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Role of Ni content in improvement of corrosion resistance of Zn–Ni alloy in 3.5% NaCl solution. Part I: Polarization and impedance studies

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Abstract: Zn plays an important role in the protection of iron and steel from corrosion in sea water, and the alloying of Zn and Ni can improve its corrosion resistance. The corrosion behavior of Zn–Ni alloys in synthetic sea water (3.5% NaCl, mass fraction) was studied using Tafel plot and electrochemical impedance spectroscopy (EIS) techniques. The corrosion resistance of the investigated alloys with various Ni contents (0.5%–10%, mass fraction) was compared with that of Zn. The results show that the corrosion resistance of Zn–Ni alloys (except 0.5% Ni) is superior to that of Zn. The 10% Ni gives the highest corrosion resistance due to the formation of γ -Zn₃Ni with γ -ZnNi phases in the alloy. In the case of alloy I (0.5% Ni), it exhibits a higher corrosion rate (less corrosion resistance) than Zn.

Key words: Zn-Ni alloy; Ni content; corrosion resistance; Cl⁻ ions; impedance; polarization

1 Introduction

Zn has been used to protect iron and steel from corrosion for long periods. Galvanostatic protection of iron or steel by Zn can take place by two methods: coating the ferrous metal with a thin layer of Zn, or attaching a sacrificial Zn anode to the steel structure in the presence of an electrolyte such as sea water (3.5% NaCl, mass fraction) or moist soils [1-6]. Historically, only commercial Zn grades were used for coating. As it is known, Zn corrosion in aqueous solution is cathodically controlled, so the rate of the cathodic hydrogen evolution limits the Zn corrosion rate. Hence, the best way to slow down the corrosion process is to reduce the hydrogen evolution rate, which can be achieved by the introduction of a small amount of Hg into Zn. However, from the ecological point of view, the use of very toxic Hg is harmful. Apart from Hg, an insignificant amount of other metals such as Bi, Pb, Al and In can be used to hinder the anodic corrosion of Zn [7]. Therefore, Zn alloys have become important because of great corrosion protection, superior engineering properties such as formability, and their ability to successfully coat different steel compositions. Zn-Ni coatings have received more attention than Zn coatings because of their higher degree of corrosion resistance to NaCl in the atmospheric environment [8]. Zn-Ni alloys have been widely used in the trades of ship craft, auto, aviation, electron and so on [9]. So they have a widespread availability foreground because of their excellent characteristic of high corrosion resistance, low hydrogen brittleness, welding capacity and machining properties [10]. Recently, the corrosion behavior of Zn in NaCl and NaOH solutions has been studied by MOUANGA et al [11,12]. They showed that the corrosion layer on surface is porous and much hydrated in NaCl solution. In spite of the presence of so many publications on the corrosion behavior of Zn-Ni alloys electro-deposition in aqueous solutions, there is nothing work on the electrochemical and corrosion behavior of synthetic Zn-Ni alloys by fusion. The aim of this work is to study the role of Ni content in the improvement of corrosion resistance of Zn-Ni alloy in synthetic sea water (3.5% NaCl). Part I (this work) deals with the electrochemical studies such as Tafel plot and electrochemical impedance spectroscopy (EIS). The obtained data using two investigated techniques were analyzed and compared. Part II deals with the anodic polarization of the same investigated metals and alloys in 3.5% NaCl solution using both galvanostatic and potentiodynamic measurements. The corrosion layer

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2808

formed on both Zn and alloy surfaces, under different anodic polarization potentials, in the examined solution were characterized using scanning electron microscopy (SEM).

2 Experimental

2.1 Materials and solution

Solution of 3.5% NaCl (analytical grade) was prepared by dissolving the appropriate mass of NaCl in double distilled water. High purity Zn and Ni (99.999%; Johnson Matthey Chemicals Ltd.) were used to prepare Zn–Ni alloys as disk electrodes (0.196 cm²) in a Gallenkamp muffle furnace using evacuated closed silica tubes at 850 °C for 24 h. The melts were shaken every 6 h to ensure the homogeneity of melting alloys and finally quenched in ice water as previously discussed [13]. Four Zn–Ni alloys were prepared with the Ni content listed in Table 1.

