— Technical Paper —

Electrochemical Impedance Spectroscopy Study on Anodic Dissolution of Fe-Ni Alloy in Sulfuric Acid Solution

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The anodic dissolution mechanism of Fe-Ni alloy was investigated by an electrochemical impedance spectroscopy (EIS). The Fe(II) and Ni(II) dissolved from Fe-Ni alloy electrode were detected simultaneously during the polarization curve measurement by a channel flow electrode system. The preferential dissolution of Fe(II) was observed at low anodic potentials, and the dissolution rate of Fe(II) was controlled by Ni content significantly. Nyquist plot of electrochemical impedance of Fe-Ni alloy electrode shows an inductive semicircle and negative resistance. These unique loci were explained by the formation of adsorbed intermediates Fe(I)_{ad} and Ni(I)_{ad} . The numerical simulation was performed for the experimental results of polarization curves, dissolution currents of Fe(II) and Ni(II) and electrochemical impedance responses. The dissolution mechanism was discussed on the basis of the kinetic parameters obtained by the simulation.

Key Words : Electrochemical Impedance Spectroscopy, Anodic Dissolution, Fe-Ni Alloy, Channel Flow Electrode

1 Introduction

Ni is one of the major elements in stainless steel, and the studies on its corrosion resistance are very significant. Therefore, many researchers have investigated the role of Ni for improvement of corrosion resistance of stainless steel using its binary alloys. The most of the reports concerning electrochemical behavior of Fe-Ni alloys are about the component and structure of the passive film. Nagasaki *et al.*¹⁾ investigated the nature of the passive film on Fe-Ni alloys by X-ray microanalysis and X-ray diffraction, and discussed the relation between passive film and sulfate ions. Okuyama and Haruyama²⁾ estimated the thickness and chemical composition of the passive film on Fe-Ni alloys in borate solution by coulometry, and examined the influence of alloy composition, electrode potential and pH of the solution on the passive film nature. Morioka and Sakiyama³⁾ investigated the influence of Ni component in Fe-Ni alloys on the anodic current and the passivation potential in sulfuric acid solution. Ponthiaux *et al.*⁴⁾ measured the polarization curve of the Fe-31 % Ni alloy in sulfuric acid solution by a rotating disk electrode. Okuyama⁵⁾ applied a rotating ring disk electrode to the investigation of anodic dissolution of Fe-Ni alloy in sulfuric acid solution, and reported the preferential dissolution of Fe(II) from Fe-Ni alloy electrode. However, important subjects have remained on the anodic dissolution of Fe-Ni alloy, *i.e.*, information regarding adsorbed intermediate and kinetic analysis of the detailed dissolution mechanism.

Keddam *et al.*⁶⁾ studied the effect of Cr component on the dissolution rate of Fe from a Fe-Cr alloy by

measuring polarization curves and electrochemical impedance spectroscopy (EIS), and proposed the dissolution mechanism of Fe-Cr alloy on the basis of experiment results. They⁶⁾ reported that the anodic dissolution potential and the passivation potential of Fe-Cr alloys shifted toward negative potential with increasing the Cr component, and obtained the kinetic parameters of the elementary reactions of anodic dissolution of the Fe-Cr alloy by the numerical simulation on the experimental results. Annegren *et al.*⁷⁾ got the information about an intermediate in Fe-Cr dissolution by the measurement of electrochemical impedance and the dissolution efficiency of Fe(II) in the frequency domain.

In the present study, channel flow electrode method is applied to the investigation of Fe-Ni alloy dissolution because the each dissolved ion can be detected independently during the measurement of polarization curve. Furthermore, EIS is applied to it in order to obtain the kinetic parameters of the detailed dissolution process of Fe-Ni alloy and the information concerning the adsorbed intermediate.

2 Experimental Method

The scheme of a channel flow electrode is shown in Fig. 1. Figure 1(a) depicts the zoom up of the double electrode system,⁸⁾ and it was used when one kind of ions which dissolved from pure Ni and Fe were detected. The collecting electrode was separated at right angle to the electrolyte flow direction in Fig. 1 (b), and the separation-type collecting electrode system⁹⁾ was used for simultaneous detection of both Fe(II) and Ni(II) which dissolved from Fe-Ni alloy. Pure Fe

Fig. 1 (a) Zoom up of channel flow double electrode in contact with the electrolyte solution. (b) Zoom up of the separation-type channel flow electrode. (c) Scheme of channel flow cell.

