Effect of nickel content on the anodic dissolution and passivation of zinc–nickel alloys in alkaline solutions by potentiodynamic and potentiostatic techniques

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Abstract. The effect of systematic increase of Ni on the anodic dissolution and passivation of Zn–Ni alloys in various concentrations of KOH solution (0.1–1 M) was investigated. The anodic dissolution and passivation behaviour for each pure Zn and Ni in the same studied solutions was also investigated, and the obtained data were compared. Potentiodynamic and potentiostatic methods were used, and the corrosion layer formed on each electrode surface was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results of the anodic potentiodynamic measurements exhibited that the polarization curves showed active/passive transition in the case of Ni and active/pseudopassive in the case of both Zn and its alloys. The results showed that the increase in Ni content increases the activation energy (E_a) and decreases the dissolution rate of the alloys in KOH solution, and the lowest dissolution rate was obtained at 10% Ni. The results of both potentiodynamic and potentiostatic measurements exhibit sudden increase in current density which is observed at certain positive potential (+0.42 V vs. SCE) in the case of the investigated alloys. This indicates that the addition of Ni to Zn promotes the electrochemical reaction (in the passive region). However, the passivation potential shifted to more positive direction with the increase in Ni content in the alloy.

Keywords. Metal; alloys; anodic dissolution; passivation; electron microscopy; X-ray diffraction.

1. Introduction

Zinc is preferred to other anode materials both in chloride and alkaline primary batteries, owing to its electrochemical and ecological merits.¹ The latter find increasing use as sources of energy in various electronic devices. However, the observed tendency of zinc to corrode during storage of batteries remains the most difficult problem. Hence its electrochemical properties in alkaline solution are under active investigation.^{2–22} It is well known that the process of zinc dissolution in alkaline media is responsible for the formation of a layer of mixed oxide and hydroxide on its surface. Nickel and nickel alloys are important materials for the design vessels in different process industries.²³ Nickel electrode is also used in different energy-producing cells in which aqueous or non-aqueous solutions are used as electrolytes. Nickel and its alloys exhibited excellent corrosion resistance in aqueous aggressive environments, which are attributed to the ability of nickel to form a stable passive film on its surface.^{24–33}

In recent years, several attempts have been made at preparing zinc coating with high corrosion resistance. In so doing, zinc alloys with the group 8 metals have been developed,^{34–39} and, among these, zinc–nickel alloys have received most

attention because of their high degree of corrosion resistance and their mechanical properties. In spite of the appearance of so many publications on the electrochemical behaviour of Zn–Ni alloy electrodeposition in aqueous solutions, but very little work on the corrosion behaviour of the synthetic Zn–Ni alloy (by fusion) has been reported in our previous work.⁴⁰ In continuation of the previous studies, the present work concerns with the effect of Ni on the anodic behaviour and passivation of Zn–Ni alloy in alkaline solutions following potentiodynamic and potentiostatic techniques.

In this work, anodic polarization of the investigated electrodes in various concentrations of KOH solution using both potentiodynamic and potentiostatic measurements was studied. The role of both Ni content and temperature on the corrosion and passivation behaviour of the alloys was examined. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used for the characterization of the corrosion layer formed on all investigated electrodes surfaces, under their anodic polarization in the examined solution.

2. Experimental

2.1 Materials and solutions

Solutions of KOH (analytical grade) were prepared by dissolving the appropriate weight in doubly distilled water.

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Zn and Ni of high purity (99.999%; Johnson Matthey Chemicals Ltd.) were used to prepare Zn–Ni alloy as disk electrodes ($A = 0.196 \text{ cm}^2$) in a Gallenkamp muffle furnace using evacuated closed silica tubes with the dimension $10 \times 1 \text{ cm}^2$ up to 1173 K (900°C) for 24 h according to the phase diagram of Zn–Ni system, has been considered by Okamoto.⁴¹ The melts were shaken every 6 h to ensure the homogeneity of melting alloys. The details of the preparation method and identification of the synthetic alloys were mentioned in our previous work.⁴⁰ The prepared alloys were analysed using X-ray photoelectron spectroscopy. For the alloys, the percentages of Zn and Ni were found in accordance with the percentage of mixing Zn and Ni.

2.2 Electrochemical measurements

The measurements were performed on planar disk electrode embedded in an Araldite holder. Before each experiment, the surfaces of the working electrodes were polished using polishing cloth (polishing machine; Buehler, Lake Bluff, Illinois, USA), until their surfaces became smooth and mirror-like bright. Then 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 are referred.

The cell description is given elsewhere.⁴² To remove any surface contamination and air formed oxide, the working electrode was kept at -1.50 V vs. SCE for 5 min in the tested solution, disconnected, shaken free of adsorbed hydrogen bubbles and anodic polarization was recorded. Potentiostat/Galvanostat (EG&G Model 273) connected with a personal computer (IBM Model 30) was used for the measurements.

2.2a Potentiodynamic technique: The potentiodynamic polarization studies were carried out with electrodes having a surface area of 0.196 cm^2 . The potential was altered automatically from the steady state of open-circuit potential (E_{corr}) up to positive potentials vs. SCE and at scan rate of 1 mV s^{-1} using software version 342C Supplied from EG&G Princeton Applied Research.

