

EFFECT OF NICKEL CONTENT ON THE ELECTROCHEMICAL BEHAVIOUR OF CUPRONICKEL ALLOY IN NEUTRAL CHLORIDE SOLUTIONS

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ABSTRACT

Voltammetric studies on copper, nickel and cupronickel alloys of various compositions in neutral chloride solutions revealed that the passivation is due to the formation of duplex film consisting of inner compact Cu_2O layer with outer chloro hydroxy layer. Under transient cyclic polarisation conditions, the presence of nickel hindered the passive film formation decreasing its thickness and ohmic conductivity. The reduction of these passive films to copper was markedly favoured by chloride ions. The presence of nickel in the alloy hindered the reduction of these passive films.

Key words: Cupronickels, Cyclic voltammetry, Passivation, Solid state model

INTRODUCTION

A study of electrochemical behaviour of cupronickel alloys in chloride solution is of basic and technological interest as most of the sea going vessels employ cupronickel alloys in heat exchangers. In saline atmospheres the corrosion rates of cupro-nickel alloys decreased sharply with increasing nickel content due to passivation [1]. The passivation was thought to be due to a critical electron-atom ratio of nickel and copper and to the structure and composition of the products formed [2,3]. Nickel alloys exhibited passivation due to protective nickel oxide layer [4]. In aerated sodium chloride solutions the protective films consisted of hydroxy chloride compound and were found to be poor in electronic conductivity [5]. In synthetic seawater the films formed on 90/10 cupronickel alloy contained mainly Cu_2O with a small amount of Ni^{2+} , Ni^{3+} and chloride ions in the inner layer [6]. This oxide film was found to grow till the potential of the outer film surface reached that of $\text{Cu}_2(\text{OH})_3\text{Cl}$. After some time, the inner layer stopped growing and a non-protective porous outer layer of $\text{Cu}_2(\text{OH})_3\text{Cl}$ was formed [7]. As

Cu_2O layer being a p-type semiconductor, was found to accept large amounts of foreign ions like nickel, iron and chlorides [8]. In natural seawater, alloys with 50 wt.% nickel, both copper and nickel dissolved simultaneously with the eventual redeposition of copper and above 50 wt.% nickel only selective dissolution of copper took place [9-13].

The present investigation focuses on the effect of nickel content in the cupronickel alloy on the formation of protective passive film and its reduction behaviour in neutral chloride solutions.

EXPERIMENTAL

High purity copper (99.99%), nickel (99.99%) and 90/10, 80/20, 70/30, cupronickel alloys were used. They were made into cylindrical rods having an area of cross section 0.385 cm^2 . The rods were embedded in Teflon gaskets and electrical connections were provided by screw and thread arrangements. The specimens were mechanically polished in 4/0 emery paper and the solutions were oxygenated by bubbling purified oxygen for an hour before experiment. A standard all glass three electrodes cell was used. A large platinum foil was used as an auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode.

Triangular potential sweep experiments were carried out using a potentiostat (EG&G 173) and a universal programmer (EG&G 175). A Rikadenki 210T X-Y recorder was used to register the I-E curves.

Sodium chloride solution of 0.5M concentration was used in this study. The cyclic voltammograms were obtained from -1000mV to $+500\text{mV}$ vs.SCE. The sweep rates (v) were resorted to 5 to 100 mV/sec. In order to obtain a clean metal surface, the electrode was kept at -1000mV vs.SCE for 5 minutes. Then the specimens were immediately polarised from -1000mV to desired values after this treatment. Experiments were carried out at $30 \pm 1^\circ\text{C}$ and in duplicate.

RESULTS

The cyclic voltammograms of pure nickel in chloride solutions is shown in Fig.1. The electrode was polarised from -900 mV (Cathodic termination potential - $E_{\lambda,c}$) to +500 mV (Anodic termination potential - $E_{\lambda,a}$). The anodic current started increasing beyond -200mV and on the reverse scan, zero current crossing potential (ZCCP) appeared at +100mV. A broad anodic peak appeared at +300 mV (pseudocapacitive in nature); on the reverse scan no cathodic peak was seen. Sweep rates had no influence on the shape of the spectrum.