(99.99 %, Johnson matthey), pure Ni (99.99 %, Nilaco) and Fe- x wt% Ni ($x=20,40,60,80$) alloys were used for the working electrode. Fe- x wt% Ni ($x=20,40,60,80$) alloys were made from 99.9 % Ni and 99.99 % Fe by the argon arc melting method. The heat-treatment condition for the working electrode materials is as follows. A furnace was cooled to the room temperature after the specimen was heated to 900 °C at a speed of 250 °C/hr in hydrogen gas stream and maintained for 10 hr at 900 °C. Glassy carbon and Pb (99.99 %, Nilaco) were used for the collecting electrodes to detect Fe(II) and Ni(II), respectively. The collecting electrodes were arranged at the downstream of the working electrode with a gap of 0.05 mm. The dimension of the working and collecting electrodes in double electrode system in Fig.1 (a) were 4 mm wide and 1 mm long to the flow direction. In the case of separation-type collecting electrode system, the dimension of two collecting electrodes was 2 mm wide and 1 mm long, and their gap held a distance of 0.05 mm. A saturated KCl-AgCl/Ag electrode (SSE) and platinum were used for reference and counter electrodes, respectively. The electrode potential in the present paper is represented by the SSE standard. The working electrode was rinsed by methanol and double distilled water successively after polishing by an emery paper of #2000. The electrolyte solution was a mixture of 0.5 kmol/m³ H₂SO₄ and 0.5 kmol/m³ Na₂SO₄, and was adjusted to pH 1. The electrolyte solution used in these experiments was prepared from the double distilled water and the analytical grade chemical reagent, and was deaerated by passing nitrogen gas for 24 hr before measurement.

In the measurement of polarization curve, the work-

ing electrode potential was scanned at 100 mV/min toward noble potential, and the working and collecting electrode currents were recorded. Fe(II) and Ni(II), which were dissolved from the working electrode, were detected on the collecting electrode at 1.4 V and -1.2 V, respectively.

The electrochemical impedance $Z(\omega)$ was measured by using frequency response analyzer (FRA). The amplitude of alternative voltage on the working electrode was 10 mV (rms), and frequency range used for the measurement was from 10 mHz to 10 kHz. The measurement was started at 20 min after the polarization at arbitrary potential. The mean flow rate of the electrolyte solution was 2 m/s in all the experiments.

3 Experimental Results

3.1 Polarization curves

Figure 2 shows the polarization curves of Fe (a) and Ni (b) in sulfuric acid solution of pH 1. The polarization curve of Fe shows a cathodic current region below an immersion potential of -0.49 V, and an anodic current region above -0.49 V. The cathodic current is related to the hydrogen evolution reaction. On the other hand, the polarization curve of Ni shows that the immersion potential (zero current potential) is approximately -0.12 V, indicating that Fe dissolves at more negative potential than Ni. The dissolution currents of Fe(II), $i_{\text{Fe(II)}}$, and Ni(II), $i_{\text{Ni(II)}}$, were determined from the collecting electrode current i_c according to the following expressions.

Fig. 2 (a) Polarization curve of Fe and Fe(II) dissolution current and (b) polarization curve of Ni and Ni(II) dissolution current in sulfuric solution (pH 1). The solid and dotted lines denote the working electrode currents and dissolution currents, respectively.

$$i_{\text{Fe(II)}} = 2i_c/N_s \quad (1)$$

$$i_{\text{Ni(II)}} = -i_c/N_s \quad (2)$$

The collection efficiencies N_s for Fe(II) and Ni(II) in the double electrode system were measured to be 0.39 and 0.35, respectively. The anodic currents of both Fe and Ni are coincided with $i_{\text{Fe(II)}}$ and $i_{\text{Ni(II)}}$, respectively.

Figure 3 shows polarization curves of the Fe-Ni alloys and $i_{\text{Fe(II)}}$ and $i_{\text{Ni(II)}}$ in the sulfuric acid solution of pH 1. N_s 's of separation-type collecting system are 0.19 and 0.17 for Fe(II) and Ni(II), respectively. The preferential dissolution of Fe(II) from Fe-Ni alloy is observed in small anodic polarizations, and this result is in good agreement with the report by Okuyama.⁵⁾ This phenomenon is more significant when the Ni component in Fe-Ni alloy is smaller. The start potentials of Fe(II) and Ni(II) dissolutions shift toward noble with increasing the amount of Ni component. Fe(II) preferential dissolution rate decreased greatly with increasing the Ni content, and however this result cannot be explained only by the decrease of Fe content. The start potential for Ni(II) dissolution becomes noble when the Ni content is larger.