2.2b Potentiostatic technique: The anodic potential was fixed at a required constant value and the variation of current density was recorded as a function of time (current density–time transients).

2.3 Surface characterization

The composition of the corrosion layer formed on each electrode surface was investigated by XRD, using a diffractometer with an iron filter and copper radiation was used with an accelerating voltage of 30 kV and a filament current of 20 mA. The morphology of the corrosion layer formed on each electrode was also examined using SEM (JEOL, model 5300).

Each experiment was performed with freshly prepared solutions and clean set of electrodes. Measurements were conducted at 298, 308, 318 and 328 K ($25, 35, 45$ and $55 \pm 0.5^\circ\text{C}$) for each investigated electrode. For this purpose ultrathermostat model Frigiter 6000 382 (SELECTA) was used.

3. Results and discussion

3.1 Potentiodynamic measurements

3.1a Behaviour of zinc: Figure 1 shows the potentiodynamic polarization curves for zinc anode in various concentrations of KOH solution ($0.25\text{--}1.0 \text{ M}$) at scan rate 1 mV s^{-1} and 25°C . The polarization curves were swept from steady state of open-circuit potential (E_{corr}) up to 0.0 V (SCE). The data revealed that the anodic polarization curves exhibit active/pseudopassive transition. The active dissolution region involves two small anodic peaks (A_I and A_{II}), followed by a passive region which extends up to 0.0 V (SCE) with slightly increase in the passive current density (I_{pass}). The first anodic peak A_I is located at about -1.382 V (SCE) in 0.25 M KOH solution, which can be associated with active oxidation of Zn under the experimental conditions could be explained based upon the reaction⁴³

The second anodic peak A_{II} located at about -1.229 V (SCE), corresponds to the dehydration of thermodynamically unstable Zn(OH)_2 to the corresponding stable ZnO occurring on zinc surface during the potential sweep to the positive direction:

Figure 1. Potentiodynamic anodic polarization curves for pure Zn in various concentrations of KOH solution at 298 K (25°C).

Further increase of potential in the positive direction leads to the formation of ZnO_2 according to

Shams El Din *et al.*⁴⁴ and Popova *et al.*⁴⁵ observed that ZnO_2 is formed in weak alkaline media only or closely to the oxygen evolution potential. When the surface is covered with the passive film, the dissolution current falls to small value (I_{pass}), indicating the onset of permanent passivation. However, with the increase in the potential in the positive direction the current density of passivation gradually increases. This behaviour may be attributed to dissolution of some ZnO or Zn(OH)_2 on the Zn surface.⁴⁶

The obtained data reveal that an increase in the concentration of KOH solution results in an increase in both the peak currents and passivation current density (I_{pass}), such behaviour was related to the decrease of Zn(OH)_2 or ZnO and ZnO_2 formed on the surface, with an increase of concentration. This was explained on the basis of the increase of the partial dissolution of oxide or hydroxide film with the increase concentration of KOH . On the other hand, the data exhibited that the peaks potential (A_I and A_{II}) shift to more positive direction with increasing concentration. However, it is observed that the peak (A_{II}) is gradually reduced with the increase in concentration of KOH , and disappears completely at highest concentration (1 M). This behaviour may be attributed to the hindrance of the transformation of Zn(OH)_2 (by dehydration) into ZnO or ZnO_2 in higher concentration of KOH solution, particularly at the mentioned potential region of peak A_{II} . In addition, ZnO is dissolved by the reaction with further hydroxide to form the zincate ion $[\text{Zn(OH)}_4]^{2-}$ according to the reaction⁴⁶

3.1b Behaviour of nickel: Figure 2 represents the potentiodynamic polarization curves for Ni electrode in various concentrations of KOH solution at scan rate 1 mV s^{-1} and 25°C . The data revealed that the anodic excursion exhibits active/passive transition. The active dissolution region involves two anodic peaks (A_I and A_{II}) prior to the permanent passive region. The first anodic peak A_I is located at about -0.201 V (SCE) in 0.25 M KOH solution may correspond to the following reactions:

and/or

The formation of HNiO_2^- may be considered as the starting process for the dissolution reaction. While the broad anodic peak A_{II} appearing at about $+1.942 \text{ V}$ vs. SCE is

Figure 2. Potentiodynamic anodic polarization curves for pure Ni in various concentrations of KOH solution at 298 K (25°C).

related to direct oxidation of Ni into NiO according to the reaction

However, the broad anodic peak A_{II} can be attributed to the competition between the anodic formation of the hydroxide or oxide and chemical dissolution of the passive oxide film on the Ni surface.^{24,25} When the surface is covered with the passive film, the dissolution current falls to very small value (I_{pass}), indicating the onset of permanent passivation. The passive currents were estimated from anodic potentiodynamic polarization curves at the minimum current density (in passive region). It seems that the passive layer increases the overpotential for oxygen evolution.⁴⁷ The current flowing through the passive region may correspond to the film formation and the replacement of chemically dissolved film materials.^{24,25} Previous works confirmed duplex nature of the passive film, which consists of both Ni(OH)_2 and NiO .^{24,25} At the same time, during the positive going polarization of Ni in KOH , transformation of Ni(OH)_2 to $\beta\text{-NiOOH}$ takes place. It has been suggested by the same authors that $\beta\text{-Ni(OH)}_2$ can be oxidized to $\beta\text{-NiOOH}$ at higher potential *via* a deprotonation reaction²⁴