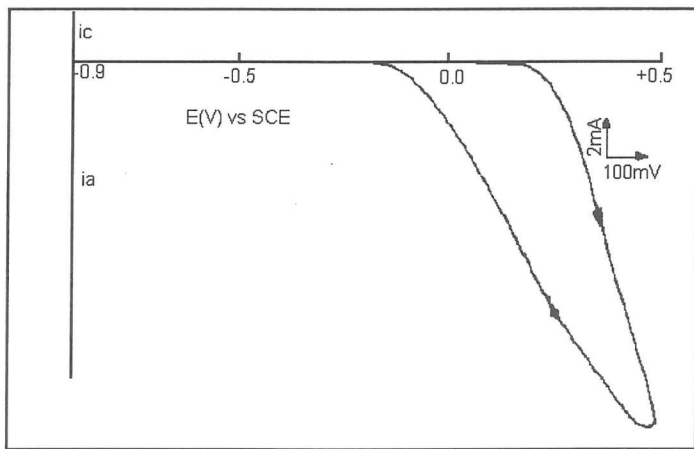


Fig.1 Cyclic voltammogram of pure nickel in 0.5M NaCl solution. Scan rate was 5 mVs^{-1} . ($E_{\lambda,c} = -900\text{mV}$; $E_{\lambda,a} = +500\text{mV}$)

The electrochemical spectrum of copper exhibited an anodic peak at +80mV followed by oxygen evolution at higher anodic potentials (> 0.3 Volt). The backward scan exhibited a cathodic peak at -240mV [Figure 2]. $\Delta E = E_{p,a} - E_{p,c} = -160\text{mV}$ was variant with sweep rate suggesting irreversible reduction and oxidation of copper species on the surface. Anodic peak current varied linearly with \sqrt{v} suggesting diffusion controlled process. If the passivation is of phase type (Formation of a new phase of oxide film) [14], the dependence of $E_{p,a}$ and $I_{p,a}$ on the square root of sweep rate [15,16] must be linear.

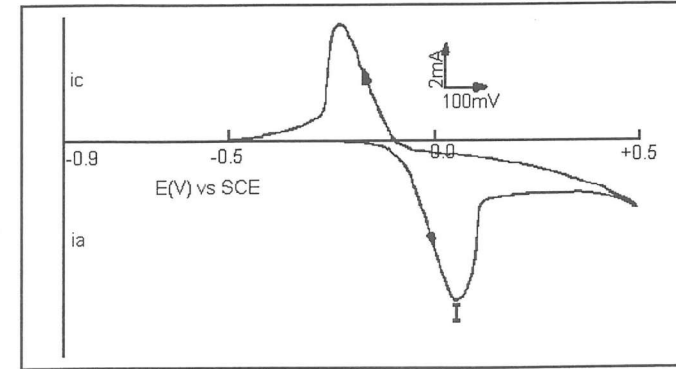


Fig.2 Cyclic voltammogram of pure copper in 0.5M NaCl solution. Scan rate was 5 mVs^{-1} . ($E_{\lambda,c} = -900\text{mV}$; $E_{\lambda,a} = +500\text{mV}$)

The electrochemical spectrum obtained for 90/10 cupronickel alloy at 5mVs^{-1} was shown in Figure 3. When polarised from -900mV to +500mV, the forward scan exhibited an anodic peak at +90mV(I) followed by another peak at +270mV(III). On reversing the scan an inverted anodic peak appeared at +200mV(II), followed by an inverted shoulder at -60mV. A distinct cathodic peak appeared at -200mV. The appearance of inverted anodic peaks (a flow of net anodic current on the reverse scan) suggests a predominant dissolution of the alloy through the pores of passive film.

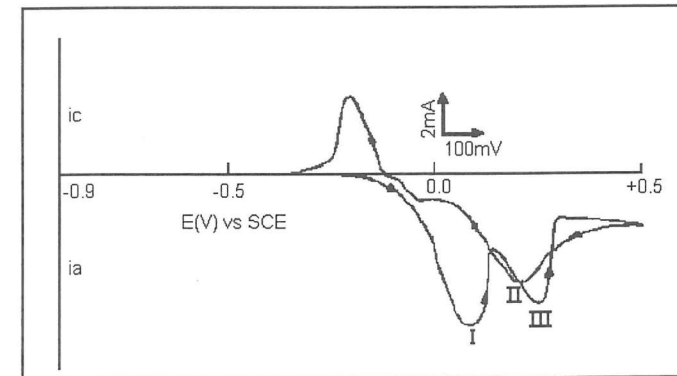


Fig.3 Cyclic voltammogram of 90/10 Cupronickel alloy in 0.5M NaCl solution. Scan rate was 5 mVs^{-1} . ($E_{\lambda,c} = -900\text{mV}$; $E_{\lambda,a} = +500\text{mV}$)

Increase of the nickel content by 10% in the above alloy exhibited interesting features [Figure 4]. The forward scan exhibited a sharp anodic peak at +130mV(I) followed by another peak at +270mV(III). The reverse scan revealed a large inverted broad anodic peak at +180mV(II) and the inverted shoulder became a distinct plateau at -30mV; the cathodic peak appeared at -190mV.

