

EFFECT OF ALKALINE SOLUTION CONCENTRATION ON THE PASSIVATION FILM OF Cu-Ni ALLOY

VPLIV KONCENTRACIJE ALKALNE RAZTOPINE NA NASTANEK PASIVNEGA FILMA NA ZLITINI Cu-Ni

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Passive films formed on a Cu-Ni alloy in various concentrations of alkaline environment were investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy and the Mott-Schottky approach. The wide passivation range of the copper-nickel alloy was tested in alkaline solutions of three concentrations. The oxide film on the specimen has a p-type semiconductor property, while the flat band potential (E_{FB}) decreased with increasing solution concentration. The film resistance of the passive films increased with increasing solution concentration. The passive films showed a duplex structure, including an inner layer of oxide (Cu_2O , NiO) and an outer layer of hydroxide ($Cu(OH)_2$, $Ni(OH)_2$).

Keywords: 90Cu-10Ni alloy, corrosion resistance, oxidation film, solution concentration, passivation potential

Raziskovali so nastajanje tanke oksidne plasti na zlitini Cu-Ni v prisotnosti različno koncentrirane alkalneraztopine. Raziskave so izvajali s pomočjo potenciodinamične polarizacije, elektrokemične impedančne spektroskopije (EIS), rentgenske fotoelektronske spektroskopije in Mott-Schottky-jevega pristopa. Pri tem so izbrali tri različne koncentracije alkalne raztopine in dosegli širok spekter pasivacije izbrane Cu-Ni zlitine. Oksidni film formiran na površini zlitine je imel lastnosti polprevodnika tipa p, ploskost pasovnega potenciala (E_{FB}) pa se je zmanjševala z naraščajočo koncentracijo oz. s povečanjem alkalnosti raztopine. Odpornost pasivnih filmov je naraščala z naraščajočo koncentracijo raztopine. Pasivni filmi so imeli duplex strukturo, ki je bila sestavljena iz notranje oksidne plasti (Cu_2O , NiO) in zunanje plasti hidroksida ($Cu(OH)_2$, $Ni(OH)_2$).

Ključne besede: zlitina 90Cu-10Ni, odpornost proti koroziji, oksidni film, koncentracija alkalne raztopine, potencial pasivacije

1 INTRODUCTION

Copper-nickel alloys play an important role in marine engineering for thermal condensers, seawater desalination equipment, water supply lines, and other pipeline applications due to their excellent physical and mechanical properties, resistance to seawater corrosion and biological fouling.¹ The excellent corrosion resistance of copper-nickel alloys, on the one hand, is due to the high standard electrode potential for copper of +0.34 V, which is difficult to ionize. On the other hand, the Ni^{2+} is incorporated into the Cu_2O film, and the ion resistance of the film is increased. In copper-nickel alloy systems, 70Cu-30Ni and 90Cu-10Ni alloys are the most widely used. The nickel content of the 70Cu-30Ni alloy is 30 %, which has better corrosion resistance and is mainly used for pipelines that withstand larger flow rates. However, compared with 90Cu-10Ni alloys, due to its higher nickel content, the cost is higher, so limiting the application range. Some issues regarding the main corrosion protection offered by the copper alloy remain to be studied further.²

Typically, the excellent corrosion resistance of a metal or an alloy is attributed to the passivation oxide film formed on the surface, possibly only a few nanometers thick, that protects the metal surface from the effects of an aggressive external environment and thus inhibits further corrosion.³ The characteristics of the passive film, including the composition, structure and thickness, will control the corrosion resistance.⁴ Some issues regarding the main corrosion protection offered by the copper alloy remain to be studied further. Because passivation plays a crucial role in material applications, investigations of the passive behavior remain topical issues in corrosion science.⁵ The presence, composition and structure of an oxide overlayer on a metallic substrate is determined by the redox conditions of the interface formed with the environment.⁶ In recent years, many scholars have devoted themselves to the study of the passivation behavior of copper and copper alloys in acidic or alkaline solutions. Kose et al.⁷ proposed that the composition of the passivation film formed on Cu-20Zn and Cu-20Ni alloys in an alkaline borate buffer can be expressed as $ZnO/Cu_2O/CuO$ and $NiO/Cu_2O/CuO$, respectively. Zaky et al.⁸ studied the passivation film of copper-nickel alloy in NaOH solution by cyclic voltammetry consisting of $Ni(OH)_2/CuO/Cu_2O/$