Confirmation of this reaction in a nickel–cadmium cell was made by Uno⁴⁸ who showed, using X-ray measurements, that Ni(OH)_2 indeed converts to the oxyhydroxide upon charging. The data also reveal that, peak current densities A_I and A_{II} of the two anodic peaks and passivation current density (I_{pass}) increase with the increase in the alkali concentration. This behaviour could be ascribed to the increase of the chemical dissolution rate with the increase in the concentration of

KOH solution. However, it is observed that the peak's potentials E_{AI} and E_{AII} seem to be not affected with the variation of KOH concentration.

3.1c Behaviour of Zn–Ni alloys: Figure 3 shows the potentiodynamic E/I curves of Zn–Ni alloy IV (as a representative alloy) in various concentrations of KOH solution at 25°C and scan rate 1 mV s^{−1}. The curves were swept from E_{corr} up to positive potential (+0.80 V vs. SCE). The polarization curves showed three active dissolution peaks, permanent passivation and finally breakdown of passive region. The three peaks (A_I , A_{II} and A_{III}) are well defined at about −1.325, −1.20 and −0.888 V vs. SCE, respectively. However, the data reveal that the anodic current of peak III is higher than that of peak I or II.

In active dissolution region, firstly zinc in the alloy dissolves as $[Zn(OH)_4]^{2-}$ ions as the following:

Further increase of potential in the positive direction leads to the formation of $Zn(OH)_2$ and/or ZnO (peaks I and II). At the same time, during the positive going polarization electrode of alloy in KOH solution, the current density increases steadily with the potential to give peak III (−0.888 V vs. SCE). This peak corresponds to simultaneous Ni dissolution on the alloy surface and oxide formation according to the reactions in eqs (7) and (8), respectively. Flowing the anodic peak, the electrode becomes passive and the current density decreases to lower values and extends over a wide potential range. The current flowing along this region is governed by the fixed rate of dissolution of the passivating film in the electrolyte. However, the film dissolution is counter balanced by film formation.⁴⁷ This is indicating that the onset of passivation can be due to the precipitation of ZnO/ZnO_2 and NiO on the surface. In other words, this behaviour can be attributed to that the mentioned oxides block the

Figure 3. Potentiodynamic anodic polarization curves for alloy IV in various concentrations of KOH solution at 298 K (25°C).

dissolution of the active sites and cause inactivation of a part of the surface towards the corrosive medium.⁴⁹ This suggestion is supported by XRD which will be discussed later. On the other hand, the results revealed that by increasing KOH solution concentration, the anodic current peaks increase and the potential corresponding to these peaks are shifted to more positive direction. Also, the current density of both permanent passivation region and breakdown of oxide layer at certain potential (+0.42 V vs. SCE) is increased as an increase of the concentration of KOH solution. These results could be explained on the basis of the dissolving power of OH^- ion on the layer formed by anodic treatment.^{40,50}

Figure 4 shows comparison between the potentiodynamic polarization curves of Zn and the investigated alloys in 0.5 M KOH solution at 25°C. It was found that the current of two peaks in the case of Zn are higher than those of the investigated alloys. It is interesting to note that, the current of peaks A_I and A_{II} gradually decreases while for peak A_{III} increases with the increase in Ni content in the alloy (figure 5). This behaviour exhibits very important results that Ni content in the alloy plays an important role in decreasing the dissolution rate of zinc in alkaline solution. For alloy electrodes, the increase in Ni content (from 0.5 to 10%) decreases both the anodic corrosion (I_{peak}) and passivation current (I_{pass}) of the alloy under the same conditions, hence improves its stability against corrosion. The peaks potentials (A_I , A_{II} and A_{III}) (the data not present here) shift to more positive direction as an increase Ni content. This behaviour confirms that the tendency of the alloy towards passivity is delayed, while the corrosion resistance of alloy increases with Ni content. Accordingly, the results show the corrosion resistance of Zn–Ni alloy is superior to that of Zn in alkaline solutions, and 10% Ni alloy gives higher corrosion resistance.³⁶ The superior corrosion resistance observed for the investigated Zn–Ni alloys compared with that of Zn could be explained

Figure 4. Comparison between potentiodynamic anodic polarization curves for Zn and Zn–Ni alloys in 0.5 M solution of KOH at 298 K (25°C).