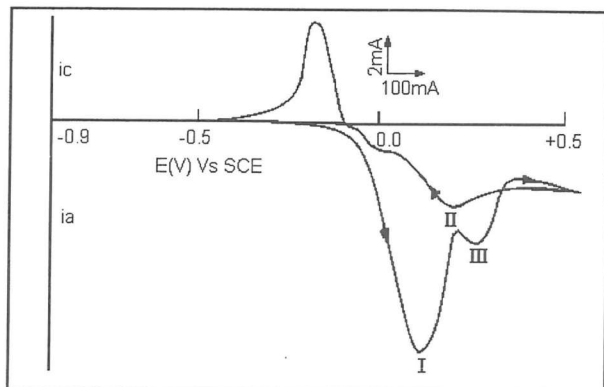


Fig.4 Cyclic voltammogram of 80/20 Cupronickel alloy in 0.5M NaCl solution. Scan rate was 5 mVs⁻¹. (E_{λ,c} = -900mV ; E_{λ,a} = +500mV)

Figure 5 presents the electrochemical spectrum of 70/30 Cu-Ni alloy obtained at 5mV/sec. The forward scan exhibited a single anodic peak at +150mV(I) while the reverse scan exhibited only an inverted shoulder at +10mV followed by a cathodic peak at -230mV.

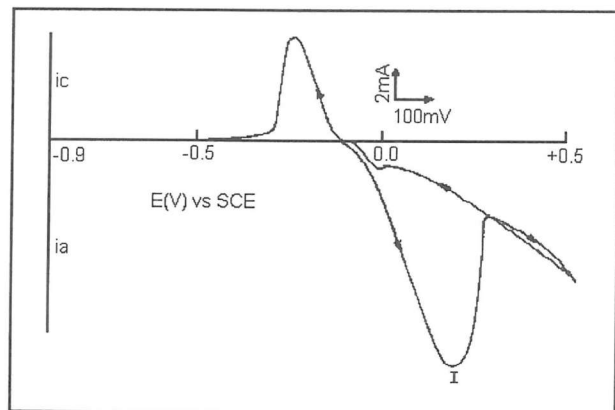


Fig.5 Cyclic voltammogram of 70/30 Cupronickel alloy in 0.5M NaCl solution. Scan rate was 5 mVs⁻¹. (E_{λ,c} = -900mV ; E_{λ,a} = +500mV)

The anodic peak potential (I) varied linearly with square root of sweep rates for copper and all the three cupronickel alloys were shown in Fig.6. The anodic peak potential (I) varied with log chloride concentration with a slope of 100mV/decade [Fig.7]. The cathodic peak potentials became more noble with the increase of the amount of copper content in the alloy suggesting that the reduction of passive film was favoured by increase of copper in the alloy. The cathodic peak potentials became more noble with chloride content and varied 100mV/decade change of chloride concentration [Fig.8]. The chloride concentration favoured the reduction of the passive film as indicated by the shift of cathodic peak potentials to more noble direction.

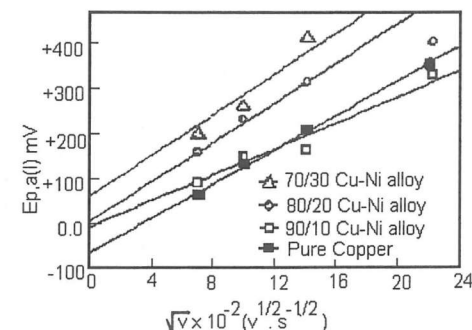


Fig.6 Anodic peak potential vs, square root of sweep rates for pure copper and various Cupronickel alloys.

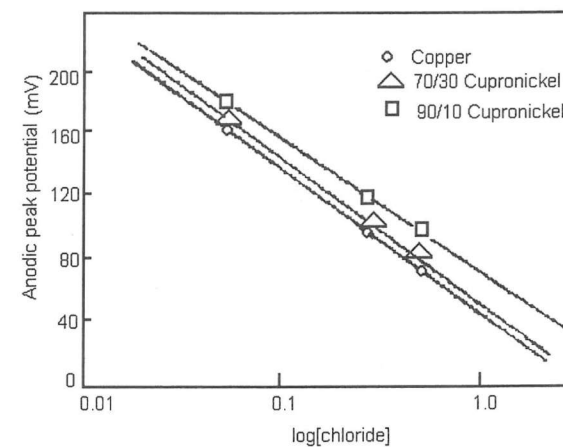


Fig.7 Anodic peak potential vs, log[chloride] for pure copper and various cupronickel alloys.