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Table 1: Chemical compositions of 90Cu10Ni alloy (w%)

Cu	Ni	Fe	Mn	Zn	S	P	C	Pb
substrate	10.55	1.76	0.80	0.031	0.0041	0.004	0.01	<0.005

$\text{Cu}(\text{OH})_2/\text{Ni}_2\text{O}_3$. The surface passivation film of copper-nickel alloy is also related to the metal substrate,^{9–13} and the results showed that the addition of Ni to Cu to form copper–nickel alloys changes the composition of the surface film; the passivation potential,^{14,15} the results showed that the corrosion resistance increased with increasing potential; i.e., the passivation time.¹² The increase of the immersion time in the solution improved the alloy stability due to the formation of a stable passive film, and the solution concentration,^{2,9,16,17} significant passivity was not observed in the un-buffered chloride solutions at pH 6. The alloys exhibited passivity in the buffered solutions at pH 10. A large number of studies were reported to explain the electrochemical behavior of the passive films on copper. However, little information about the effect of solution concentration on the composition of these passive films is available.

In the alkaline solution, by controlling the passivation potential parameters, the solution composition and concentration, pH, temperature and time, substances with effective protection properties can be obtained. In the present work the electrochemical properties of the passive films formed into Cu-Ni alloy in alkaline solutions were further studied in the concentrations range 0.01–0.35 mol/L using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and the Mott–Schottky approach. The chemical composition and the element state of the passive film were investigated with X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL

2.1. Materials and solutions

In this study the main chemical composition (w%) of 90Cu-10Ni alloy is shown in **Table 1**. The plate thickness of 3 mm is cut into (10 × 10) mm specimens and then embedded in the epoxy resin. The surface sanded with sandpaper to 2000# and mirrored with diamond abrasive paste, and then rinsed with methanol. Three electrodes were used in this experiment. The saturated calomel electrode (SCE) was used as the reference electrode and the platinum electrode was used as the counter electrode. The working electrode is a 90Cu-10Ni specimen. The test solutions are 0.01 mol/L NaOH+0.125 mol/L $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 0.1 mol/L NaOH+0.125 mol/L $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 0.35 mol/L NaOH+0.125 mol/L $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ borate buffer solution at 22 °C.

2.2. Electrochemical measurements

In this experiment the electrochemical data were measured using the CHI660E electrochemical workstation. Before all the electrochemical experiments, the sur-

face of the sample was initially pretreated cathodically at $-0.8 \text{ V}_{\text{SCE}}$ for 15 min to reduce the air-formed oxide film.¹⁸ Then the potentiodynamic polarization experiments were performed at a scan rate of 1 mV/s, the scanning range is -0.25 V (vs E_{OCP}) to 1 V. Before the EIS measurement, the specimens were first passivated for 1 h at $0.1 \text{ V}_{\text{SCE}}$, $0.2 \text{ V}_{\text{SCE}}$, $0.3 \text{ V}_{\text{SCE}}$, and $0.4 \text{ V}_{\text{SCE}}$ to ensure that a sufficiently stable film is formed on the specimen. The EIS experiment is a signal from 10^5 Hz to 10^{-2} Hz with an amplitude signal of 5 mV. ZSimpWin software was used to fit the EIS experimental data. The Mott-Schottky plot is obtained by scanning in both the positive and negative directions at a frequency of 1000 Hz with an amplitude signal of 5 mV, a potential range of 0 V_{SCE} to 1 V_{SCE} , and a potential step of 10 mV. XPS analyses were performed using a Thermo Scientific K-Alpha photo-electron spectrometer. Photo-electron emission was excited by a monochromatic Al K_{α} source operated with an initial photo energy of 1486.6 eV. The C 1s peak at contaminative carbon at 284.8 eV was used as a reference to correct the charging shifts. The quantification of the species in the oxide films was performed using XPSPEAK software fitting peak.