Figure 5. Dependence of the peaks current density I_{peak} on Ni content in the alloy in 0.50 M KOH solution at 298 K (25°C).

by the barrier protection mechanism theory during acts as a barrier to further attack. This behaviour can be attributed to the presence of single γ -phase structure and hence the absence of local cells between different phases. In addition, the presence of Ni in the alloy shows slow down the dehydration of Zn(OH)_2 (as a product of corrosion) to ZnO. The hydroxide has a lower level of electronic conductivity than the oxide; therefore the corrosion is slower.⁵¹ However, it is observed that, the values of passive current in the case of the investigated alloys are higher than that of pure Ni under the same conditions. This behaviour could be attributed to the solubility of some Zn oxides or hydroxide film on the surface in KOH solution with shift the potential to more positive direction, which in turn, decreased the thickness of the film.

3.1d Effect of temperature: Figure 6 represents the potentiodynamic polarization curves for alloy IV in 0.5 M KOH solution at different temperatures. It can be seen that the temperature enhanced peaks A_I , A_{II} and A_{III} of alloy IV towards higher current densities, and shifted $(E_p)_{A_I}$, $(E_p)_{A_{II}}$ and $(E_p)_{A_{III}}$ towards more positive values. On the other hand, the passivation current density increases also with the increase in the temperature. Similar effect of temperature in the case of pure zinc or nickel is observed to that mentioned of alloy IV. This indicates that an increase in temperature accelerates the rate of diffusion and migration of the reactant and product species,⁵² and consequently the corrosion reactions and the dissolution of oxide film.

Table 1 shows the values of the apparent activation energy (E_a) values for Zn and its investigated alloys in 0.5 M KOH solution at both peak A_{II} and passivation current (at 0.2 V vs. SCE). These values are determined from the slope of Arrhenius plots ($\log I_{\text{peak}}$ or $\log I_{\text{pass}}$ vs. $1/T$ plots) as shown in figures 7 and 8 applying the equation

$$\log I = \log A - \frac{E_a}{2.33R} \frac{1}{T}, \quad (10)$$

Figure 6. Potentiodynamic anodic polarization curves for alloy IV in 0.50 M solution of KOH at different temperatures (25–55°C).

Table 1. Apparent activation energy in kJ mol^{-1} of Zn and Zn–Ni alloys in 0.50 M KOH solution.

Metal and alloy	E_a (kJ mol^{-1}) I_p vs. $1/T$ (at peak A_{II})	E_a (kJ mol^{-1}) I_{pass} vs. $1/T$ (at $E = 0.20$ V vs. SCE)
Zn	23.04	21.2
Alloy I (0.5% Ni)	32.16	29.54
Alloy II (2.0% Ni)	35.35	31.23
Alloy III (5.0% Ni)	37.97	33.26
Alloy IV (10.0% Ni)	44.45	40.81

Figure 7. Arrhenius plots for Zn and Zn–Ni alloys corrosion in 0.50 M solution of KOH ($\log I_{\text{peak}} (A_{II})$ vs. $1/T$).

Figure 8. Arrhenius plots for Zn and Zn–Ni alloys corrosion in 0.50 M solution of KOH ($\log I_{\text{pass}}$ vs. $1/T$).

where I is the peak current or passivation current, A the frequency factor, E_a the activation energy and T the absolute temperature. It can be observed that the values of E_a gradually increases with the increase in the Ni content in the alloy, and the maximum value is obtained in the case of alloy **IV** at both peak and passivation current densities. This provides that the activation energy increases with the increase in the Ni content in alloy. This observed higher energy barrier would be attributed to the hindrance of dissolution process by increasing Ni content in the alloy.⁴⁹ These data support our suggestion that the corrosion resistance of Zn–Ni alloy in KOH solution increases with the increase in the Ni content.

3.2 Potentiostatic measurements

Figure 9a–c shows the current–time transient curves of Zn, Ni and alloy **IV** in 0.5 M KOH solution at different applied anodic potentials and at 25°C. It is observed that the current density decreases with time (except in the case of alloy **IV** at certain positive potential) at different applied potentials. The results show clearly that the currents measured of the investigated electrodes in the examined solution at more positive potentials are significantly reduced in comparison with the currents obtained at more negative potentials. This behaviour confirms that the tendency of the investigated electrodes towards passivity increases with shifting applied potential to more positive direction. However, in the case of alloy **IV**, it is observed that the current density vs. time at certain positive potential (+0.42 V vs. SCE) gives opposite behaviour to that observed for pure Zn and Ni. That is, after certain time of immersed alloy **IV** in 0.5 M KOH solution, the current density rises suddenly. This exhibits that the oxide film formed on the alloy surface tends to breakdown, and reactivation of the alloy surface takes place at certain positive potential.⁵³ This observation means that

Figure 9. Potentiostatic transient's current vs. time curves for (a) pure Zn, (b) pure Ni and (c) alloy **IV** in 0.50 M KOH solution at different applied potentials.