3.2 Electrochemical impedance response

The Nyquist plots of electrochemical impedance responses $Z(\omega)$ of Fe- x wt% Ni ($x=20, 40, 60, 80$) in the sulfuric acid solution (pH1) are shown in Figs. 4-7. In Fig. 4, capacitive and inductive semicircles are observed on $Z(\omega)$ of Fe-20 wt% Ni alloy below -0.3 V, and the shape is similar to that of Fe.¹⁰⁾ It was shown that the preferential dissolution of Fe(II) occurred below -0.3 V in Fig. 3. From these results, the Fe(II) dissolved by a consecutive dissolution mechanism and the inductive semicircle originated from the adsorbed intermediate of Fe¹¹⁾ in this potential region. On the other hand, when potential is at -0.25 V and -0.2 V, the second capacitive semicircle appears on $Z(\omega)$. Because the dissolution of Ni(II) begins at -0.3 V in Fig. 3, the second capacitive semicircle

Fig. 3 Polarization curves of Fe- x wt% Ni ($x=20, 40, 60, 80$) alloy and dissolution currents of Fe(II)_{sol}, Ni(II)_{sol} in sulfuric acid solution (pH 1).

could be explained by adsorption of the species in the dissolution process of Ni.

In Fig. 5, the capacitive and inductive semicircles are observed on $Z(\omega)$ of Fe-40 wt% Ni alloy at -0.25 V. The two capacitive semicircles and one inductive semicircle appear on $Z(\omega)$ above -0.2 V. This behavior is as the same as that of Fe-20 wt% Ni alloy.

In Fig. 6, $Z(\omega)$ of Fe-60 wt% Ni shows the same behavior as those presented in Figs. 4 and 5 below -0.2 V. On the other hand, a negative resistance, which is locus moving toward a negative real axis with decreasing the frequency on the complex plane, is observed in the $Z(\omega)$ plots at 0.1 V.

In Fig. 7, a negative resistance is observed on the $Z(\omega)$ plots of Fe-80 wt% Ni alloy above -0.05 V. Generally the negative resistance originates from passivation,¹²⁾ however the polarization curve of Fe-80 wt% Ni doesn't show passivation at the potentials where $Z(\omega)$'s are measured as shown in Fig. 3. At the

Fig. 4 Experimental results of electrochemical impedance of Fe-20 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials.

Fig. 5 Experimental results of electrochemical impedance of Fe-40 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials.

Fig. 6 Experimental results of electrochemical impedance of Fe-60 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials.

Fig. 7 Experimental results of electrochemical impedance of Fe-80 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials.

conditions in which the negative resistance appears, the dissolution rate of Ni(II) is sufficient large comparing with that of Fe(II) in Fig. 3. This result means that the dissolution process of Ni is related with the negative resistance.

4 Discussion

4.1 Dissolution model of Fe-Ni alloy and derivation of electrochemical impedance

The following consecutive reactions¹³⁾ are used to represent the Fe(II) dissolution process from Fe-Ni alloy in the present paper.

where K_1 is a reaction rate constant, and has the

following relation with the electrode potential E . The subscript "ad" means adsorbed intermediate.

$$K_1 = k_1 \exp(b_1 E) \quad (5)$$

where k_1 is a constant, and b_1 is a Tafel constant. According to the previous paper,¹⁴⁾ the active dissolution of Ni proceeds by the following reactions.

(oxidation rate constant: K_3 , reduction rate constant: K_{-3})

On the basis of the above reactions, the simulation is performed for the electrochemical behavior of Fe-Ni alloys obtained in the present paper with the following assumptions.

- 1) Adsorption and charge transfer happen on the two-dimensional electrode surface.
- 2) The interaction among adsorbed species is neglected.
- 3) The reaction rate changes exponentially with the electrode potential (equation(5)).