3 RESULTS AND DISCUSSION

3.1 Cu-Ni alloy thin-film preparation

Figure 1 shows potentiodynamic polarization curves for the B10 alloy in 0.01 mol/L, 0.1 mol/L and 0.35 mol/L NaOH solutions. All three curves have obvi-

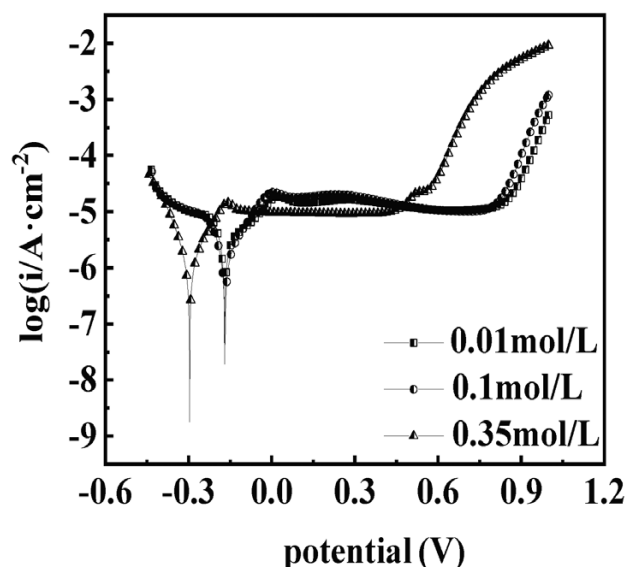


Figure 1: Potentiodynamic polarization curves for B10 alloy in NaOH solution

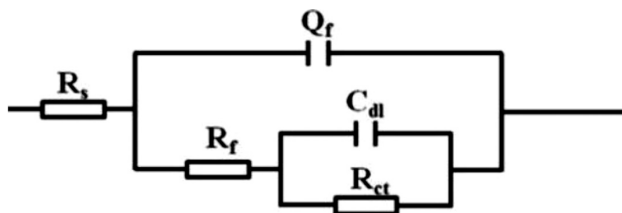


Figure 2: Equivalent electron circuit used to fit the impedance spectra

ous passivation ranges. In the 0.35 mol/L solution, the potential polarization curve has a significant primary passivation and secondary passivation. The current densities were very small, and its specific value is shown in Table 2, so exhibiting a better corrosion resistance. According to the potentiodynamic polarization curves, 0.1 V, 0.2 V, 0.3 V and 0.4 V were selected as passivation potentials.

Table 2: Corrosion potential and current density of B10 alloy in NaOH solution with different concentrations

Concentrations (mol/L)	E_{corr} (V)	I_{corr} ($\times 10^{-5}$ A·cm $^{-2}$)
0.01	-0.170	1.21
0.1	-0.169	0.39
0.35	-0.296	0.14

3.2 Evaluation of corrosion resistance

To evaluate the influence of the solution concentrations on the corrosion resistance of the coatings obtained, experiments were carried out using the electrochemical impedance spectroscopy (EIS) techniques.¹⁹ EIS has been widely used to study and characterize passive films formed into pure metals or alloys.²⁰ According to the characteristics of the polarization curve, 0.1 V, 0.2 V, 0.3 V and 0.4 V potentials were selected for passivation for 1200 s, 2400 s and 3600 s, respectively. The applied potentials were within the passive range. After stabilization, the electrochemical impedance was measured. The equivalent circuit is shown in the Figure 2. In the circuit, R_s is the solution resistance, Q_f is the constant-phase element (CPE) of the passive films, R_f is the passive film resistance, C_{dl} is the double-layer capacitance and R_{ct} is the charge-transfer resistance. The CPE was used as the non-ideal capacitance ($n < 1$) of the passive film caused by surface heterogeneities and toughness, as given by:

$$Z_{CPE} = [Y_0(jw)^n]^{-1} \quad (1)$$

where Q is the admittance of CPE, n is the CPE exponent, and w is the angular speed. The higher values of R_{ct} and R_f indicate a better corrosion resistance, thus it