the passive layer on the alloy surface is destroyed and initiation of corrosion is occurred, where the metal oxides (M_xO_y) may be dissolved into M^{n+} ($M = \text{Zn}^{-1}$ and/or Ni) in solution.⁵⁴ Sato and Okamoto⁵⁵ attributed the dissolution of oxide film to the presence of active patches in the passive oxide layer. We proposed that the reason why the passive film formed on the alloy surface has ability to breakdown at certain positive potential in 0.5 M KOH solution, as due to that some Ni(II) is precipitated in ZnO lattice.⁵⁶ Such behaviour can be explained by the interaction between OH^- and Ni(II) which is precipitated in ZnO lattice. This interaction enhances the rate of diffusion of metal ions from the metal/film interface to the film/solution interface leading to the formation of cation vacancies, which lead in turn to breakdown of the passive film.⁵⁷ A similar behaviour for the other investigated alloys (**I–III**) under the same conditions (the data are not presented here) is observed. The same breakdown potential of oxide film on the alloy **I** (0.5% Ni) in high concentration of KOH (7 M) was obtained by the authors.⁵⁸ This behaviour indicates that reactivation of the alloy surface takes place in the passivation region.

3.3 Structures and properties of anodic passive film

3.3a X-ray diffraction: The composition of the corrosion layer formed on the surfaces of Zn, Ni and Zn–Ni alloys after anodic potentiostatic polarization treatment in 0.5 M KOH solution for 20 min at different formation potentials was examined. The passive electrode was withdrawn carefully, washed with doubly distilled water, dried and finally examined by XRD. Figure 10a represents XRD of the corrosion layer formed at peak potential of Zn electrode for peak A_I (−1.382 V vs. SCE) in 0.5 M KOH. The data confirm the existence of Zn as a major, but Zn(OH)₂ and ZnO as minor constituents. These results indicate that the peak potential of zinc in KOH solution is related to the formation of Zn(OH)₂/ZnO system on the electrode surface. In addition, XRD data for peak A_{II} (at −1.229 V (SCE); figure 10b), indicate that the surface contains small amounts of ZnO/ZnO₂. These data support our suggestion that peak A_{II} of Zn is related to the formation of ZnO and traces from ZnO₂ system on the electrode surface.

X-ray data for Ni electrode, treated potentiostatically in 0.5 M KOH at first peak potential A_I (−0.209 V (SCE); figure 11a), indicate that the surface contains Ni and

Ni(OH)₂. This confirms that the first peak A_I could be attributed to Ni(OH)₂ formation on the Ni surface. However, the data for Ni electrode, treated at +1.460 V vs. SCE (peak A_{II}; figure 11b), show that the surface contains large amount from NiOOH and small amount Ni(OH)₂. This exhibits that the surface is completely covered by mixed oxides of NiOOH/Ni(OH)₂, and the amount of NiOOH is higher compared with that of Ni(OH)₂ at this investigated peak potential. This result confirms that peak potential (A_{II}) is related to the conversion of Ni(OH)₂ to NiOOH. While, the data obtained at +3.50 V vs. SCE (passive region; figure 11c) show the existence of a mixture of oxides as NiOOH, NiO and Ni₂O₃. This indicates that Ni surface is completely covered by a thick film from oxides mixture (NiOOH, NiO and Ni₂O₃). This behaviour can be attributed to the conversion of NiOOH to Ni₂O₃ according to the following equation:

These data support our suggestion that the very small current density which is observed in the passive region of potentiodynamic measurements can be attributed to formation of

Figure 10. X-ray diffraction analysis for the corrosion layer on Zn electrode surface formed anodically in 0.50 M solution of KOH at applied potential (a) −1.382 V (SCE) peak A_I and (b) −1.229 V (SCE) peak A_{II} and at 298 K (25°C).

Figure 11. X-ray diffraction analysis for the corrosion layer on Ni electrode surface formed anodically in 0.50 M solution of KOH at applied potential (a) -0.209 V (SCE) peak A_I, (b) $+1.460$ V (SCE) peak A_{II} and (c) $+3.50$ V (SCE) passive region and at 298 K (25°C).

very thick oxide layer which covered the whole Ni surface. Therefore, there are not data obtained by XRD related to Ni metal at this region.

The data in figure 12a for the alloy **IV** treated potentiostatically at -1.20 V vs. SCE (peak A_{II}) in 0.5 M KOH solution at 25°C reveal that the surface contains Zn, γ -Zn₃Ni, and small amounts of Zn(OH)₂ and ZnO. This confirms that the data in figure 12a for the alloy **IV** treated potentiostatically at -1.20 V vs. SCE (peak A_{II}) in 0.5 M KOH solution at 25°C reveal that the surface contains Zn, γ -Zn₃Ni, and small amounts of Zn(OH)₂ and ZnO.