The mass balance of Fe(I)_{ad} and Ni(I)_{ad} are written as below according to the equations (3), (4), (6) and (7).

$$\beta(d\theta_{\text{Fe}}/dt) = K_1(1 - \theta_{\text{Fe}} - \theta_{\text{Ni}}) - K_2\theta_{\text{Fe}} \quad (8)$$

$$\beta(d\theta_{\text{Ni}}/dt) = K_3(1 - \theta_{\text{Fe}} - \theta_{\text{Ni}}) - (K_4 + K_{-3})\theta_{\text{Ni}} \quad (9)$$

where θ_{Fe} and θ_{Ni} are the fractional coverages of Fe(I)_{ad} and Ni(I)_{ad} , respectively, and β is surface concentration (mol cm⁻²) as monolayer on the electrode when $\theta = 1$. At the steady-state:

$$d\theta_{\text{Fe}}/dt = 0, \quad (10)$$

$$d\theta_{\text{Ni}}/dt = 0. \quad (11)$$

From the equations (8) and (9), the steady-state coverages of Fe(I)_{ad} , θ_{Fe} , and Ni(I)_{ad} , θ_{Ni} , are:

$$\theta_{\text{Fe}} = (K_1 K_4 + K_1 K_{-3}) / (K_1 K_4 + K_1 K_{-3} + K_2 K_4 + K_2 K_{-3} + K_2 K_{-3}) \quad (12)$$

$$\theta_{\text{Ni}} = K_2 K_3 / (K_1 K_4 + K_1 K_{-3} + K_2 K_4 + K_2 K_{-3} + K_2 K_{-3}) \quad (13)$$

The equations (8) and (9) are transformed into the frequency domain and by Taylor expansion as follows.

$$(j\omega\beta + K_1 + K_2)\Delta\theta_{\text{Fe}}/\Delta E + K_1\Delta\theta_{\text{Ni}}/\Delta E = b_1 K_1(1 - \theta_{\text{Fe}} - \theta_{\text{Ni}}) - b_2 K_2\theta_{\text{Fe}} \quad (14)$$

$$K_3\Delta\theta_{\text{Fe}}/\Delta E + (j\omega\beta + K_3 + K_{-3} + K_4)\Delta\theta_{\text{Ni}}/\Delta E = b_3 K_3(1 - \theta_{\text{Fe}} - \theta_{\text{Ni}}) - (b_4 K_4 + b_{-3} K_{-3})\theta_{\text{Ni}} \quad (15)$$

From the charge balance in reactions (3), (4), (6) and (7), the working electrode current i_w and the dissolution currents of Fe(II), $i_{\text{Fe(II)}}$, and Ni(II), $i_{\text{Ni(II)}}$, are written as follows.

$$i_w = F \{ (K_1 + K_3)(1 - \theta_{\text{Fe}} - \theta_{\text{Ni}}) + K_2\theta_{\text{Fe}} + (K_4 - K_{-3})\theta_{\text{Ni}} \} \quad (16)$$

$$i_{\text{Fe(II)}} = 2FK_2\theta_{\text{Fe}} \quad (17)$$

$$i_{\text{Ni(II)}} = 2FK_4\theta_{\text{Ni}} \quad (18)$$

The equation (16) is transformed into:

$$\Delta i_w/\Delta E = F \{ (b_1 K_1 + b_3 K_3)(1 - \theta_{\text{Fe}} - \theta_{\text{Ni}}) + b_2 K_2\theta_{\text{Fe}} + (b_4 K_4 - b_{-3} K_{-3})\theta_{\text{Ni}} \} + (-K_1 + K_2 - K_3)(\Delta\theta_{\text{Fe}}/\Delta E) + (-K_1 - K_3 - K_{-3} + K_4)(\Delta\theta_{\text{Ni}}/\Delta E) \quad (19)$$

The Faradaic impedance $Z_F(\omega)$ is calculated by:

$$Z_F(\omega) = \Delta E / \Delta i_w \quad (20)$$

4.2 Simulated results of $Z(\omega)$ of Fe-Ni alloy

The electrochemical impedance $Z(\omega)$ of liquid/solid interface is composed of $Z_F(\omega)$ and the capacitance of electric double layer C_{dl} .

$$1/Z(\omega) = 1/Z_F(\omega) + j\omega C_{dl} \quad (21)$$

The $Z(\omega)$'s of Fe-20 wt% Ni alloy simulated according to the calculation method in the previous section are shown in Fig. 8. The one pair of capacitive and inductive semicircles is shown below -0.3 V. The inductive behavior is explained by the formation of the adsorbed intermediate Fe(I)_{ad} in the reactions (3) and (4). Above -0.25 V, two capacitive semicircles and one inductive semicircle are simulated. The locus and its potential dependence of the simulated $Z(\omega)$ agree well with the results in Fig. 4. However, the frequency for each plot is not agreement with that in Fig. 4 perfectly. In this simulation, since five pairs of b_i and K_i were determined at the same time, the accuracies of the parameters were not high. The discrepancy between Figs. 4 and 8 originates from the parameters K 's were obtained to one significant digit due to low accuracy. Though a capacitive semicircle is explained by the time constant of reaction resistance and C_{dl} generally, the second capacitive semicircle, which appears on $Z(\omega)$ above -0.25 V, originates from the action of adsorbed intermediate Ni(I)_{ad} .