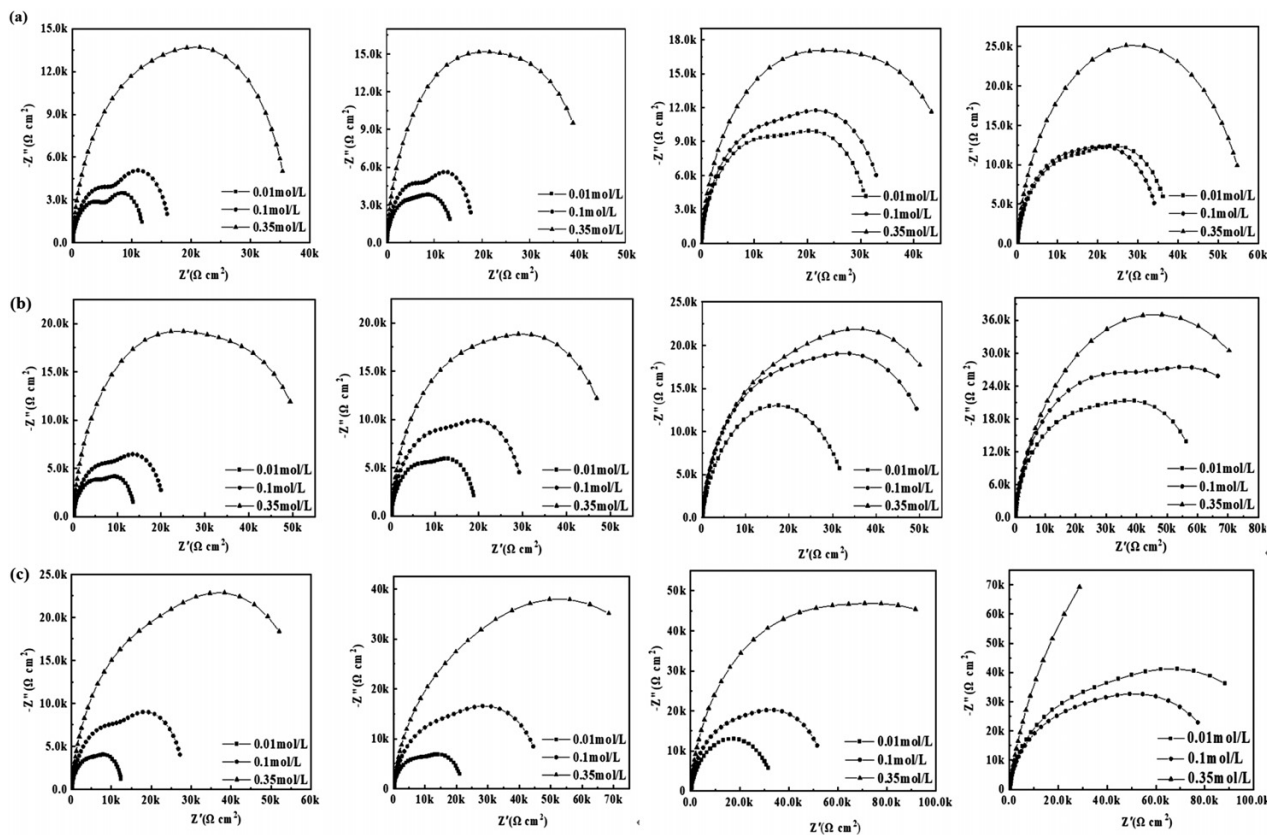


Figure 3: Nyquist diagram of 90Cu-10Ni in NaOH solution: a) 0.1 V, 0.2 V, 0.3 V, 0.4 V passivation for 1200 s, b) 0.1 V, 0.2 V, 0.3 V, 0.4 V passivation for 2400 s, c) 0.1 V, 0.2 V, 0.3 V, 0.4 V passivation for 3600 s