Table 1 Ni content in Zn–Ni alloys (mass fraction, %)

Alloy No.	Ι	II	III	IV
Ni content	0.5	2	2	10

The prepared alloys were analyzed using X-ray photoelectron spectroscopy. For the alloys, the fractions of Zn and Ni were found in accordance with the fraction of mixing Zn and Ni. The microstructure of the studied alloys was investigated in the previous work [14] using X-ray diffraction and SEM micrographs. The data of X-ray diffraction exhibited that, alloys I and II contain one intermetallic compound (γ -Zn₃Ni) in addition to Zn as the separated elemental phase. While, alloys III and IV contain two intermetallic compounds (γ -Zn₃Ni and γ -ZnNi) in addition to the Zn matrix.

2.2 Electrochemical measurements

The measurements were performed on planar disk electrodes embedded in an Araldite holder. Before each experiment, the surfaces of the working electrodes were polished with a series of emery paper (grade 320–400–600–800–1000–1200) and then by polishing cloth (polishing machine; Buehler, Lake Bluff, Illinois USA) until their surfaces became smooth and mirror like bright. Then the working electrodes were degreased in pure ethanol and washed in running bidistilled water before being inserted in the polarization cell. The reference electrode was a saturated calomel electrode (SCE) to which all potentials were referred.

The cell description was given elsewhere [15]. To remove any surface contamination and oxide, the working electrode was kept at -1500 mV (vs SCE) for 5 min in the tested solution, disconnected, and shaken free of adsorbed hydrogen bubbles. The stabilization

period before measurements was 45 min (steady state of open circuit potential). Then cathodic and anodic polarization was recorded. A potentiostat/Galvanostat (EG&G Model 273) connected with a personal computer (IBM Model 30) was used for the measurements. Before measurement, the electrode was immersed in aerated NaCl solution without stirring at natural potential for 1 h until a steady state was reached.

2.2.1 Tafel polarization technique

The extrapolation of cathodic and anodic Tafel lines was carried out in a potential range of ±200 mV with respect to the corrosion potential (φ_{corr}) at scan rate of 1 mV/s using software version 342C supplied from EG&G Princeton Applied Research. Each experiment was performed with freshly prepared solution and a set of clean electrodes. The measurements were conducted at (25±0.5), (35±0.5), (45±0.5) and (55±0.5) °C for each investigated electrode in the examined solution. For this purpose, an ultrathermostat model Frigiter 6000 382 (SELECTA) was used.

2.2.2 Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) measurements were performed with a phase-sensitive detector (amplifier) (Model 5208) driven by a potentiostat/galvanostat apparatus (Model 273) from EG&G Instruments. The electrochemical software of this model is 378. Each electrode was held at both open circuit potential (OCP) and ± 100 mV (vs OCP) for 10 min, in order to reach steady state before the impedance measurements. The EIS was acquired at different applied potentials (0 and ± 100 mV (vs OCP)) in the frequency ranging from 100 kHz to 5 Hz with a 5 mV amplitude sine wave generated by a frequency response analyzer.

3 Results and discussion

3.1 Tafel plot measurements

Figures 1-4 show the polarization curves of Zn, Ni,



Fig. 1 Tafel polarization curves for pure Zn in 3.5% NaCl solution at different temperatures



Fig. 2 Tafel polarization curves for pure Ni in 3.5% NaCl solution at different temperatures



Fig. 3 Tafel polarization curves for alloy I in 3.5% NaCl solution at different temperatures



Fig. 4 Tafel polarization curves for alloy IV in 3.5% NaCl solution at different temperatures

alloys I and IV (as representative alloys) in synthetic sea water (3.5% NaCl) at different temperatures and scan rate of 1 mV/s. The corrosion parameters were calculated on the basis of cathodic and anodic potential versus the current density characteristics in the Tafel plot potential region [16]. The values of the corrosion current density (J_{corr}) for Zn, Ni and Zn–Ni alloys (I–IV) were determined by the extrapolation of the cathodic and anodic Tafel lines to the corrosion potential (φ_{corr}). A marked shift in both cathodic and anodic branches of the polarization curves towards high current densities is observed as the temperature increases. This indicates that the rate of hydrogen evolution reaction and anodic dissolution increases with increasing the temperature.

