The use of beta-carotene as environmentally safe inhibitor for Cu-Al-Ni alloys corrosion in sulfide polluted chloride solutions

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Abstract

The stability of Cu-Al-Ni alloys used in the manufacture of NaCl in Egypt was investigated in sulfide polluted chloride solutions. Three different alloys, namely, Cu-10Al-5Ni, Cu-10Al-10Ni and Cu-10Al-45Ni were investigated in chloride containing sulfide$^-$ions using different electrochemical techniques including polarization and electrochemical impedance spectroscopy. The presence of sulfide ions in the chloride solution accelerates the corrosion of Cu-Al-Ni alloys, whereas the increase of the nickel content in the alloy improves its corrosion resistance.β-carotene as eco-friendly corrosion inhibitor was used to protect the Cu-10Al-Ni alloys from corrosion in presence of sulfide ions. The corrosion inhibition efficiency reached >95% at 50 ppm of β-carotene. The alloy surface was investigated by the scanning electron microscope and the surface constituents were analyzed by EDAX.

Keywords: Corrosion; chloride, Cu-Ni alloys; EIS; sulfide pollution.

1. Introduction

The Cu-Ni alloys possess attractive mechanical properties, high thermal and electrical conductivities and good corrosion resistance in a variety of environments at moderately elevated temperatures (60-80 ^{0}C) [1, 2]. The addition of aluminum to these binary alloys improves the light weight of the alloy and increases its corrosion resistance, especially in sea water and salt solutions. It provides good wear properties, better workability and resistance to high temperature oxidation]. The good corrosion resistance of the Cu-Al-Ni alloys is due to the formation of a protective layer of alumina, which builds up quickly on the surface post-exposure to the corrosive environment [3, 4]. The passivation of the alloy is based on the fact that aluminum has a greater affinity toward oxygen than copper and considerable stability of Al_2O_3 than Cu_2O in neutral solutions [5,6]. The essential role of Ni in the passivation of Cu-Ni alloys is attributed to its incorporation into the Cu (I) oxide which is formed as corrosion product during the corrosion of the alloy [7,8]. The incorporation of nickel ions reduces the number of cation vacancies that normally exist in Cu (I) oxide. The substitution of Ni in the Cu (I) oxide increases with the increase in the Ni content of the alloy at least up to 30%. Copper/nickel alloys have tremendous applications indifferent industries, where chloride containing water is always used [9, 10].

The presence of certain pollutants, such as sulfides in the seawater may jeopardize cooling systems. In chloride medium, purged of air, the presence of sulfide ions accelerates the corrosion rate of Cu-Ni alloys[9, 11, 12]. The presence of sulfide ions is reported to be dangerous only when the corroding medium contains dissolved oxygen. Also, Cu-10Ni alloy was found to resist corrosion in seawater free from sulfide, but when 0.01 ppm of sulfide was added to the solution, the corrosion rate became significant. There is a general acceptance that the sulfide ions weakens the protective film by the formation of $Cu(H_2S)_{ads}$ complex or the establishment of sulfur and Cu linkage that weakens Cu and O or (OH) bonding of the barrier film leading to the acceleration of the corrosion process [13, 14].

One of the important methods to combat corrosion is the use of inhibitors. This method was extensively studied to reduce the corrosion of copper and its alloys in water transport systems. A large number of organic compounds ranging from long chain alkyl benzene derivatives to heterocyclic organic compounds containing nitrogen or sulfur were used as inhibitors for the corrosion of copper and copper alloys in different media [15-17].Nowadays, there is an increased attention to the environment and the use of eco-friendly compatible corrosion inhibitors.

