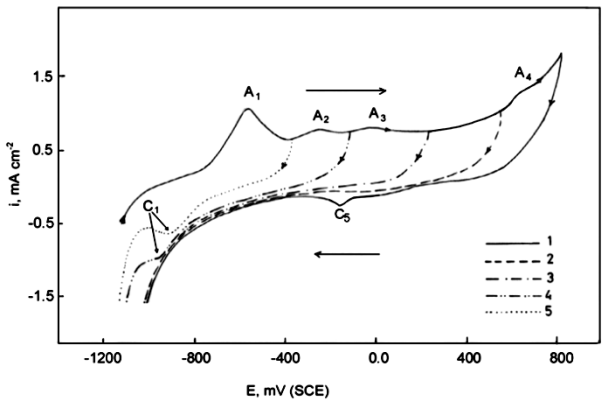

Figure 6. Cyclic voltammograms of alloy II in 0.1 M Na_2SO_4 at 25ºC, scan rate 50 mV s^{-1} and various reversing anodic potentials: (1) -400 mV, (2) -150 mV, (3) 200 mV , (4) 500 mV and (5) 800 mV

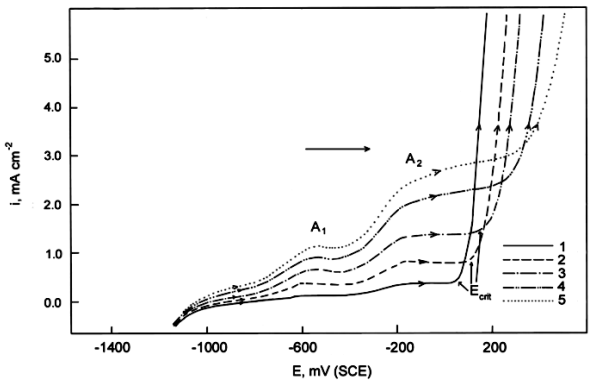

Figure 7. Potentiodynamic anodic polarization of alloy I in 0.1 M Na_2SO_4 at 25ºC and different scan rates: (1) 10 mV s^{-1}, (2) 25 mV s^{-1}, (3) 50 mV s^{-1}, (4) 75 mV $s^{-1}$and (5) 100 mV s^{-1}

In order to obtain more information about the electrochemical behaviour of copper-nickel alloys in Na_2SO_4 solution, potentiostatic current/time transients were carried out at different anodic step potentials, E_s. Figure 11 represents the current transients of alloy II in 0.1 M Na_2SO_4. It is seen that the current density decreases rapidly with time at first and then reaches a steady-state value. As the value of the potential is made more positive, both of the instantaneous and steady-state current values increase due to and increase in the thickness of the anodically formed layers. Plotting the current density vs. $t^{-1/2}$ for the descending part of the current transients gives straight lines passing by the origin, Fig. 12. When E_s at -500 mV, these is two slopes as one could be expect, owing to the formation of two different layers, NiO and $Ni(OH)_2$. If E_s is fixed at -200, 0.0 mV, the line consists of three portions with three different slopes due to the formation of three different layers (NiO, $Ni(OH)_2$ andCu_2O) with three different potentials. Four different layers with four different potentials NiO, $Ni(OH)_2$, Cu_2O and CuO are expected when E_s was fixed at 200 mV where a line with four portions with four different slopes. When E_s was fixed at 200 mV a line with five portions with five different slopes was obtained due to the formation of NiO, $Ni(OH)_2$, Cu_2O, CuO and Ni_2O_3. These linear relations support the suggestion that the growth of the NiO, $Ni(OH)_2$, Cu_2O, CuO and Ni_2O_3 layers are diffusion-controlled processes and obey the following equation [17,18] where $P = z.c.D^{1/2}/\pi^{1/2}$, where z is the number of exchanged electrons, c is the concentration of the electrolyte and D is the diffusion coefficient of the diffusing species.

$$i = P / t^{1/2}$$

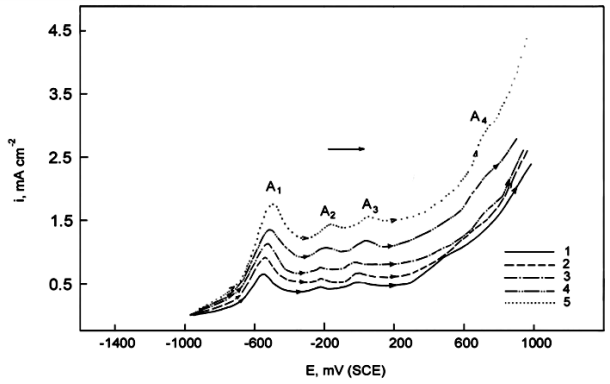

Figure 8. Potentiodynamic anodic polarization of alloy II in 0.1 M Na_2SO_4 at 25ºC and different scan rates: (1) 10 mV s^{-1}, (2) 25 mV s^{-1}, (3) 50 mV s^{-1}, (4) 75 mV $s^{-1}$and (5) 100 mV s^{-1}