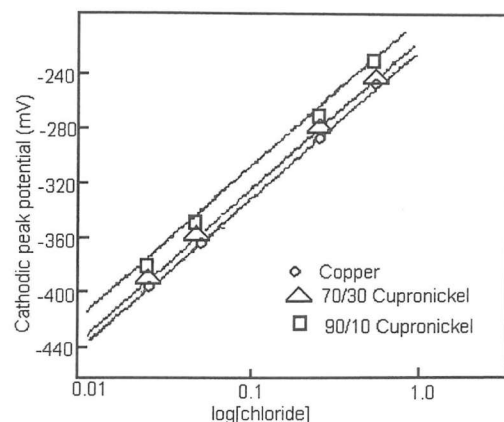
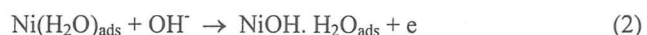


Fig.8 Cathodic peak potential vs. log[chloride] for pure copper and various cupronickel alloys.

DISCUSSION

Passivation of nickel

The initial portion of the anodic curve is assigned to a steady electrodisolution leading to passivation. Before the appearance of the anodic peak at +300mV, an initial surface oxidation can take place. The participation of water and OH⁻ ions may lead to



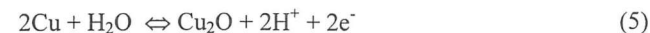
The appearance of peak at +300mV is due to Ni(OH)₂ or NiO and further anodic polarisation thickens the film. In chloride solutions, the dissolution and passivation may lead to the formation of NiCl₂ as



Passivation of copper

In the passive region copper forms Cu₂O which has been confirmed by X-ray analysis [17].

The passivation reaction is



The subsequent oxidation of Cu₂O to CuO

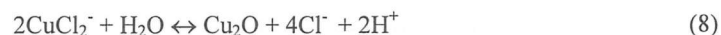


[Cu₂O + 3H₂O ⇌ 2Cu(OH)₂ + 2H⁺ + 2e⁻] may also occur.

In presence of chloride ions, the reaction



which is pH independent but chloride ion dependent. The solid Cu₂O product may be formed via the hydrolysis of CuCl₂⁻ complex as



According to Muller's passivation model [18,19] the passive film starts forming only at certain points on copper and extends over the surface as a layer of uniform thickness (δ). This film formation is said to be under ohmic resistance control. If the total area of the electrode is A_o and θ_p is the degree of coverage of the electrode the resistance of the solution in the pores threading the layer is R_p.

$$R_p = \delta / KA_o (1 - \theta_p) \quad (9)$$

Where,

δ = thickness of the film

K = specific conductivity of the solution inside the pores

The expressions for peak current and peak potential are

$$i_{p,a} = [(\sqrt{nF\rho K} / \sqrt{M})] A_o (1 - \theta_p) \sqrt{v} \quad (10)$$

$$E_{p,a} = E_o + [(\sqrt{nF\rho K} / \sqrt{M})] \{(\delta / K) + R_o A_o (1 - \theta_p)\} \sqrt{v} \quad (11)$$

Where,

n = number of electrons involved in the electrochemical reaction

ρ = film density

R_o = resistance of the solution external to the film

As predicted by the above equations the anodic peak current reaches zero as the sweep rate goes to zero. The anodic peak potentials were extrapolated to zero sweep rates. This value E_a^o can be defined as the minimum potential needed for current flow i.e. film formation potential. The presence of nickel in the alloy shifted the E_a^o to more noble values indicating the hinderance in the formation of oxide. An estimation of surface coverage after the first peak can be obtained by assuming ρ = density of the CuCl₂ =

3.386 g/c.c.; M = molecular weight of $\text{CuCl}_2 = 134.45 \text{ g/mol.}$; and $K = 10^{-2} \text{ ohm}^{-1}\text{cm.}^{-1}$ in the above equations. The value of $[E_{p,a}(I) - E_a^0 / i_{p,a}(I)]$ has the dimensions of resistance and θ_p was found to be ≈ 1 . Table I summarises the E_a^0 , δ , R of various materials used. The increase in nickel content decreased the thickness and ohmic resistance of the passive film.