The corrosion mechanism of Zn–Ni alloy in 3.5% NaCl solution can be suggested as follows.

The anodic dissolution of Zn,

$$Zn \rightarrow Zn^{2+} + 2e$$
 (1)

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2$$
⁽²⁾

and/or

$$Zn^{2+}+2Cl^{-} \rightarrow ZnCl_2$$
(3)

and the cathodic process, which is the reduction of molecular oxygen:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{4}$$

LIN and HUANG [17] illustrated that the compositions of the rust layer on the surface of electroplating Zn–Ni alloy were $Zn(OH)_2$ and $ZnCl_2$, which confirmed the products of corrosion mechanism. Therefore, both processes were markedly retarded by the addition of Ni to Zn metal to form Zn–Ni alloy which is not easily attacked by CI^- ions.

But, in the case of Ni, the results show that the cathodic and anodic branches seem to be equal. This indicates that the rate of both hydrogen evolution and anodic dissolution are approximately equal, maybe due to the fact that Ni has ability to resist the corrosive action of Cl^{-} ions. Consequently, the dissolution process of Ni to Ni²⁺ ions in NaCl solution is slow. Accordingly, Ni exhibits high corrosion resistance in aqueous aggressive environments. This means that, the anodic dissolution and hydrogen evolution processes are slow on the surface [18].

The comparison among Tafel plots of both Zn and investigated alloys in 3.5% NaCl solution at 25 °C is shown in Fig. 5. It is observed that the cathodic and anodic branches shift to lower current densities in the case of alloys (except alloy I) compared with those of pure Zn, and the shift increases with increasing the Ni content. Therefore, compared with Zn, the positive shift of corrosion potential (φ_{corr}) with the simultaneous decrease of corrosion rate of alloys (except alloy I) can be ascribed to the polarization action of γ -Zn₃Ni phase. This phase was recorded using X-ray diffraction on the alloy surface [14]. Since the hydrogen overpotential on the particles of γ -Zn₃Ni phase may be higher than that of pure Zn [19]. It is concluded that the presence of γ -Zn₃Ni phase in the alloy as a separated phase or in pearlitic structure acts as the cathodic sites on the alloy surface. Therefore, it is assumed that the presence of Ni as alloying element decreases the density of active sites on the alloy surface and the amount of these active sites decreases with increasing the Ni content. This behavior can be interpreted on the basis that the increase of Ni content in the alloy leads to higher formation of γ -Zn₃Ni phase (alloy II) or γ -Zn₃Ni and γ -ZnNi phases (alloys III and IV). Consequently, the corrosion resistance against the attack of Cl⁻ ions is improved. CHOUCHANCE et al [20] demonstrated that, the solid solution of Zn which contains more Ni content could be more efficient against corrosion in NaCl solution.



Fig. 5 Comparison between Tafel polarization curves of pure Zn and Zn–Ni alloys in 3.5% NaCl (mass fraction) solution at $25 \text{ }^{\circ}\text{C}$

However, in the case of alloy I (0.5% Ni), it is observed that the cathodic and anodic branches shift to higher current densities compared with those of pure Zn, It is assumed that the presence of Ni as a minor alloying element increases the density of active sites on the surface, and consequently increases the rate of both hydrogen evolution reaction and anodic dissolution [21]. Accordingly, the higher corrosion rate of alloy I (0.5% Ni) compared with that of pure Zn and the investigated alloys (II-IV) can be attributed to lower formation of y-Zn₃Ni phase in the alloy, leading to heterogeneous surface [22]. Consequently, the depolarization action is higher, and the attack of active sites on the alloy surface by Cl⁻ ions is easier at lower Ni content (0.5% Ni). In addition, the roughness factor describes the initial surface irregularity. Therefore, the rough surfaces expose more weekly bonded sites and exhibit higher dissolution rates, particularly in the presence of corrosive medium [20].