In a series of publications, we have investigated the role of Ni in the stability of the passive film formed on the Cu-Ni and Cu-Al-Ni alloys in chloride free, chloride containing and chloride/sulfate neutral solutions, which represent the main solutions for the production of NaCl and Na_2SO_4 by the Emethal Company at Fayoum-Egypt [10, 18-20]. Since these alloys are always used as condenser tubes for heat exchangers and reservoirs for aggressive acidic and basic solutions, it was important to investigate the electrochemical behavior and the role of Ni in the stability of these alloys in chloride solution polluted by sulfide ions [21]. The inhibition of the corrosion process with environmentally friendly compounds was also one of our tasks [22-24].The present work deals essentially with the corrosion inhibition of Cu-Al-Ni with different Ni content in sulfide polluted chloride solutions using natural β-carotene secreted by the alga, which is practically present in large amounts in Quaron Lake water, Fayoum, Egypt]. The artificial culturing of this alga is also undertaken in metallic ponds. The present investigation showed that β-carotene, being an ecologically acceptable natural product, can act as an effective inhibitor for the corrosion of Cu or Cu-Ni alloys.

2. Experimental

The working electrodes were made from commercial grade Cu-Al-Ni rods, mounted into glass tubes by two component epoxy resin leaving a surface area of 0.2 cm^2 to contact the solution. The alloys under investigation were prepared in our metallurgical workshop to match the application in the manufacturing of NaCl from Lake Qaroun in Egypt and the mass spectrometric analysis of these alloys is presented in Table 1 [18].

Table 1: Mass spectrometric analysis for the different electrode materials in mass%.

Sample	Cu	Al	Ni	Zn	Mn	Sn	Fe	Si	Mg	Ti
Cu-Al-05Ni	81.16	11.15	4.98	0.11	0.02	0.14	2.22	0.21	0.01	-----
Cu-Al-10Ni	76.00	11.28	9.95	0.10	0.02	0.14	2.26	0.24	0.01	------
Cu-Al-45Ni	43.31	9.56	46.01	------	------	0.04	0.72	0.35	-----	0.01

β-carotene was obtained as a secretion of the alga, which is present in large amounts in Quaron Lake water, Fayoum, Egypt. The molecular formula of this material is presented in Fig. 1. The electrochemical cell was a three-electrode all-glass cell, with a large area platinum counter electrode and saturated calomel, SCE, reference electrode. Before each experiment, the working electrode was polished mechanically using successive grades emery papers down to 2000 grit. The electrode was washed thoroughly with distilled water, and transferred quickly to the cell. The electrochemical measurements were carried out in a stagnant, naturally aerated neutral 3.5 mass% NaCl solution containing 2 ppm S^{2-}in absences or presence of the inhibitor. Polarization measurements and electrochemical impedance spectroscopic investigations, EIS, were performed using a Voltalab PGZ 100 "*All-in-one*" potentiostat/galvanostat. The potentials were measured against and referred to the standard potential of the SCE(0.245 V vs. the standard hydrogen electrode, SHE). The total impedance, Z, and phase shift, θ, were recorded in the frequency domain 0.1-10^5 Hz. The superimposed ac-signal was 10 mV peak to peak amplitude. The surface morphology and the constituent elements of the surface film were investigated by SEM/EDAX (model ISPECT S 2006, FEI Company, Holland). Each experiment was carried out at least twice and details of experimental procedures are as described elsewhere[25,26].The extraction of β-carotene from a culture of the alga Dunaliella Salina was made using 90vol% acetone and details of the extraction process are presented previously [27].

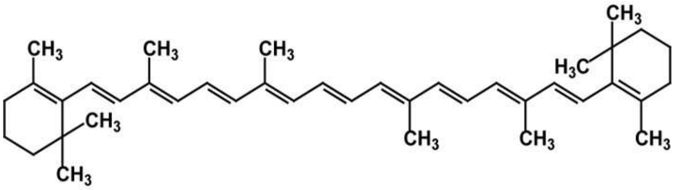

Fig. 1: Chemical structure of β- carotene

3. Results and discussion

3.1. Polarization measurements

The potentiodynamic polarization measurements of the three alloys under investigation were carried out in stagnant naturally aerated neutral 3.5 mass % NaCl solutions containing 2 ppm S^{2-}at a scan rate of 5 mV s^{-1} and 25°C in absence and presence of 50 ppm of β-carotene. Fig. 2 presents a comparison between the three different alloys in chloride solutions containing sulfide, it shows clearly that the increase of the Ni content shifts the corrosion potential towards more positive values and at the same time decreases the corrosion current density. Fig. 3 is typical presentation to show the effect of β-carotene on the polarization curve of Cu-10Al-10Ni alloy. The other two alloys show the same trend.