The simulated $Z(\omega)$'s of Fe-40 wt% Ni alloy are shown in Fig. 9. The two capacitive and one inductive semicircles are simulated, and in agreement with the experimental results in Fig. 5. In experiment results in Fig. 5, however, the third capacitive semicircle is

Fig. 8 Simulated results of electrochemical impedance of Fe-20 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials. The parameters for the simulation are as follows:

$$\beta = 10^{-8} \text{ mol cm}^{-2}, \quad b_1 = 38 \text{ V}^{-1}, \quad b_2 = 7 \text{ V}^{-1}, \quad b_3 = 13 \text{ V}^{-1}, \quad b_{-3} = -13 \text{ V}^{-1}, \quad b_4 = 18 \text{ V}^{-1},$$

$$(a) \quad K_1 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 3 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(b) \quad K_1 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 3 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(c) \quad K_1 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 3 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(d) \quad K_1 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 2 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 1 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}.$$

Fig. 9 Simulated results of electrochemical impedance of Fe-40 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials. The parameters for the simulation are as follows:

$$\beta = 10^{-8} \text{ mol cm}^{-2}, \quad b_1 = 38 \text{ V}^{-1}, \quad b_2 = 7 \text{ V}^{-1}, \quad b_3 = 13 \text{ V}^{-1}, \quad b_{-3} = -13 \text{ V}^{-1}, \quad b_4 = 18 \text{ V}^{-1},$$

$$(a) \quad K_1 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 1 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(b) \quad K_1 = 8 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 8 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 8 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 8 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(c) \quad K_1 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 2 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(d) \quad K_1 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_3 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_4 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}.$$

observed at low frequency range around 10 mHz. Though the simulation assuming the third adsorbed intermediate, which has very low formation rate, is necessary to represent the third capacitive semicircle, it is neglected in the present analysis for a simplification.

The simulated $Z(\omega)$'s of Fe-60 wt% Ni alloy are shown in Fig. 10. Below 0.0 V, the $Z(\omega)$ shows the similar behavior to those of Fe-20 wt% Ni and Fe-40 wt% Ni alloys. Furthermore, negative resistance observed in 0.1 V is reproduced. Above-mentioned simulation results agree with experiment results shown with Fig. 6. The simulated $Z(\omega)$'s of Fe-80 wt % Ni alloy are shown in Fig. 11. The negative resistance is reproduced above 0.05 V, and agrees with experiment results in Fig. 7.

When the potential becomes nobler in all cases of Ni contents, a values of K_1 and K_3 become larger, as indicated by equation (5) in small anodic polarizations. In large anodic polarizations, the values K_1 and K_3 of deviate from the relation of equation (5). This deviation originates from the change of surface activity of alloy element due to rapid dissolution in large anodic polarizations. Though the surface activities were not determined in this paper, the surface concentration of alloy element is significant parameter to discuss the active dissolution of alloy. For example, the value of K_1 at -0.2 V is getting smaller with

Fig. 10 Simulated results of electrochemical impedance of Fe-60 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials. The parameters for the simulation are as follows:

$$\beta = 10^{-8} \text{ mol cm}^{-2}, \quad b_1 = 38 \text{ V}^{-1}, \quad b_2 = 7 \text{ V}^{-1}, \quad b_3 = 13 \text{ V}^{-1}, \\ b_{-3} = -13 \text{ V}^{-1}, \quad b_4 = 18 \text{ V}^{-1}$$

$$(a) \quad K_1 = 3 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 3 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(b) \quad K_1 = 3 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 4 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 3 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(c) \quad K_1 = 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 7 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(d) \quad K_1 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(e) \quad K_1 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 3 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 3 \times 10^{-3} \text{ mol cm}^{-2} \text{ s}^{-1}.$$

increasing the Ni component. Because the value of K_1 contains surface activity of Fe, the decrease should be caused by Fe component in the alloy. The degree of the decrease is more remarkable than a change of the Fe component. The above-mentioned result indicates that the formation rate of the adsorbed intermediate Fe(I)_{ad} (reaction (3)) and the dissolution rate from Fe(I)_{ad} are controlled by the addition of Ni into Fe.