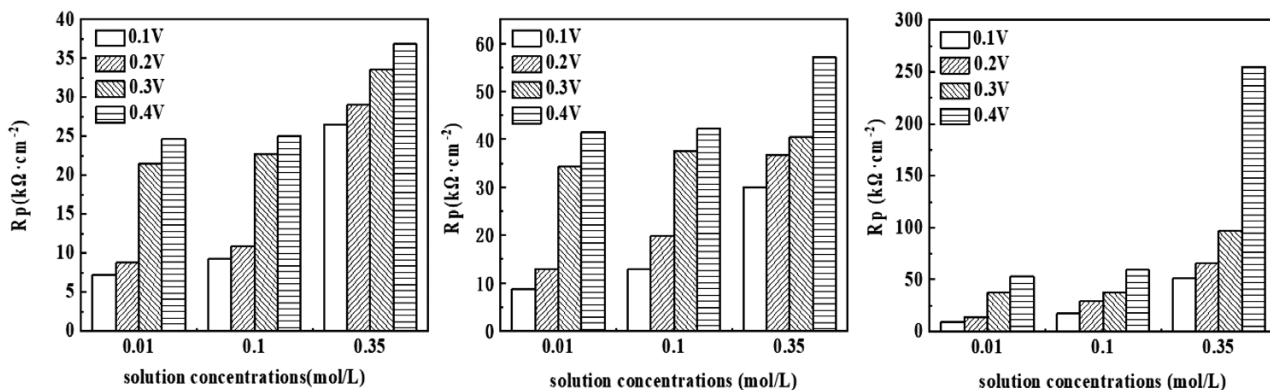


Figure 4: Electrochemical impedance spectroscopy fitting yields R_p . Passivation time is: a) 1200 s, b) 2400 s, c) 3600 s

can be used to evaluate the corrosion resistance of the samples.

On the one hand, according to **Figure 3**, the Nyquist diagram of 90Cu-10Ni in NaOH solution, with an increase of the applied potential, the radius of capacitive resistance arc increases. And the R_p of passive film fitting data shows in **Figure 4** that as the concentration increases, R_p and R_{ct} increase. So, the corrosion resistance increases. This can be explained as follows: the applied potential is the driving force for oxide formation, the growth and crystallisation of the passive film. There was a competition between nucleation and growth; at lower applied potential, there were fewer nucleation sites, and the grains grew slowly to a large scale, whereas at higher applied potential, more susceptible nucleation sites were activated, and the grains tended to have a refined structure. On the other hand, there was a formation of a protective film on the copper alloy surface when it was immersed in the alkaline solution. In the alkaline solution, increases in the solution concentration depend on the concentration of hydrogen ions. And, this is known as one of the factors affecting the corrosion rate. The changes in concentration can either induce or modify electrochemical reactions.²¹ The increases in solution concentration relate to the increases in stability of the formed corrosion product, most likely as an oxide. These oxides can form protective films, slowing down the anodic activity.²² The corrosion resistance of the passivation film increases with an increase of the solution concentration, while the passivation time and the passivation potential remain unchanged. This is because the inner layer of the passivation film is mainly copper oxide and a small amount of nickel oxide, and the outer layer is copper oxide and hydroxide. Generally, the outer layer is relatively loose and porous, and has strong protection without the inner layer.

3.3 Semiconductor performance of passive film

The semiconductor property of the passivation film can be described with the Mott-Schottky theory. The linear region of the plots is due to the variation on the width

of the space-charge layer of the oxide film on the specimen with the applied potential, according to:

- p-type:

$$\frac{1}{C^2} = -\frac{2}{\epsilon\epsilon_0 eN_A} \left(E - E_{FB} - \frac{kT}{e} \right) \quad (2)$$

- n-type:

$$\frac{1}{C^2} = -\frac{2}{\epsilon\epsilon_0 eN_D} \left(E - E_{FB} - \frac{kT}{e} \right) \quad (3)$$

where E is the applied potential (V_{SCE}), E_{FB} is the flat-band potential (V_{SCE}), ϵ_0 is the permittivity of free space ($F \cdot cm^{-1}$), ϵ is the relative dielectric constant, N_D is the donor density (cm^{-3}), N_A is the accept density (cm^{-3}), A is the surface area of the sample (cm^2), k is the Boltzmann constant ($1.38 \times 10^{-23} J/K$), T is the absolute temperature and e is the charge of the electron ($1.6 \times 10^{-19} C$).

Table 3: Accept densities N_A of passive films at different solution: a) 1200 s, b) 2400 s, c) 3600 s

(a)				
$N_A(10^{20}cm^{-3})$	0.1V	0.2V	0.3V	0.4V
0.01 mol/L	5.27	5.59	5.5	3.4
0.10 mol/L	3.72	4.65	3.7	3.3
0.35 mol/L	7.48	8.86	5	6.4
(b)				
$N_A(10^{20}cm^{-3})$	0.1V	0.2V	0.3V	0.4V
0.01 mol/L	5.05	4.9	3.8	4.7
0.10 mol/L	3.44	3.23	2.2	1
0.35 mol/L	6.31	4.64	9.1	5.5
(c)				
$N_A(10^{20}cm^{-3})$	0.1V	0.2V	0.3V	0.4V
0.01 mol/L	2.18	4.2	4.2	0.4
0.10 mol/L	2.8	2.2	4.2	3.4
0.35 mol/L	6.09	4	14	9.8