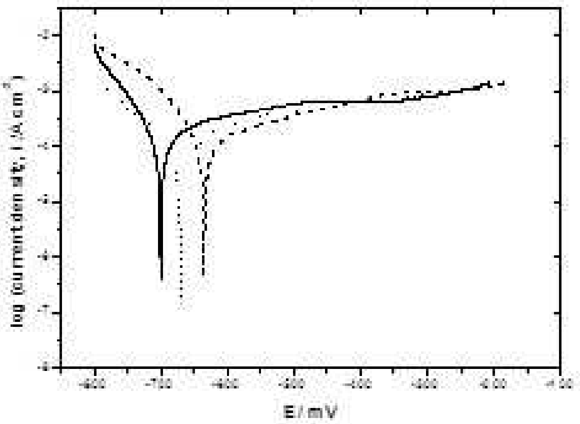

Fig. 2: Potentiodynamic polarization curves for Cu-Al-5Ni (—),Cu-Al-10Ni (---) and Cu-Al-45Ni (…) alloys in a stagnant naturally aerated 3.5 % NaCl solution containing 2 ppm S^{2-} at 25 ◦C.

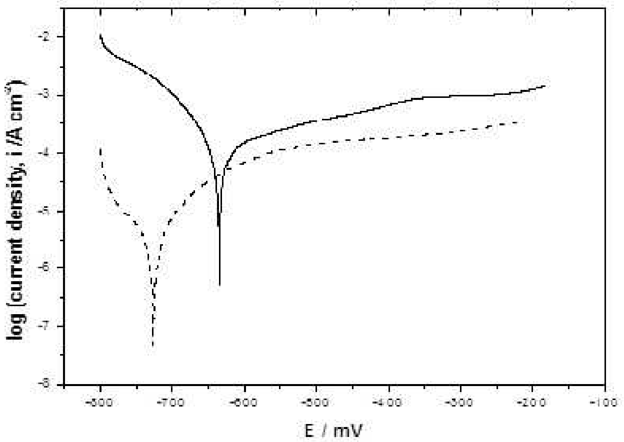

Fig. 3: Potentiodynamic polarization curves for Cu-10Al-10Ni alloy in a stagnant naturally aerated neutral 3.5 % NaCl solution containing 2 ppm S^{2-} in absence (—) and presence (-----) of 50 ppm β-Carotene at 25 ◦C and scan rate of 5 mV s^{-1}.

The corrosion parameters calculated from the different polarization curves i.e. the corrosion potential, E_{corr}, the corrosion current density, i_{corr}, the anodic, $ß_a$ and cathodic, $ß_c$. Tafel slopes of the three alloys are presented in Table 2 for carotene free and Table 3 for carotene containing solutions. The general and clear trend is that i_{corr} decreases remarkably in the presence of β-carotene.

Table 2: Polarization parameters of the different Cu-Al-Ni alloys after electrode immersion in stagnant naturally aerated neutral 3.5 % NaCl containing 2 ppm S^{--} at 25 °C.

Alloys	E_{corr}/ mV	i_{corr} /µA cm^{-2}	$ß_a$/mV	$ß_c$ /mV
Cu-10Al-5Ni	-700	144.3	251	-65.0
Cu-10Al-10Ni	-634	100.5	209	-60.8
Cu-10Al-45Ni	-670	61.8	115	-78.6

The decrease in the corrosion rate by increasing the Ni content was attributed to the incorporation of Ni ions in the mobile vacancies of the Cu_2O film decreasing the possibility of Cu dissolution from the alloy surface [22].

Table 3: Polarization parameters of the different Cu-Al-Ni alloys after electrode immersion in stagnant naturally aerated neutral 3.5 % NaCl containing 2 ppm S^{-} and 50 ppm ß-Carotene at 25 °C.

Alloys	E_{corr}/ mV	i_{corr} /µA cm^{-2}	$ß_a$/mV	$ß_c$ /mV	η %
Cu-10Al-5Ni	-765	5.9	47.5	-18.8	95.9
Cu-10Al-10Ni	-725	3.1	94.6	-85.1	97.4
Cu-10Al-45Ni	-647	1.0	53.3	-46.4	98.2

Fig. 4 shows the collective polarization curves of the three alloys under the same conditions, where the effect of both the Ni content and β-carotene is clear. The presence of ß-carotene in the electrolyte does not change the general features of the polarization curves but remarkably decreases the corrosion current density i.e. the corrosion rate.