4. 3 Simulated results of polarization curves of Fe-Ni alloy and the fractional coverages of Fe(I)_{ad} and Ni(I)_{ad}

Figure 12 shows the simulated results of polarization curves of Fe-Ni alloy and their dissolution currents $i_{\text{Fe(II)}}$ and $i_{\text{Ni(II)}}$ calculated according to equations (12), (13), (16), (17) and (18). These simulated results agree with the measurement results presented in Fig. 3 qualitatively. The steady-state coverages of Fe(I)_{ad} , Θ_{Fe} , and Ni(I)_{ad} , Θ_{Ni} calculated by equations (12) and (13) are shown in Fig. 13. The preferential dissolution

Fig. 11 Simulated results of electrochemical impedance of Fe-80 wt% Ni in sulfuric acid solution (pH 1) at various electrode potentials. The parameters for the simulation are as follows:

$$\beta = 10^{-8} \text{ mol cm}^{-2}, \quad b_1 = 38 \text{ V}^{-1}, \quad b_2 = 7 \text{ V}^{-1}, \quad b_3 = 13 \text{ V}^{-1}, \\ b_{-3} = -13 \text{ V}^{-1}, \quad b_4 = 18 \text{ V}^{-1}$$

$$(a) \quad K_1 = 2 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 2 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 2 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 2 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(b) \quad K_1 = 2 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 2 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 2 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 2 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 2 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(c) \quad K_1 = 2 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 2 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 2 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 2 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(d) \quad K_1 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 3 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 6 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(e) \quad K_1 = 3 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 4 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 1 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 4 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1},$$

$$(f) \quad K_1 = 4 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_2 = 2 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_3 = 5 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}, \quad K_{-3} = 3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_4 = 4 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}.$$

of Fe(II) is reproduced for the alloy of small Ni component in Fig. 12, and coverage of Ni(I)_{ad} , Θ_{Ni} is very small at the low anodic potentials. The calculated results in Fig. 13, which show that the almost adsorbed species are Fe(I)_{ad} at low anodic potential, confirm that the inductive behavior of $Z(\omega)$ originates from the formation of Fe(I)_{ad} . In the case of Fe-20, 40, 60 wt% Ni alloy, the second capacitive semicircle is observed in Figs. 4-6. The potential at which the second capacitive semicircle appears corresponds to the potential at which the Θ_{Ni} become large beyond 10^{-2} , indicating that the second capacitive semicircle is caused by the formation of Ni(I)_{ad} . Moreover, Θ_{Ni} decreases at noble potentials, and Θ_{Fe} increases with the increase of Ni content. These results could influence on the passivation of Fe-Ni

Fig. 12 Simulated results of polarization curves of Fe- x wt% Ni ($x=20,40,60,80$) alloy and the dissolution currents of Fe(II), Ni(II) in sulfuric acid solution (pH 1). The parameters for the simulation are referred to Figs. 8-11.

Fig. 13 Simulated results of steady-state coverages of the adsorbed species Fe(I)_{ad} (Θ_{Fe}), Ni(I)_{ad} (Θ_{Ni}) of Fe- x wt% Ni on alloy. The parameters for the simulation are referred to Figs. 8-11.

alloy.

5 Conclusion

First of all in the present paper, *in situ* detection of Fe(II) and Ni(II) dissolved from Fe-Ni alloy electrode was done by separation type channel flow electrode, and the effect of Ni content on the alloy dissolution

behavior was discussed. In the case of low Ni content, Fe-Ni alloy showed a preferential dissolution of Fe(II) at anodic side near the immersion potential. The dissolution rate of Fe(II) was controlled significantly by Ni content.

In the analysis by EIS, the features of electrochemical impedance, *i.e.*, two capacitive semicircles,

an inductive semicircle and negative resistance, was discussed theoretically. The inductive semicircle was explained by the Fe(I)_{ad} formation, and two capacitive semicircles were related to the time constants of the Ni(I)_{ad} formation and of the reaction resistance and the double layer capacitance. The numerical simulation was performed for experimental results of $Z(\omega)$ and polarization curve. On the basis of kinetic parameters obtained by the simulation, the steady-state coverage Θ_{Fe} and Θ_{Ni} were calculated. The Θ_{Ni} is quite small comparing with Θ_{Fe} at low anodic potential, indicating that Ni product does not inhibit the dissolution rate of Fe(II) by Ni addition but changes the free energy of Fe-Ni alloy, as the reason why the immersion potential of Fe-Ni alloy shifts toward positive with the increase of Ni content. The negative resistance in Z appears when Θ_{Ni} became larger than Θ_{Fe} .

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