This confirms that the peak potential at -1.20 V vs. SCE may be attributed to the formation of Zn(OH)₂/ZnO on the alloy surface. This indicates that the alloy surface is partially covered by mixed film of Zn(OH)₂ and ZnO. However, the data of the same alloy, treated at -0.888 V vs. SCE (peak A_{III}; figure 12b), show that the surface contains small amounts of Zn and a large amounts of Ni(OH)₂ and ZnO and small amount from ZnO₂. Accordingly, the data reveal that the peak potential (peak A_{III}) of alloy **IV** is related to the formation of Ni(OH)₂/NiO and ZnO/ZnO₂ on the electrode surface. These results support our suggestion that the

Figure 12. X-ray diffraction analysis for the corrosion layer on alloy **IV** surface formed anodically in 0.50 M solution of KOH at applied potential (a) -1.20 V (SCE) peak A_{II}, (b) -0.888 V (SCE) peak A_{III}, (c) $+0.10$ V (SCE) passive region and (d) $+0.420$ V (SCE) and at 298 K (25°C).

investigated peak potential (A_{III}) is related to the formation of Ni(OH)₂/NiO on the electrode surface. The data for the same alloy **IV** treated at $+0.1$ V vs. SCE (passive region;

figure 12c) reveal that the surface is covered by ZnO as a major and NiO or ZnO₂ as minor constituents. By comparing the analysis data of both Ni and Zn–Ni alloy **IV**, it is

Figure 13. SEM photographs of the corrosion layer on the Zn surface formed anodically in 0.50 M KOH solution at (a) -1.229 V vs. SCE (peak A_{II}) and (b) $+1.0$ V (SCE).

Figure 14. SEM photographs of the corrosion layer on the Ni surface formed anodically in 0.50 M KOH solution at (a) -0.209 V vs. SCE (A_I), (b) $+1.942$ V vs. SCE (A_{II}) and (c) $+3.500$ V vs. SCE (passive).

observed that Ni_2O_3 and NiOOH are not formed in the case of alloy. This behaviour can be attributed to alloying Zn with Ni retards the formation of NiOOH or Ni_2O_3 , when the alloy surface is passivated at more positive potential. Figure 12d shows XRD data of alloy **IV** treated at $+0.420 \text{ V vs. SCE}$ (at breakdown potential of oxide layer). The data infer that the surface contains Zn in a large amount and ZnO and NiO as minor constituents. Comparison between X-ray data for the presence of ZnO and NiO amounts on the surface of the alloy at both $+0.1 \text{ V vs. SCE}$ (less positive potential) and $+0.420 \text{ V vs. SCE}$ (more positive potential), reveals that large amounts of ZnO/ ZnO_2 and NiO are formed at less positive potential compared with those amounts formed at more positive potential. This provides that at more positive potential, all ZnO_2 and most NiO dissolve in KOH solution and leads to reactivation of the electrode surface.⁵⁸ Therefore, XRD results are in good agreement with both potentiodynamic and potentiostatic measurements, in which the current density increases suddenly at the investigated potential ($+0.420 \text{ V vs. SCE}$).

3.3b Microscopic examination: Figure 13a and b shows the micrographs of the corrosion layer formed potentiostatically on surface of Zn in 0.5 M KOH solution at applied potentials -1.229 (peak A_{II}) and $+1.0 \text{ V vs. SCE}$. It may appear from figure 13a that the surface is partially covered by the passive film (mixture form ZnO and ZnO_2) and the electrode surface may be seen. The oxide patches of the layer exhibit the same shapes. The oxide patches of this layer are not compact, i.e., there are vacancies between them. These observations are in agreement with the data of XRD that the corrosion layer is related to ZnO/ ZnO_2 . However, the photograph of Zn treated anodically at $+1.0 \text{ V vs. SCE}$ (passive region; figure 13b), recognized that the surface contains some pores and the oxide patches are smaller and the amount is greater than that at more negative potential (peak A_{II}). The oxide patches of the layer become more adhered on the surface, and are not compact, i.e., there are vacancies between them. Therefore, SEM results support the potentiodynamic measurements that high current density in the passive region is obtained. This behaviour may be

Figure 15. SEM photographs of the corrosion layer on alloy **IV** surface formed anodically in 0.50 M KOH solution at (a) -1.20 V vs. SCE (peak A_{II}), (b) -0.888 V vs. SCE (peak A_{III}), (c) $+0.10 \text{ V vs. SCE}$ (passive) and (d) $+0.42 \text{ V vs. SCE}$.

due to an amount from this layer dissolved in the bulk of solution.

Figure 14a–c shows the micrographs of the corrosion layer formed potentiostatically on surface of Ni in 0.5 M KOH solution at applied potentials -0.209 , $+1.942$ and $+3.50$ V vs. SCE. It may appear from figure 14a (Peak A_I) that the surface is partially covered by the passive film. One layer is observed on the electrode surface. The oxide patches of the layer exhibited different shapes. The oxide patches of this layer are not compact, i.e., there are vacancies between them. These observations are in agreement with the data of XRD that the layer is related to Ni(OH)₂. Figure 14(b) shows SEM photographs of Ni treated at $+1.942$ V vs. SCE, it is found that the surface is almost completely covered by the corrosion layer. The oxide patches exhibit different shapes. Therefore, the electrode surface seems to be completely covered by NiOOH with Ni(OH)₂, and this is suggested by XRD. However, at higher potential $+3.50$ V vs. SCE (passive region; figure 14c), it is observed that the most of the surface is covered by some oxide patches. Two layers are observed on the electrode surface. The oxide patches of the upper layer exhibited small amounts may be Ni₂O₃, and the amount of underneath layer is increased and the distance between them becomes less widely compared with those in figure 14b. These observations are in agreement with the data of XRD that, the surface contains a mixture of oxides (Ni₂O₃, NiO and NiOOH).