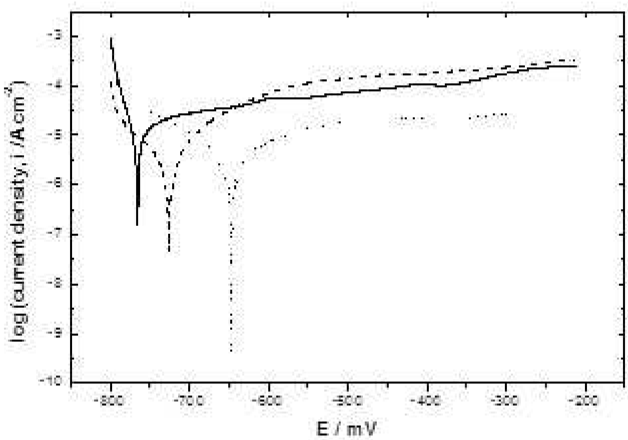

Fig. 4: Potentiodynamic polarization curves for Cu-10Al-5Ni (—), Cu-10Al-10Ni (----) and Cu-10Al-45Ni (……) alloys in a stagnant naturally aerated neutral 3.5 % NaCl solution containing 2 ppm S^{2-} and 50 ppm β-Carotene solution at 25 ◦C and scan rate of 5 mV s^{-1}.

This means that the inhibitor molecules do not affect the mechanism of the corrosion process but decrease both the cathodic and anodic current densities, which means that ß-carotene acts as a mixed inhibitor. The significant decrease of the corrosion rate by the small addition of ß-carotene (50 ppm) indicates clearly that it can act as excellent inhibitor for Cu-Al-Ni alloys regardless of the Ni content. The inhibition corrosion efficiency, η, was also calculated from the values of the measured current densities in absence of inhibitor, i_{corr}, and in its presence r, $i_{corr, inh,}$ according to [24]:

$$\eta = [i_{corr} - i_{corr(inh)}] / i_{corr} \times 100 \qquad (1)$$

The calculated values are included in Table 3 and confirm the strong corrosion inhibition character of ß-carotene.

3.2. Electrochemical impedance spectroscopic investigations, EIS

EIS is a powerful tool for measuring corrosion rates, especially for coatings, passive films and adsorbed layers. An important advantage of this technique is the use ofa small ac signal without significantly disturbing the electrode surface morphology or the properties being recorded. Also, it is possible to simulate the experimental impedance results to pure electronic models that can verify or role out mechanistic models and enable the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system [22, 28-30].

The impedance data of the different alloys recorded after1h of electrode immersion in stagnant, naturally aerated neutral 3.5 mass %NaCl sulfide free, 3.5 mass % NaCl containing 2 ppm S^{2-} ions and 3.5 % NaCl containing 2 ppm S^{2-} ions and 50 ppm ß-carotene solutions for Cu-10Al-45Ni alloy are presented as Bode plots in Fig. 5. The Bode plots of the other two alloys show similar trend. The presented Bode plots show mainly a single phase maximum, especially at higher Ni content (cf. Fig. 5). Also, the increase of the phase angle and broadening of the phase maximum as the Ni content increases indicates a decrease in the corrosion rate of the alloys, which appears clearly in the presence of carotene with the different Ni contents [19, 28]. A clear comparison of the effects of S^{2-} ions and carotene on Cu-Al10-Ni45 is presented in the Nyquist presentation of Fig.6. The other two alloys show the same behavior.