From Equation (2) the slope of the plot of the experimental C^{-2} as a function of E can determine N_A , and the extrapolation of the linear portion to $C^{-2} = 0$ can obtain E_{FB} . The data of N_A is shown in **Table 3**. Different types of defects exist within the barrier layer, including anion vacancies, cation interstitials, and cation vacancies, re-

sulting in different types of electronic, semiconducting films.²³ The slope of the straight line is negative, showing p-type semiconductor characteristics. It is suggested that the passive oxide layers formed on the Cu-Ni alloy depend on the predominant defect present in the passive film. The cation vacancy was the dominant defect in the film. According to the electron band theory of solids, if the number of holes in the valence band is more than that of electrons in the conduction band of oxides, the oxides are considered as a p-type semiconductor such as Cu_2O , Ni_2O_3 and NiO .

Figure 5 is the Mott-Schottky diagram of the sample in different concentration solutions. It can be seen from the comparison of the flat-band potential (E_{FB}) in all figures that the value of the flat band potential (E_{FB}) decreases with the increase of the solution concentration. In other words, the breaking potential (E_b) increases with the decrease of the flat band potential (E_{FB}), and the corrosion resistance of the metal matrix increases accordingly. This conclusion is consistent with that of the electrochemical impedance.

3.4 XPS Analysis of the Surface Layers

The XPS spectra of the 90Cu10Ni alloy after passivation at 0.4 V for 3600 seconds in different solutions are shown in **Figure 6**. The fitting of the peaks ob-

tained from the XPS results showed that the metallic and oxidized states of Cu 2p, Ni 2p and O 1s appeared in the passivation film. This was to obtain high-resolution spectra, in order to study the composition of the passivation film more carefully.

Figure 6 shows XPS spectra of the passivation film formed on the surface of the 90Cu-10Ni alloy in different concentrations of NaOH solution after 0.4 V passivation for 3600 s. Cu species were detected in the passivation film. The high-resolution spectra of Cu 2p is shown in the **Figure 6a**, the Cu 2p spectra can be deconvoluted into three peaks, the metallic state (Cu(met)) peak, the cuprous species peak and the bivalent (Cu 2p) species peak. It is observed that the solution concentrations play a crucial role in the composition oxide species, they will be altered at different solution concentrations. Cu (0) was detected in the XPS spectrum of the passivation film formed by the 0.01 mol/L solution. The relative peak heights of Cu (I) and Cu (II) indicate that Cu (II) is the primary oxidized species or hydroxyl in the passive film. The relative peak intensity of Cu (I) increased in the XPS spectra of 0.10 mol/L solution passivation film. Compared with the passivation film formed in the 0.01 mol/L solution, the passivation film is more compact. The relative peak intensity of Cu (I) in the passivation film increases with the increase of the solution concentration. For the passivation film formed in