Figure 15a–d shows the micrographs of the corrosion layer formed potentiostatically on surface of alloy IV in 0.5 M solution of KOH at applied potentials -1.20 , -0.888 , $+0.10$ and $+0.42$ V vs. SCE. It would be recognized from figure 15a that the treated surface at -1.20 V vs. SCE (peak A_{II}) is covered by the passive layer. Two layers are observed on the electrode surface, and its oxide patches exhibited different shapes compared with those of pure zinc (peak A_{II}). However, the higher corrosion resistance of the alloy leads to lower current density of peak A_{II} than that of pure Zn. Figure 15b shows SEM photographs of the same alloy treated at -0.888 V vs. SCE (peak A_{III}). It is found that the surface is almost completely covered by adhered passive oxides. Two layers are observed on the electrode surface. The oxide patches of the upper layer exhibited similar shapes. The second layer seems to lie below the upper layer and their oxide patches size is smaller. These observations are in agreement with the data of XRD that, the upper layer is related to ZnO/ZnO₂, while the underneath layer is due to Ni(OH)₂ or NiO formation. For the electrode surface treated anodically at $+1.0$ V vs. SCE (more positive potential; figure 15c), it appears two layers of the oxide patches on the alloy surface (double nature). It is observed that the amount of the oxide patches at the upper layer decreases and becomes more distant apart than those in figure 15b, the quantity of the oxide patches in the underneath layer increases with smaller size. Whereas the oxide patches of the upper layer become loosely bound to the alloy surface, and an amount from this layer dissolves in the bulk of the solution. In addition the oxide patches of the underneath layer are dispersed on the

whole surface. Figure 15d shows SEM photographs of alloy IV treated at $+0.42$ V vs. SCE (at the breakdown potential of oxide layer). The data show that the oxide film formed on the alloy surface is less than that formed at more positive potential (figure 15c). Thus some parts of the alloy surface can be seen. Therefore, SEM results are in good agreement with both potentiodynamic and potentiostatic measurements, in which the current density increases suddenly at the investigated potential ($+0.42$ V vs. SCE).

4. Conclusions

Potentiodynamic oxidation of Zn and its investigated alloys exhibits active/pseudopassive transition state, while Ni exhibits active/passive one in various concentrations of KOH solution. The active dissolution of Zn, Ni and their alloys increases with the increase of both concentration of KOH and temperature. However, the results show that the increase in Ni content in the alloy decreases the dissolution rate in KOH solution, consequently the maximum corrosion resistance is obtained at 10% Ni content (alloy IV). Passivation of zinc is due to precipitation of a thin film of ZnO and ZnO₂. However, passivation of Ni is due to the formation of thick film from NiOOH, NiO and Ni₂O₃ on the electrode surface. Passivation of Zn–Ni alloys can be attributed to the formation of a thin film from ZnO, ZnO₂ and NiO. It is observed that Ni₂O₃ and NiOOH are not formed on the alloy surface. The results show that the corrosion resistance of Zn–Ni alloy is superior to that of Zn in alkaline solutions. The results of both potentiodynamic and potentiostatic measurements exhibit sudden increase in current density which is observed at certain positive potential ($+0.42$ V vs. SCE) in the case of the investigated alloys. This indicates that the addition of Ni to Zn promotes the electrochemical reaction (in the passive region). Therefore Zn–Ni alloy can be used as anodes in the alkaline batteries due to its high corrosion resistance and reactivation of the alloy surface in the passive region. The values of activation energy (E_a) at both peak and passivation current densities gradually increase with the increase in Ni content in the alloy, and the maximum value is obtained in the case of alloy IV (10% Ni). This observed higher energy barrier would be attributed to the hindrance of dissolution process by increasing Ni content in the alloy.

References

1. Dobryszewski J and Bialozor S 2001 *Corros. Sci.* **43** 1309
2. Baugh L M and Baikie A R 1985 *Electrochim. Acta* **30** 1173
3. Baugh L M and Higginson A 1985 *Electrochim. Acta* **30** 1163
4. Bialozor S and Dobryszewski J, Proc Eurocorr'98, Utrecht, Holland, 28 September–1 October 1998
5. Bockris J O' M, Nagy Z and Damjanovic A 1972 *J. Electrochem. Soc.* **119** 285
6. Brodd R J and Leger V E, in: Bard A J (ed), *Encyclopedia of electrochemistry of the elements* (New York: Marcel Dekker) vol. 5 (Chapter V-1) 1974