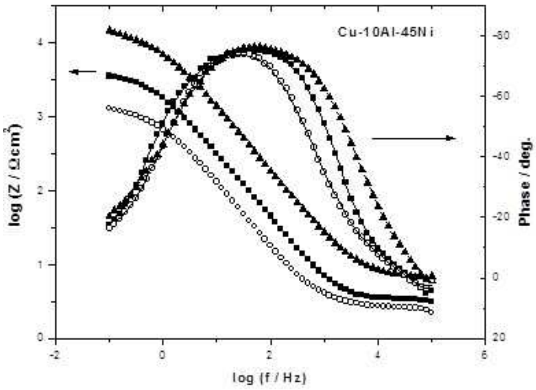

Fig. 5: Bode plots of Cu-10Al-45Ni alloy after 1 h immersion in stagnant naturally aerated 3.5% NaCl (■■■), 3.5% NaCl containing 2 ppm S^{2-}(○○○) and 3.5% NaCl containing 2 ppm S^{2-} and 50 ppm of *β*-carotene (▲▲▲) solutions at 25 ◦C.

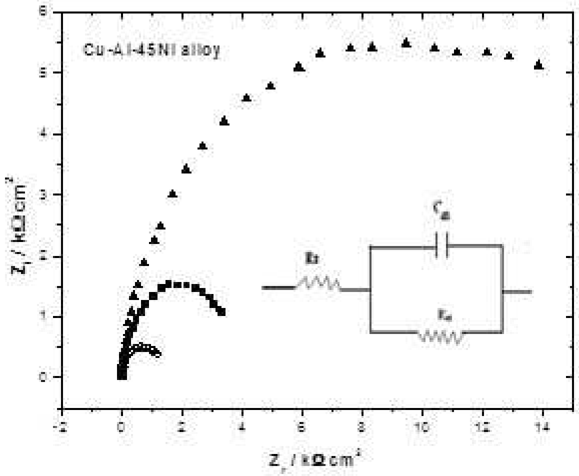

Fig. 6: Nyqusit plots of Cu-10Al-45Ni alloys after 1 h immersion in stagnant naturally aerated 3.5% NaCl (■■■), 3.5% NaCl containing 2 ppm S^{2-} (○○○) and 3.5% NaCl containing 2 ppm $S^{2-}$and 50 ppm of *β*-carotene (▲▲▲) solutions at 25 ◦C.

Fig. 6(inset): Equivalent circuit model used for impedance data fitting. R_s= solution resistance, R_{ct} = charge transfer resistance, C_{dl} = double layer capacitance.

The main features of the Nyquist plot are the presence of a depressed capacitive loop at intermediate frequencies and a single semicircle. This behavior is attributed to a single time constant comprising relaxation effects due to adsorption phenomena and indicates that the corrosion process is under charge transfer control [23, 24,28].The semicircle at high frequency is generally, associated with the relaxation of the double layer capacitance and the diameter of this semicircle represents the charge-transfer resistance [31, 32].

The impedance data were analyzed using software provided with the impedance system where the dispersion formula (Eq. 2) was used. For a simple equivalent circuit model consisting of a parallel combination of a capacitor, C_{dl}, and a resistor, R_{ct}, in series with a resistor, R_s, representing the solution resistance, the electrode impedance, Z, is represented by the mathematical formulation:

$$Z = R_s + [R_{ct}/ \{1+ (2\pi f R_{ct}C_{dl})^{\alpha}\}] \qquad (2)$$

where α denotes an empirical parameter (0 < α < 1) and *f* is the frequency in Hz. This formula takes into account the deviation from the ideal RC-behavior in terms of a distribution of time constants due to surface inhomogeneity, roughness effects, and adsorption phenomena [33, 34]. The experimental impedance data were fitted to theoretical data according to the simple equivalent circuit model shown in Fig. 6 (inset). The procedure of data fitting was carried out for the experimental impedance data obtained for all investigated alloys after 1h immersion in stagnant naturally aerated neutral 3.5 mass % NaCl solutions free and containing 2 ppm $S^{2-}$and presented in Table 4. The equivalent circuit parameters after the addition of 50 ppm β-carotene under the same conditions are presented in Table 5.

Table 4: Equivalent circuit parameters for Cu-Al-Ni alloys after 1h of immersion in 3.5% NaClsolution with and without sulphide ions at 25 °C.