The polarization results (Table 2) exhibit that the corrosion current density (J_{corr}) values decrease, while the φ_{corr} values shift to positive direction with increasing the Ni content (except alloy I). Therefore, the corrosion

current density values of both alloy IV (10% Ni) and pure Zn are 7.3 and 115 μ A/cm², respectively, in synthetic sea water (3.5% NaCl) at 25 °C. This behavior shows that the addition of 10% Ni (mass fraction) to Zn leads to the corrosion rate of alloy IV significantly reduced by a factor of 15 times. This indicates that, as a result of increasing Ni content in the alloy, the aggressive action of Cl⁻ ions on the alloy surface is suppressed. This result can be interpreted on the basis that, the presence of Ni content in the alloy plays an important role to suppress the corrosion rate of Zn–Ni alloy. Thus, the alloy with high content of Ni (10%) presents more noble corrosion potential and low corrosion rate, and this is in agreement with the previous study [23].

The data exhibit that, the corrosion current density (J_{corr}) increases, while φ_{corr} shifts to more positive potentials with rising the temperature for all the investigated metals and alloys. This behavior could be attributed to the increase of rate of both hydrogen evolution reaction and anodic dissolution with increasing the temperature. The results show that an increase in the temperature accelerates the rate of diffusion and migration of the reactant and product species [24], and consequently the corrosion reactions increase. Such effects of temperature on cathodic and anodic processes may be attributed to the increase of both catalytic hydrogen evolution reaction and solubility of Zn or Ni with increasing the temperature. However, in the case of this investigated alloy (10% Ni), the corrosion current density value (36.6 μ A/cm²) is very low compared with that of pure Zn (992 µA/cm²) at 55 °C. This behavior exhibits that the addition of Ni (10%) to Zn has ability to reduce the corrosion rate of Zn in 3.5% NaCl solution, approximately by a factor of 27 times. This indicates that the presence of Ni with Zn (10% Ni) to form Zn-Ni alloy reduces the corrosion rate by 96%. Therefore, the results reveal that the effect of aggressive anions on the general corrosion of alloy IV may be negligible compared with that of Zn in NaCl solution. This result can be interpreted by the increased corrosion resistance of the alloy compared with the base metal [25] in 3.5% NaCl solution at 55 °C. Consequently, as a result of very high corrosion resistance of Zn-Ni alloy (10% Ni) in 3.5% NaCl compared with that of Zn particularly at high temperature (55 °C), the mentioned alloy can be used in different applications instead of Zn [8]. This behavior can be interpreted on the basis that the increase of γ -Zn₃Ni with γ -ZnNi phases in the alloy [14] leads to the improvement of corrosion resistance. This is due to the fact that the density of active sites on the alloys surface is significantly reduced compared with that of Zn. In other words, the presence of γ -Zn₃Ni and γ -Zn₂Ni phases in the alloy have the ability to resist the aggressive Cl⁻ ions.