7. Cabot P L I, Cortes M, Centellas F A, Garrido J A and Perez E 1987 *Electrochim. Acta* **32** 1321
8. Cachet C, Saidani B and Wiart R 1992 *J. Electrochem. Soc.* **139** 644
9. Cai M and Park S M 1996a *J. Electrochem. Soc.* **143** 2125
10. Cai M and Park S M 1996b *Electrochim. Acta* **143** 3895
11. Chang Y C and Prentice G A 1989 *Electrochim. Acta* **136** 3398
12. Chang Y C and Prentice G A 1984 *Electrochim. Acta* **131** 1465
13. Cyrankowska M and Szczesniak B 1994 *Prog. Batteries Battery Mater.* **3** 233
14. Dirkse T P and Hampson N A 1972 *Electrochim. Acta* **17** 1113
15. Hutchison P F and Turner J 1976 *J. Electrochem. Soc.* **123** 185
16. Kannan A R S, Muralidharan S, Sarangapani K B, Balaramachandran V and Kapali V 1995 *J. Power Sources* **57** 93
17. Keily T and Sinclair T J 1981 *J. Power Sources* **6** 47
18. Maja M, Penazzi N, Farnia G and Sandona G 1993 *Electrochim. Acta* **38** 1453
19. Mansfeld F and Gilman S 1970 *J. Electrochem. Soc.* **117** 1328
20. Müller B and Imblo G 1996 *Corros. Sci.* **38** 293
21. Nartey V K, Binder L and Kordes K 1994 *J. Power Sources* **52** 217
22. Scholl P, Shan X, Bonham D and Prentice G A 1991 *Electrochim. Acta* **138** 895
23. Singh D D N and Banerjee M K 1986 *Corros. NACE* **42** 156
24. Abd El Aal E E 2003a *Corros. Sci.* **45** 641
25. Abd El Aal E E 2003b *Corros. Sci.* **45** 759
26. Chao C and Szklarska-Smialowska Z 1980 *Surf. Sci.* **96** 426
27. MacDougall B and Cohen M 1976 *J. Electrochem. Soc.* **123** 191
28. Okuyama M and Haruyama S 1974 *Corros. Sci.* **14** 1
29. Ord J L, Clayton J C and DeSmet D J 1977 *J. Electrochem. Soc.* **124** 1754
30. Paik W and Szklarska-Smialowska Z 1980 *Surf. Sci.* **96** 401
31. Sato N and Kudo K 1974 *Electrochim. Acta* **19** 461
32. Seghioeur A, Chevalet J, Barhoun A and Lantelme F 1998 *J. Electroanal. Chem.* **422** 113
33. Vissker W and Barendrecht E 1983 *Surf. Sci.* **135** 436
34. Barcelo G, Garcia E, Sarret M and Müller C 1998 *J. Appl. Electrochem.* **28** 1113
35. Elhajjani A, Gigandet M P, De Petris-Wery M, Catonne J C, Duprat J J, Thiery L, Raulin F, Starck B and Remy P 2008 *Appl. Surf. Sci.* **255** 1654
36. Heydarzadeh Sohi M and Jalali M 2003 *J. Mater. Process. Technol.* **138** 63
37. Hotellaz B, Bonino J P and Rousset A 1999 *J. Mater. Sci.* **34** 881
38. Lin C-C and Huang C-M 2006 *JCT Res.* **99** 3
39. Petrauskas A V, Grintsyavichene L S, Cheshunene A V and Matulenis E L 2003 *Prot. Met.* **39** 454
40. El-Sayed A, Mohran H S and Abd-Elateef H M 2011 *Metall. Mater. Trans. A* online: 6 October 2011
41. Okamoto H 2003 *J. Phase Equilibria* **24** 280
42. Abd El Rehim S S, Hassan H H and Mohamed N F 2004 *Corros. Sci.* **46** 1071
43. Amin M A 2005 *Electrochim. Acta* **50** 1265
44. Shams El Din A M, Abd El Wahaab F M and Abd El Haleem S M 1973 *Werkst. Korros.* **24** 389
45. Popova T I, Bagotskii V S and Kabanov B N 1992 *Russ. J. Phys. Chem.* **36** 770
46. Abd El Aal E E 1999 *Corros. NACE* **55** 582
47. Abd El Aal E E and Abd El-Haleem S M 2005 *Chem. Eng. Technol.* **28** 1158
48. Uno S F 1960 *J. Electrochem. Soc.* **107** 661
49. Mohran H S, El-Sayed A and Abd El-Lateef H M 2009 *J. Solid State Electrochem.* **13** 1279
50. El-Sayed A, Shaker A M and Gad El-Kareem H 2003 *Bull. Chem. Soc. Jpn.* **76** 1527
51. Wilcox G D and Gabe D R 1993 *Corros. Sci.* **35** 1251
52. Foad El-Sherbini E E and Abd El Rehim S S 2000 *Corros. Sci.* **42** 785
53. Hassan H H, Abd El-Rehim S S and Mohamed N F 2002 *Corros. Sci.* **44** 37
54. Refaey S A M, Taha F and Hasanin T H A 2006 *Electrochim. Acta* **51** 2942
55. Sato N and Okamoto G 1963 *J. Electrochem. Soc.* **110** 605
56. Xu J, Liu X, Li X, Barbero E and Dong C 2006 *J. Power Sources* **155** 420
57. Badawy A W, Ismail K M and Fathi A M 2005 *Electrochim. Acta* **50** 3603
58. El-Sayed A, Mohran H S and Abd El-Lateef H M 2010 *J. Power Sources* **195** 6924