	Alloys	R_s/Ω	R_{ct}/kΩ cm^2	C_{dl}/ µF cm^{-2}	α
3.5% NaCl	Cu-Al-5Ni	1.5	1.33	455.8	0.99
	Cu-Al-10Ni	0.7	1.67	477.7	0.99
	Cu-Al-45Ni	0.95	4.05	76.34	0.99
3.5% NaCl + 2 ppm S^{--}	Cu-Al-5Ni	3.5	0.44	1146	0.99
	Cu-Al-10Ni	3.3	0.91	705.8	1.00
	Cu-Al-45Ni	1.1	1.04	161.2	0.99

Table 5: Equivalent circuit parameters for Cu-Al-Ni alloys after 1h of electrode immersion in 3.5% NaCl + 2 ppm S^{2-} solution in presence of β-carotene at 25 ◦C.

Alloys	R_s/Ω	R_{ct}/kΩ cm^2	C_{dl}/ µFcm^{-2}	α	η%
Cu-Al-5Ni	12.6	13.5	38.1	1.0	96.7
Cu-Al-10Ni	13.3	15.6	28.4	1.0	96.2
Cu-Al-45Ni	5.6	21.9	23.9	0.99	95.3

The value of R_{ct} decreases in presence of sulfide ions but increases as the Ni content increases. The recorded high corrosion resistance values at higher Ni content can be attributed to the formation of a uniform passive layer on the alloy surface that is related to the complex metallurgical structure of alloys of Ni content higher than 30% [10]. The calculated value of α is approximately 1, which means that the barrier layer is behaving like an ideal capacitor [19, 34]. The presence of β-carotene in the solution increases the charge transfer resistance up to 20 times for the high Ni content alloy i.e. from 1.04 to 21.9 kΩ cm^2. At the same time the value of C_{dl} decreases remarkably in the presence of the inhibitor molecules (from 161.2 to 23.9 µFcm^{-2} for the same alloy), which means that the thickness of the double layer was increased due to the adsorption of the inhibitor molecules [22, 23]. The calculated inhibition efficiency exceeds 95%, which means that β-carotene is an effective inhibitor for the corrosion of the Cu-Al-Ni alloys and at the same time it does not change the corrosion mechanism. These results are consistent with those of the polarization experiments.

3.3. SEM and EDAX analysis

The surface of the different investigated alloys after 1h immersion in stagnant naturally aerated neutral 3.5% NaCl solutions containing 2 ppm S^{2-} free and containing 50 ppm β-carotene was investigated by SEM and EDAX. The results show that the presence of sulfide ions leads to the formation of corrosion patterns, mainly localized, and flawed regions which are very remarkable in the low Ni content alloys. EDAX analysis indicates the presence of small S and O peaks beside the Cl, Al, Cu and Ni peaks, which implies that the sulfide ions are also adsorbed on the alloy surface like the chloride ions [21, 30]. The presence of S and O peaks may lead to the acceptance that Cu_2S may be produced, as previously reported [35]. The addition of β-carotene repairs the corrosion spots and flawed regions and the surface morphology becomes smooth. Fig. 7 presents the SEM images of the high Ni content alloy after long immersion in the sulfide containing chloride solution (A) and in the presence of carotene (B).

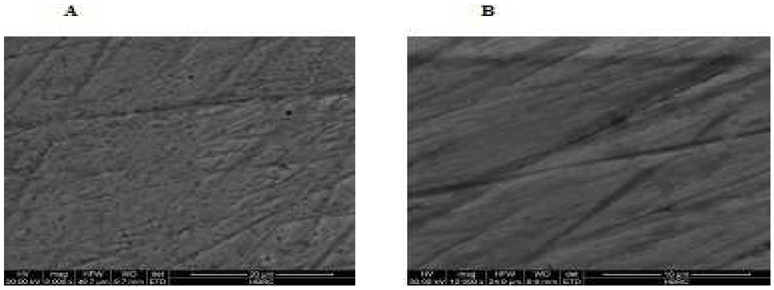

Fig. 7A: SEM images of Cu-10Al-45Ni alloy after 1h immersion in stagnant naturally aerated neutral 3.5% NaCl solution containing 2 ppm S^{2-} at 25 ◦C.