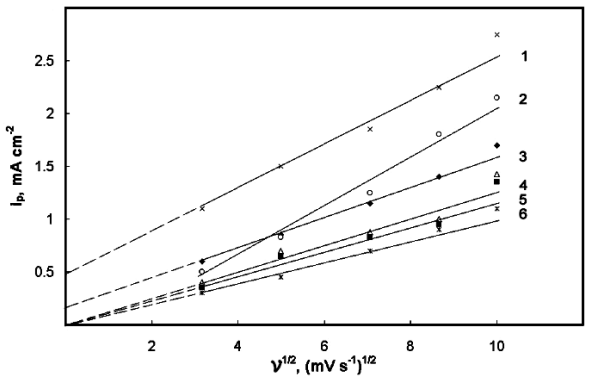

Figure 9. Relation between the peak current density, i_p, and the root of scan rate for the anodic peaks of: (1) A_1 alloy I, (2) A_2 alloy I, (3) A_1 alloy II, (4) A_3 alloy II, (5) A_2 alloy II and (6) A_4 alloy II

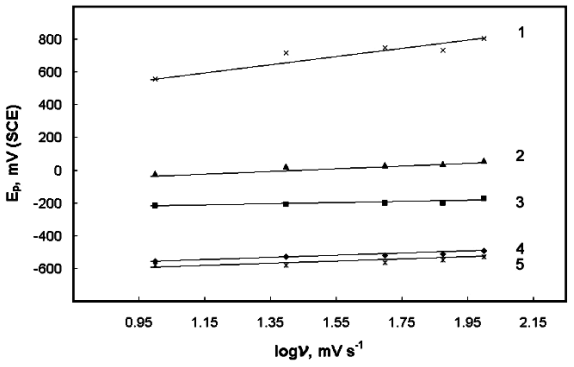

Figure 10. Relation between peak potential of the anodic peaks $E_p$and log ν in 0.1 M Na_2CO_3 at 25ºC of alloy II: (1) A_4, (2) A_3, (3) A_2, (4) A_1 and of alloy I (5) A_1

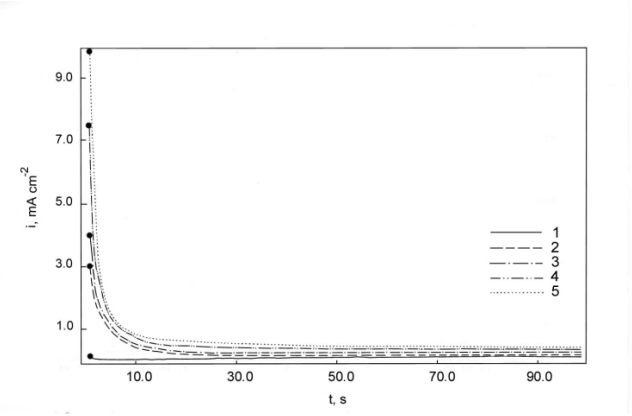

Figure 11. Current transients vs. time recorded for alloy II in 0.1 M Na_2SO_4 at 25°C and constant anodic step potentials: (1)600 mV, (2)200 mV, (3) 0.0 mV, (4) -200 mV and (5) -500 mV

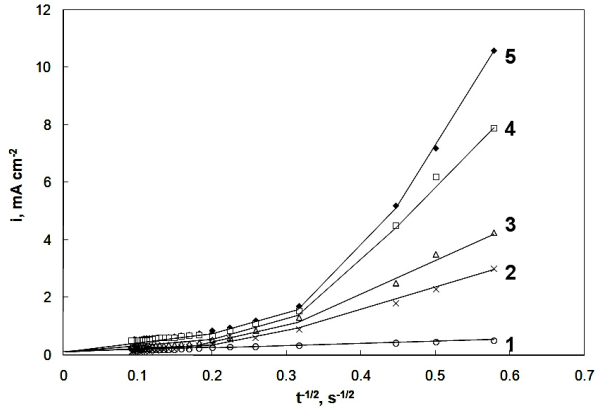

Figure 12. Dependence of the current density on $t^{-1/2}$ for the descending portions of the current transients for alloy II in 0.1 M Na_2SO_4 at 25°C and constant anodic step potentials: (1)600 mV, (2)200 mV, (3) 0.0 mV, (4) -200 mV and (5) -500 mV

4. Conclusions

Two alloys of different composition are used to study the electrochemical behaviour of copper-nickel system sodium sulphate solutions using cyclic voltammetric, potentiodynamic anodic polarization and potentiostatic current \time transient techniques.

The forward sweep was characterized by the appearance of two well-defined potential regions separated by the critical potential E_{crit}; the selective dissolution potential region and the simultaneous dissolution potential region.

The dissolution of the alloys in the first region follow the dissolution – redeposition mechanism where both copper and nickel dissolves initially followed by the redeposition of the more noble component, copper. This region was characterized by the appearance of the anodic peaks A_1 and A_2 where $Ni(OH)_2$ and NiO, and CuO are formed respectively.

The simultaneous potential region was characterized by surface enlargement and the appearance of two anodic peaks $A_3$and A_4 , which are related to the formation of Cu_2O and Ni_2O_3, respectively.

The SEM micrograph showed surface enlargement and pits formation.

The reverse sweep was characterized by the appearance of five catholic peaks C_5, C_4, C_3, C_2 and C_1, which are related to the reduction of Ni_2O_3 to Ni^{+2}componds, CuO to Cu_2O,Cu_2O to Cu,NiO to Ni and $Ni(OH)_2$ to Ni, respectively.

Potentiostatic current/time transient measurements reveal that the formation of $Ni(OH)_2$, NiO, Cu_2O, CuO and Ni_2O_3 layers involves a nucleation and growth mechanism under diffusion control.

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