The values of Tafel slopes $(b_a \text{ and } b_c)$ show that

Table 2 Corrosion parameters obtained from Tafel polarization for pure Zn, Ni and Zn-Ni alloys in 3.5% NaCl solution at different temperatures

Metal or alloy	t/°C	$-\varphi_{\rm corr}$ (vs SCE)/mV	$J_{\rm corr}/(\mu {\rm A}{\cdot}{\rm cm}^{-2})$	$b_{\rm a}/({\rm mV}{\cdot}{\rm dec}^{-1})$	$-b_{\rm c}/({\rm mV}\cdot{\rm dec}^{-1})$	α
Pure Zn	25	1075	115	52	142	0.41
	35	1072	232	53	143	0.43
	45	1066	403	53	143	0.44
	55	1063	992	54	144	0.45
	25	262	0.38	101	180	0.33
Pure	35	261	0.49	102	182	0.33
Ni	45	258	0.64	102	183	0.34
	55	256	0.86	103	183	0.34
Alloy I (0.5% Ni)	25	1057	221	60	108	0.54
	35	1052	502	60	108	0.55
	45	1050	749	61	109	0.56
	55	1048	1096	61	109	0.56
	25	1050	75	69	129	0.45
Alloy II	35	1047	121	69	129	0.46
(2.0% Ni)	45	1045	244	70	129	0.47
	55	1042	441	70	130	0.47
Alloy III (5.0% Ni)	25	1044	54	75	145	0.40
	35	1042	90	76	145	0.41
	45	1040	148	76	145	0.42
	55	1038	242	76	145	0.42
Alloy IV (10.0% Ni)	25	1032	7.30	80	159	0.37
	35	1030	12.18	81	159	0.37
	45	1028	22.10	82	160	0.38
	55	1027	36.60	83	161	0.38

these values of b_a and b_c (Table 2) increase with increasing the Ni content, and seem to not be changed with rising the temperature. However, the cathodic Tafel slopes (b_c) are found to be greater than the corresponding anodic Tafel slopes (b_a). These observations are correlated with the fact that the cathodic exchange current density values are less than those of the anodic counter parts. The corresponding value for the cathodic transfer coefficient (α) lies between 0.45 and 0.40 in the case of Zn and alloys I–III, indicating that the processes correspond to a simple discharge mechanism for hydrogen evolution reaction [19].

3.2 Effect of Ni content on activation energy

The Arrhenius plots for Zn, Ni and the investigated Zn–Ni alloys in 3.5% NaCl solution are shown in Fig. 6. The activation energy can be obtained by Arrhenius equation:

$$\lg J_{\rm corr} = \lg A - \frac{E_{\rm a}}{2.303RT} \tag{5}$$

where A is the prexponential constant, E_{a} is the apparent activation energy, R is the universal gas constant and T is the thermodynamic temperature. The values of apparent activation energy (E_a) of Zn, Ni and their alloys for corrosion, determined from the slope of lg $J_{\rm corr}$ versus 1/T plots, are given in Table 3. The data show that, the value of apparent activation energy (E_a) of Ni is higher than those of both Zn and the investigated alloys, indicating that Ni has the highest corrosion resistance in NaCl solution. However, the activation energy values of alloys II-IV are higher than that of Zn, and increase with increasing the Ni content in the alloy. The maximum value is obtained in the case of alloy IV. This behavior may be attributed to the presence of γ -Zn₃Ni phase which enhances the activation energy barrier of the corrosion [19]. The increase of activation energy values of Zn-Ni alloys with increasing the Ni content can be interpreted on the basis of phase type formed in the alloy. The X-ray diffraction exhibited that alloys I and II contain one phase (y-Zn₃Ni), while alloys III and IV contain two phases (y-Zn₃Ni and y-ZnNi) [14]. Therefore, the

presence of one phase in alloy II and two phases in alloys III and IV enhances the activation energy barrier of the corrosion, whereby reduces the corrosion rate [16]. The higher values of E_a of Zn–Ni alloys (II–IV) run parallel with their lower corrosion rates. This behavior may be ascribed to the lower active sites and/or the decrease of anodic to cathodic area ratio [26]. However, the value of E_a of alloy I is lower than that of pure Zn, indicating that alloy I has the lowest corrosion rate. This value supports the result that the corrosion rate of alloy I is higher compared with that of Zn.