Fig. 7B: Scanning electron micrograph of Cu-10Al-45Ni alloy after 1 h immersion in stagnant naturally aerated neutral 3.5% NaCl solution containing 2 ppm S^{2-} and 50 ppm *β*-carotene at 25 ◦C.

Although the presence of high Ni content decreases the corrosion rate, it is clear that the surface has corrosion spots and flawed regions, which are much more remarkable in the low Ni content alloys. The EDAX analysis of the surface after immersion in sulfide containing solutions is presented in Fig. 8, where the different peaks are clearly recorded. The presence of β-carotene in the solution, for the same time of immersion, leads to a smooth surface in which no corrosion patterns can be recognized (cf. Fig. 8).

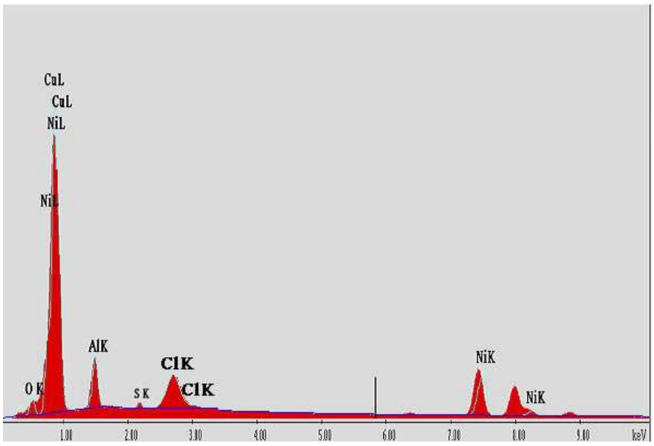

Fig. 8: EDAX analysis of Cu-10Al-45Ni alloy after 1 h immersion in stagnant naturally aerated neutral 3.5% NaCl solution containing 2 ppm S^{2-} at 25 ◦C.

4. General discussion

Generally, the corrosion behavior of the Cu-Al-Ni alloys is based on the common system of oxidation resistant materials, where Al has greater affinity towards oxygen than Cu. Under standard conditions,Al_2O_3 is almost eleven times more stable than Cu_2O relative to their metals in the zero oxidation state [8]. For Cu-10%Al alloys, thermal oxidation is based on a rapid initial production of Cu_2Othen formation of Al_2O_3 at the alloy/oxide interface due to the depletion of Cu [33]. In neutral solutions, alumina forms as a protective oxide which is highly impermeable to the passage of Cu (I) ions which can no longer enter the outermost layer. The higher the aluminum content of the alloy, the greater the corrosion resistance due to the protective Al_2O_3 film since the limiting mole fraction is achieved over a shorter exposure time and is maintained at lower copper dissolution rates [35]. Keeping the Al% constant and changing the ratio of Ni, enrichment of Ni to the metallic surface takes place .Ni is more active than Cu in nucleophilic reaction; it should preferentially dissolve:

$$Ni \rightarrow Ni^{2++} + 2e^- \quad (3)$$

From the reduction of dissolved oxygen, OH^- ions are released according to:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (4)$$

$$2\,Ni + 6OH^- \rightarrow 3H_2O + Ni_2O_3 + 6e^- \quad (5)$$

Ni will passivate the alloy surface [35]. The passive film is a dense oxide film, preventing the exchange of materials on both sides. In Ni-rich alloys, the Ni percent on the surface is much higher than the low Ni content alloys, and hence higher corrosion resistance for copper alloy could be expected. Thus, the initial surface of the alloy is free of Cu_2O and it is covered with a thin Ni_2O_3 and Al_2O_3 film [36, 37]. In this case, Cu will be involved in nucleophilic reactions and reacts with OH^- and Cl^-. The corrosion products can then be CuCl, $CuCl^{-2}$and Cu_2O. The possible reactions [37] of copper alloys are:

$$2\,Cu + 2OH^- \rightarrow Cu_2O + H_2O + 2e^- (6)$$

$$Cu + Cl^- \rightarrow CuCl + e^- \quad (7)$$

Reaction (7) followed by the formation of Cu (I) complex

$$CuCl + Cl^- \rightarrow CuCl_{2-} \quad (8)$$

Cl^- loses electrons easier than OH^- under the same conditions; therefore $CuCl_{2-}$is easily formed and goes into the solution. So during the first minutes of immersion, Cu oxidizes to Cu(I) and nickel will enrich at the alloy surface. The dissolution of Cu(I)species as $CuCl_{2-}$, decreases the Cl^- concentration at the interface leading to the formation of CuCl which hydrolysis to Cu_2O [10]. That is why the Cu (I) was detected in most EDAX spectra. Due to the defective structure of Cu_2O being a p-type semiconductor, it can be further oxidize to Cu (II) species [6, 14].