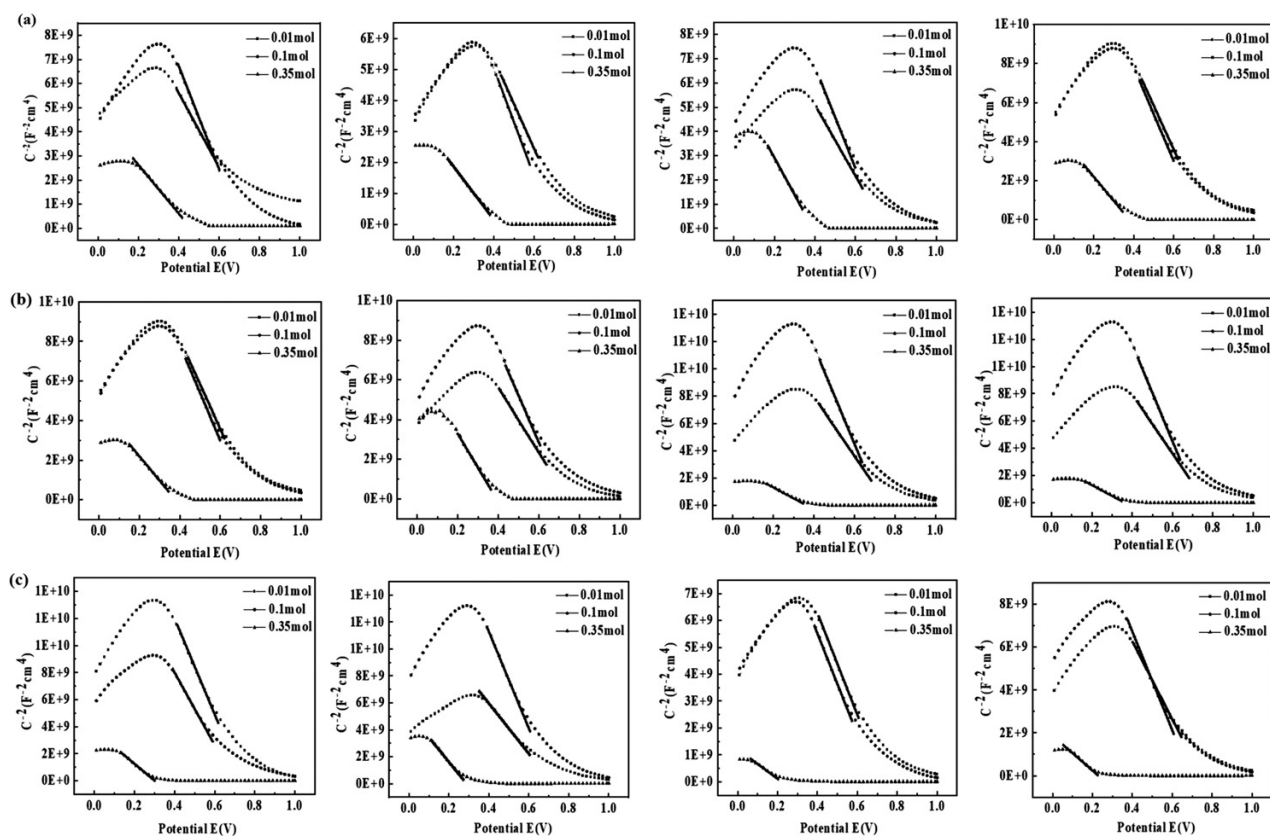


Figure 5: Mott-Schottky plots of Cu90Ni10 alloy in NaOH solution: a) 0.1 V, 0.2 V, 0.3 V, 0.4 V potentiostatic passivation for 1200 s, b) 0.1 V, 0.2 V, 0.3 V, 0.4 V potentiostatic passivation for 2400 s, c) 0.1 V, 0.2 V, 0.3 V, 0.4 V potentiostatic passivation for 3600 s

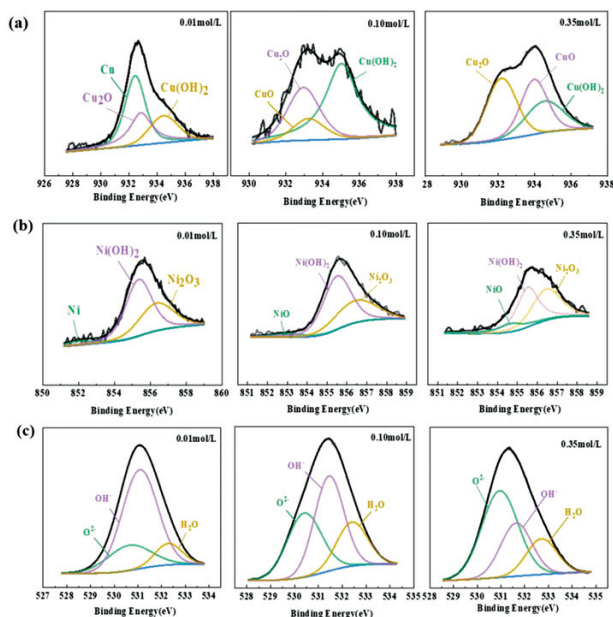


Figure 6: XPS spectra of the passivation film formed on the surface of 90Cu-10Ni alloy in NaOH solution after 0.4 V passivation for 3600 s

0.35 mol/L solution, Cu mainly exists in the form of Cu (I) oxide. At this time, the compactness of the passivation film is further strengthened.