Fig. 6 Arrhenius plots for pure Zn, Ni and Zn–Ni alloys corrosion in 3.5% NaCl solution

Table 3 Apparent activation energy of Zn, Ni and their alloys in3.5% NaCl solution

Metal or alloy	$E_{\rm a}/({\rm kJ}\cdot{\rm mol}^{-1})$	
Zn	17.22	
Ni	35.20	
Alloy I	16.51	
Alloy II	20.50	
Alloy III	22.10	
Alloy IV	24.05	

3.3 Electrochemical impedance spectroscopy (EIS)

In order to get more information about the effect of Ni content on the corrosion resistance of Zn–Ni alloy in 3.5% NaCl solution, the impedance measurements were studied and compared with the results obtained from Tafel plots. The impedance of Zn, Ni and the investigated alloys were studied in 3.5% NaCl solution at different applied potential values around the steady state of open circuit potential (OCP). Figures 7–10 show the Nyquist plots of Zn, Ni and alloys I and IV (as representative alloys) at potential selected from –100 to +100 mV with respect to the OCP, in order to confirm that the anodic process of the investigated electrodes is higher than the cathodic one (similar trend to that



Fig. 7 Nyquist plot for pure Zn in 3.5% NaCl solution at different applied potentials and 25 °C (Amplitude of AC is 5 mV and frequency ranges from 100 kHz to 5 Hz)



Fig. 8 Nyquist plot for pure Ni in 3.5% NaCl solution at different applied potentials and 25 °C (Amplitude of AC is 5 mV and frequency ranges from 100 kHz to 5 Hz)



Fig. 9 Nyquist plot for alloy I in 3.5% NaCl solution at different applied potentials and 25 °C (Amplitude of AC is 5 mV and frequency ranges from 100 kHz to 5 Hz)



Fig. 10 Nyquist plot for alloy IV in 3.5% NaCl solution at different applied potentials and 25 °C (Amplitude of AC is 5 mV and frequency ranges from 100 kHz to 5 Hz)

observed in the Tafel plots). An analysis of the impedance in the examined potential range was made. The data of the charge transfer resistance (R_{ct}) and the capacity of double layer (C_{dl}) were estimated using both the Nyquist and Bode plots of the impedance spectrum (Table 4). However, the Warburg impedance (Z_w) was determined from the following equations [27]:

$$Z_{\rm w} = \sigma \frac{1}{\omega^{1/2}} - j \frac{\sigma}{\omega^{1/2}} \tag{6}$$

$$|Z_{\rm w}| = \sqrt{2}\sigma/\omega^{1/2} \tag{7}$$

The Warburg coefficient, σ , can be determined from the slope of the Warburg plot (the slope of $(|Z_w|$ versus $1/\omega^{1/2}$, $\omega=2\pi f$), or by fitting to an equivalent circuit model which includes a Warburg impedance. However, most equivalent circuit modeling programs return " Z_w " rather than σ (Table 4). The value of σ can be calculated from the following equation:

$$\sigma = \frac{\sqrt{2}}{2} |Z_{\rm w}| \,\omega^{1/2} \tag{8}$$

Table 4 Impedance parameters obtained for corrosion of pure Ni, Zn and Zn–Ni alloys in 3.5% NaCl solution at OCP and 298 K (25 °C)

Metal or alloy	$R_{\rm ct}/$	$C_{\rm dl}/(10^{-9}{\rm F}{\rm \cdot cm}^{-2})$	$Z_{\rm w}/$
	(32 CIII)	(10 1 cm)	(32 CIII)
Pure Zn	95	167	0.669
Alloy I	78.5	202	0.827
Alloy II	135	117	1.157
Alloy III	183	87	1.305
Alloy IV	415	38	1.978
Pure Ni	10000	1.5	_

The recorded spectra show one capacitive loop at high frequency range (HF) followed by the Warburg tail at low frequency values (LF), as can be seen in the case of Zn and the investigated alloys (Figs. 7, 9, and 10). The Warburg impedance observed can be attributed to the diffusion of soluble metal species from the electrode surface to the bulk solution.