Table I Parameters derived from polarisation curves

Material	E_a^0 mV vs.SCE	Film thickness (δ) x 10^{-4} cm.	Ohmic resistance (R) x 10^3
Copper	-70	32	16.67
Cu/Ni alloy 90/10	-10	25	13.19
Cu/Ni alloy 80/20	+5	19	10.00
Cu/Ni alloy 70/30	+25	14	7.43

Passivation of cupronickel alloys

The semi quantitative EDXA of the corrosion product formed on 90/10 cupronickel alloy in alkaline solution containing chloride ions [20], presented that one atom of chloride accompanies with four atoms of copper. On higher chloride concentrations, XRD patterns revealed that the corrosion product contained Cu_2O [cuprite] and $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ [atacomite].

In the present study, the appearance of the first anodic peak was due to the formation of Cu_2O formed by hydrolysis of CuCl_2 . Further polarisation in the noble direction favours the inclusion of nickel in the Cu_2O and at extreme anodic potentials, nickel ions would leave the film and form soluble NiCl_2 and copper can also be precipitated out as $\text{Cu}_2(\text{OH})_3\text{Cl}$. The passive film may be found to consist of a compact inner Cu_2O layer and an outer layer of cupric hydroxy chloride. The passive film now contains inner Cu_2O layer and outer $\text{Cu}_2(\text{OH})_3\text{Cl}$ containing nickel.

Solid state model of passivation

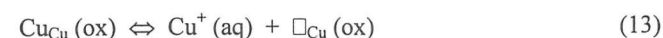
The structure of Cu_2O is cubic with the Cu^+ and O^{2-} ions being contained in two inter penetrating cubic lattices. The space group of the compound is P_n3m . The bulk form of Cu_2O is a highly defective "p-type" semiconductor and its electronic resistance is low.

This is because the electron exchange between Cu^+ and Cu^{2+} ions requires little energy. Cu_2O can accept large amounts of foreign ions e.g. nickel.

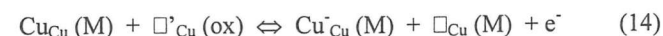
During anodic polarisation, the chloride ion adsorbs on the surface vacancy of Cu_2O film



where Cl^- is chloride ion in the aqueous solution and $\text{Cl}^-\text{O}(\text{ox})$ is the positively charged chloride ion occupying an oxygen lattice site. To preserve electroneutrality an equivalent number of cation vacancies must form through dissolution of the cation in the solutions

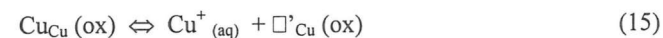


An absorption of chloride ions leads to an enhanced flux of cation vacancies from the oxide/solution towards metal/oxide interface. Here they are annihilated as



With prolonged polarisation, the amount of incorporated chloride ions increase; the oxygen vacancies occupied by chloride ions also increase. Thus an increased concentration of additionally created cation vacancies is directed towards the inner metal/oxide interface. If the concentration of these vacancies is so high that they cannot be consumed, the excess vacancies coalesce to form a cation vacancy condensate. When the condensate exceeds a critical size, the film becomes unstable and localised breakdown occurs.

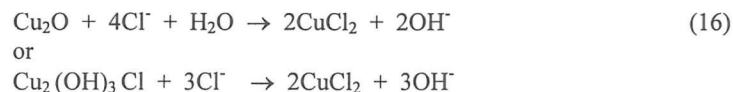
In the case of Cupronickel alloy, incorporation of nickel ions and absorption of chloride ions at the Cu_2O /solution interface causes additional cation vacancies.



These additional cation vacancies can be annihilated through reaction with host copper atoms as well as nickel atoms. It seems reasonable that a critical threshold concentration of cation vacancies above which a vacancy condensate formed has become now larger. This explains why an inclusion of nickel in copper alloy hinders the stability and formation of Cu_2O film.

Reduction of the passive film

For copper containing alloys in chloride solutions, the passive films were found to contain Cu_2O or $\text{Cu}_2(\text{OH})_3\text{Cl}$. The presence of chloride ions in solution shifted the cathodic peak potential to more nobler values suggesting that chloride ions favour reduction of the passive film.



The CuCl_2 thus formed undergoes reduction as



On Cupronickel alloys the formation of nickel chloride is simultaneously favoured which causes hinderance to CuCl_2 formation and its reduction to copper.

CONCLUSION

Voltammetric studies on copper, nickel and cupronickel alloys of various compositions in neutral chloride solutions revealed that the passivation is due to the formation of duplex film consisting of inner compact Cu_2O layer with outer chloro hydroxy layer. Under transient cyclic polarisation conditions the presence of nickel hindered the passive film formation decreasing its thickness and ohmic conductivity. The reduction of these passive films to copper was markedly favoured by chloride ions. The presence of nickel in the alloy hindered the reduction of these passive films.

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