$$Cu_2O + 3/2O_2 + 2Cl^- + 4H_2O \rightarrow 2Cu\,(OH)_3\,Cl + 2OH^- \,(9)$$

Passivity in chloride solutions is established by the formation of an oxide film consisting of an outer layer of Cu (II) hydroxy-chloride, $Cu(OH)_3Cl$, overlaying a compact inner layer of Cu_2O and impurity oxide [9]. The corrosion product film that consists of $Cu(OH)_3Cl$ andCu_2O, is fragile and easy rupture. After alloy immersion, the surface may crack since some zones mainly composed of impurity oxide, which has been evidenced by SEM analysis as a result of partial dissolution of copper. This is in agreement with a growth mechanism involving selective copper dissolution.

In sulfide containing solution, the S^{2-} ions will damage the passivation layer. The nucleophilic attack of $S^{2-}$is stronger than Cl^-, and so it will be the main nucleophilic factor and will attack the active regions of the alloy forming Cu_2S, which is the most possible corrosion product in sulfide polluted sea water [14].

$$2\,Cu + S^{2-} \rightarrow Cu_2S \qquad (10)$$

Because of the formation of Cu(I) sulfide which is insoluble in water, the surface film becomes fragile and poorly protective, and hence the process of corrosion is accelerated. The presence of β-carotene in the solution suppresses the corrosion process by blocking the active corrosion centers and flawed or fragile regions by the adsorption of its molecules on the alloy surface as was clearly presented by the polarization, impedance and SEM results. The effect of the inhibitor is very clear on the recorded values of the charge transfer resistance, R_{ct}, and also the double layer capacitance, C_{dl}, as presented in tables 4 and 5.

The double layer capacitance was calculated using Eq. 11 [38]:

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \qquad (11)$$

where f_{max} is the frequency value at which the imaginary component (Z″) of impedance is maximum [28]. The increase of R_{ct} values is ascribed to the adsorption of β-carotene, which displaces water molecules or any other anions originally adsorbed on the alloy surface. Thus, a protective film is formed, which impedes the charge-transfer across the metal/solution interface and hence the corrosion process is suppressed On the other hand, the decrease in the value of C_{dl} could be related to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [19]. Since the value of $(1/R_{ct})$ is directly proportional to the corrosion rate, the inhibition efficiency (η %) of β-carotene can be calculated from R_{ct} values obtained from impedance data using the following equation [28].

$$\eta\,\% = [1 - (R_{ct}/R^{o}_{ct})] \qquad (12)$$

where R_{ct} and R^{o}_{ct} are the charge-transfer values calculated in presence and in absence of the inhibitor, respectively. At a low concentration of 50 ppm of β-carotene, the three investigated alloys show higher corrosion resistance, especially Cu-Al-45Ni alloy. Either the polarization curves or the impedance diagrams did not show remarkable changes in the general trend after the addition of the inhibitor, which emphasizes that, no change in the corrosion mechanism occurs due to the inhibitor addition.

4. Conclusions

The corrosion resistance of the Cu-10Al-xNi alloy in the chloride solutions polluted with sulfide ions increases with the increase of the Ni content. The high Ni content leads to the enrichment of the surface with Ni, which decreases the vacancies in the Cu (I) oxide and hence increases the alloy corrosion resistance. The presence of sulfide ions in the chloride solution decreases the corrosion resistance of the Cu-Al-Ni alloys. The addition of small concentration of β-carotene was found to decrease the rate of corrosion of the Cu-Al-Ni alloys in the chloride solutions containing sulfide ions. A corrosion inhibition efficiency of 95-99%at a concentration of 50 ppm of carotene was recorded.

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