The equivalent model used to fit the experimental data is shown in Fig. 11 as previously reported [28]. The measured complex plane impedance plot is similar to that calculated results by the equivalent circuit model. The charge transfer resistance (R_{ct}) , the Warburg impedance (Z_w) and the capacity of the double layer (C_{dl}) are determined by the analysis of the complex plane impedance plot and the equivalent circuit model. It is observed that, the values of R_{ct} and Z_w decrease, while the values of C_{dl} increase with shift the potential to the positive direction. This indicates that the corrosion process at the anodic potential is higher than that at the cathodic one. This behavior can be attributed to the fact that the potential of anodic dissolution process (+100 mV vs OCP) is higher than that of cathodic hydrogen evolution reaction (-100 mV vs OCP). Therefore, the data of the Tafel extrapolation are in agreement with the impedance parameters. That is, the charge transfer resistance is lower, while the capacitance of double layer $(C_{\rm dl})$ is higher at more positive potential (+100 mV vs OCP) compared with those at more negative potential (-100 mV vs OCP) under the same conditions. On the other hand, it is observed that Nyquist plots for Zn and the investigated alloys in NaCl solution seem not to be changed in the shape of impedance plot. But, the values of impedance parameters are different at the same examined potentials.



Fig. 11 Equivalent circuit model used to fit impedance data

This behavior can be discussed on the basis that, the spectra presented in Fig. 12 show at least two time constants. The first time constant recorded at high frequency, where the properties of electrode/electrolyte interfaces are particularly reflected, displays as a depressed incomplete semicircle. The electrical equivalent circuit (EEC) parameters, describing the process included in this time constant, are $R_{\rm ct}$ and $C_{\rm dl}$. The second time constant, depicted at low frequency, corresponds to a straight line (Fig. 12). This linear dependence between the imaginary and real parts of the capacitance is related to the diffusion process of soluble

species (Zn or Ni ions), which is called Warburg impedance. Therefore, the EEC parameters describing the process included in the second time constant clearly indicate the diffusion control of the soluble species from the electrode surface to the bulk of solution [29,30]. Consequently, the impedance measurements show that the corrosion process is controlled not only by charge transfer, but also by the diffusion process [31].



Fig. 12 Comparison between Nyquist plots of pure Zn and Zn–Ni alloys in 3.5% NaCl solution at OCP and 25 °C (Amplitude of AC is 5 mV and frequency ranges from 100 kHz to 5 Hz)

The Nyquist plots of Zn and the investigated alloys (I-IV) in 3.5% NaCl at OCP and 25 °C are compared (Fig. 12). It is found that the semicircle diameter increases with increasing the Ni content (except alloy I) in the alloy. The maximum semicircle diameter is obtained in alloy IV (10% Ni). This behavior exhibits very important result that the Ni content in the alloy has significant influence on the decrease of corrosion rate in NaCl solution. Consequently, the corrosion resistance increases as the Ni content increases (except 0.5% Ni) in the alloy. This is beneficial because it leads to low loss of anode material and a small penetration of hydrogen into steel causing hydrogen embrittlement [32]. Also, in that respect, the alloy should provide a better protection than pure Zn, as used for sacrificial anodes of anticorrosion paint.

Table 4 presents the values of charge transfer resistance (R_{ct}), the Warburg resistance (Z_w) and the capacity of double layer (C_{dl}) of Zn, Ni and the investigated alloys, which were estimated from the impedance measurements at OCP. It is observed that the R_{ct} and Z_w values increase, while the C_{dl} values decrease with increasing the Ni content (except 0.5% Ni) in the alloy. Accordingly, the results show that the corrosion resistance of Zn–Ni alloy is superior to that of Zn in Cl⁻ ions, and 10% Ni content in the alloy gives high corrosion resistance [16]. The superior corrosion resistance observed for the investigated alloys (II-IV) compared with Zn could be explained by the barrier protection mechanism theory (acts as barrier to further attack). As mentioned above (Tafel plot), this behavior can be attributed to the presence of single phase $(\gamma - Zn_3Ni)$ structure in alloy II and two phases $(\gamma - Zn_3Ni)$ and γ -ZnNi) in alloys III and IV. Hence, the high content of two phases in the alloy IV improves its stability against corrosion. SOHI and JALALI [33] showed that the presence of γ phase in the electrodeposited Zn–Ni alloy improves its corrosion resistance and shows the lowest self-corrosion rate. This means that the presence of y-Zn₃Ni and y-ZnNi in the alloy IV have significant effects on the retarding of both cathodic evolution reaction and anodic dissolution of the alloy in NaCl solution.