The passive films also detected the Ni species. The three graphs in **Figure 6b** show the spectra of Ni 2p in solutions of three concentrations. The Ni 2p spectra can be deconvoluted into three peaks, the metallic state (Ni(met)) peak, the bivalent peak and trivalent species peak. The peak at 554.3 eV is attributed to the NiO.²⁴ The XPS spectra of the passivation film Ni 2p formed in three solutions were compared, the relative intensity of the NiO peak increased with the increase of the solution concentration. The main composition of the passivation film is changed from nickel hydroxide to oxide. This makes the passivation film more corrosion resistant. In addition, the peak at 855.6 eV is Ni(OH)₂.

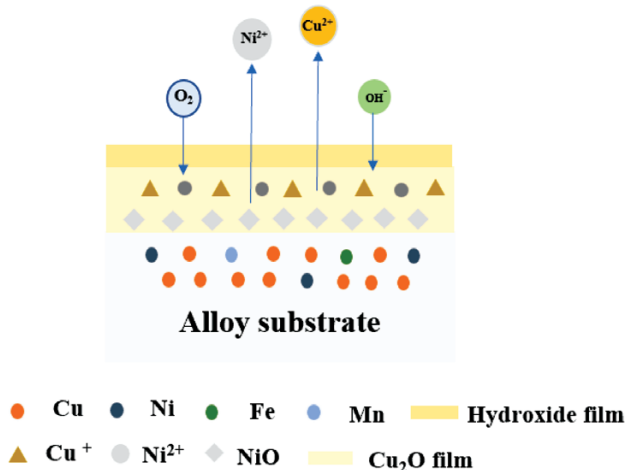


Figure 7: Formation of passive film on Cu-Ni alloy in solution

The O 1s spectra can also be split into three components, i.e., O²⁻, OH⁻ and H₂O. It can be seen that OH⁻ (531.8 eV)¹⁷ is the primary constituent of the passive film in 0.01 mol/L and 0.10 mol/L solution, which corresponds to the formation of Cu(OH)₂ and Ni(OH)₂. At the same time, O²⁻ (530.2 eV)^{24,25} is the primary constituent of the passive film in the 0.35 mol/L solution, which corresponds to the formation of the Cu₂O, CuO, NiO and Ni₂O₃ species. The peak at 533 eV represents H₂O in the passive film.¹⁷ The peak at 533 eV represents H₂O in the passive film. In comparison with the O²⁻ and OH⁻, it can be concluded that the OH⁻ is the primary species in the passive film in the 0.01 mol/L and 0.10 mol/L solution. However, as the concentration increases to 0.35 mol/L, the O²⁻ became the primary constituent of the passive film. So, the main components of the passivation film are NiO, Cu₂O and other protective substances.

According to the XPS data, the physical structure and ion-transfer process of the passive film formed by 90Cu-10Ni in a NaOH solution are shown in **Figure 7**. The passivation film shows a double-layer structure. The inner layer is relatively dense Cu₂O and NiO, and the outer layer is porous hydroxide and CuO. The oxide film of the inner layer plays a major role in protection. The content of oxide produced in 0.35 mol/L solution is higher. Therefore, with an increase of the solution concentration, the protection of the passivation film to the body increases. This conclusion is consistent with the results of electrochemical impedance and the Mott-Schottky analysis.

4 CONCLUSIONS

The passive films on a Cu-Ni alloy in alkaline solutions were investigated in the concentration range from 0.01 mol/L to 0.35 mol/L using potentiodynamic curves, electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy and Mott-Schottky plots. The following conclusions can be drawn:

- 1). There is a wide passivation range of copper nickel alloy in alkaline solutions of three concentrations. The passive films have p-type bipolar semiconductors characteristics. The flat band potential (E_{FB}) decreased with an increasing solution concentration. This indicates that the passivation film has better corrosion resistance.
- 2). The film's resistance value increased when increasing NaOH concentration and the applied potential, due to the increase in the Cu dissolution of 90Cu-10Ni alloy. The passivation film forms a stable oxide and is protective.
- 3). The passivation film is composed of stable oxides and hydroxides, which are protective. With an increase of the solution concentration, the content of Cu₂O and NiO in the film increases, and the formation ability of passive film increases in 0.35 mol/L solution.

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