However, Alloy I exhibits opposite behavior of those mentioned alloys (II-IV). That is, lower semicircle is observed compared with those of both Zn and other investigated alloys. The data in Table 4 exhibit that the charge transfer resistance (R_{ct}) of this alloy (I) is less than those of Zn and alloys II, III and IV. This trend is in good agreement with that obtained from the Tafel measurements. In other words, the corrosion current density gradually decreases (using Tafel plot technique), while the charge transfer resistance increases and the capacity of double layer decreases (using impedance technique) as the Ni content increase in the alloy. This behavior is attributed to the solid solution effect and the precipitation of γ -Zn₃Ni in the Zn matrix [14]. The addition of Ni into Zn is found to refine the effective grain size and consequently improve the corrosion resistance. The effect of Ni content on the corrosion resistance of electrodeposited Zn-Ni alloy was studied by LIN and HUANG [17]. They found that finer grain size provides greater corrosion resistance.

4 Conclusions

1) Zn–Ni alloys have better corrosion resistance in synthetic sea water (3.5% NaCl) than pure Zn, and Zn–10%Ni has the best corrosion resistance. The effect of aggressive anions on the general corrosion of alloy IV may be negligible compared with that of pure Zn in NaCl solution.

2) The observed corrosion resistance of Zn–Ni alloy is due to the formation of γ -Zn₃Ni phase in alloy II and γ -Zn₃Ni with γ -ZnNi phases in alloys III and IV.

3) The corrosion rate of Zn-10%Ni in 3.5% NaCl solution at both 25 and 55 °C is significantly reduced by a factor of 15 and 27 times, respectively, compared with those of pure Zn at the same temperatures. Therefore, the corrosion resistance of Zn-Ni alloy suggests that it can be used in different applications in NaCl medium,

particularly at high temperature.

4) The impedance measurements show that the corrosion process is controlled not only by charge transfer, but also by the diffusion process. The data obtained from Tafel plot are in agreement with the parameters of impedance measurements. The activation energy (E_a) of alloy increases with increasing the Ni content, and this runs with its low corrosion rate.

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Ni 含量对提高 Zn-Ni 合金在 3.5%NaCl 溶液中 耐腐蚀性能的影响(I):极化和阻抗研究

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摘 要: Zn 在保护钢铁材料不被海水腐蚀方面发挥重要作用。Zn 和 Ni 的合金化能改善它的耐腐蚀性能。通过 Tafel 曲线和电化学阻抗谱(EIS)研究 Zn-Ni 合金在合成海水(3.5% NaCl,质量分数)中的腐蚀行为,并比较不同 Ni 含量(0.5%~10%,质量分数)合金和纯 Zn 的耐腐蚀性能。结果表明:Zn-Ni 合金的耐腐蚀性能优于纯 Zn,只有 Ni 含量为 0.5%的合金除外。Ni 含量为 10%的合金具有最好的耐腐蚀性能,这是由于在合金中形成了 γ-Zn₃Ni 和 γ-ZnNi 相。但 Ni 含量为 0.5%的合金比纯 Zn 具有更高的腐蚀速率(更差的耐腐蚀性能)。 关键词:Zn-Ni 合金; Ni 含量; 耐腐蚀性能;Cl⁻离子;阻抗;极化

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