Effects of solution temperature on the kinetic nature of passive film on Ni

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Effects of solution temperature on the kinetic nature of passive film on Ni were investigated using polarization test, Mott–Schottky analysis and electrochemical impedance spectroscopy to reveal why the corrosion resistance of Ni is degraded with an increase in solution temperature. The increase in the corrosion rate of Ni with solution temperature was confirmed by the increase in the passive current density and also in the steady-state current density. Mott–Schottky analysis revealed that the passive film formed on Ni exhibits a p-type semiconducting characteristics irrespective of the solution temperature, and the concentration of cation vacancy in the passive film increases with temperature. By optimizing the reduced PDM (point defect model) on the experimental impedance data, base rate constants and transfer coefficients for the charge transfer reactions occurring at the metal/film and film/solution interfaces were extracted, and the Warburg coefficient for the cation vacancy transport was also determined. According to the calculated kinetic parameters (rate constants for the interfacial reactions, diffusivity of cation vacancy, etc.), the mechanism for the degradation of corrosion resistance of Ni with solution temperature was explained.

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1. Introduction

Ni and Ni-based alloys have been used as structural materials in aqueous environments at high temperatures due to their high corrosion resistance [1–3]. However, the passivity or the corrosion resistance of Ni and Ni-based alloys is degraded with an increase in solution temperature, as confirmed by the increase in the passive current density \((i_p)\) or the decrease in the resistance to film breakdown with temperature [4–6].

Numerous studies have been conducted to elucidate the effects of the solution temperature on the passivity or the corrosion behavior of metals, including Ni and its alloys. Hur and Park suggested that the composition and structure of passive film on Alloy 600 are affected by the solution temperature [5]; as solution temperature increased, the portion of non-productive nickel hydroxide/oxide in the passive film increased at the expense of the portion of the protective chromium-rich film. The change in the composition and structure of the passive film was found to be responsible for the degradation in the corrosion resistance of Alloy 600. Carranza and Alvarez showed that passive films on Alloy 800 become more porous and less protective with increasing temperature, thereby decreasing the corrosion resistance [7]. However, in spite of the numerous studies on the influence of temperature on the properties of passive film and the corrosion behavior of metals and alloys, the mechanistic explanation for the temperature effects on the corrosion behavior of a metal or an alloy still remains unclear. It is due mainly to that there are limitations in analyzing the atomic-scale details of the processes that may occur within the passive films because of the lack of in situ experimental techniques having the spatial and temporal resolution enough to probe the passive film.

However, the limitation in the direct examination of the properties of passive film can be complemented by employing the appropriate and verified passivity model. The point defect model (PDM), one of the proposed models on passivity developed by MacDonald et al. provides an analytical description for the growth and breakdown of passive film on the atomic scale, in terms of formation, annihilation, and transport of point defects in the passive film [8–13]. Moreover, in the recent studies [14–16], PDM has been found to account successfully for the properties of passive film and corrosion phenomena at a quantitative level by estimating the kinetic parameters such as rate constants for the electrochemical reactions occurring at the metal/film (m/f) and film/solution (f/s) interfaces (Fig. 1) or diffusivity of point defects. Thus, based on the PDM, the effects of temperature on the corrosion behavior of Ni can be analyzed by exploring the influence of solution temperature on the kinetic parameters for the passive film on Ni.

The research objective of present work is to elucidate the influences of solution temperature on the corrosion properties of Ni by analyzing the temperature effects on the kinetic nature for the electrochemical reactions occurring at the m/f interface or at the f/s interface.
2. Experimental

High purity Ni sheet (99.99%) was used as a working electrode. The working electrode was mounted in an epoxy resin with an exposed area of 0.12 cm², and then grinded with SiC paper to 2000 grit, and finally polished to 1 μm diamond suspension. All the electrochemical tests were carried out in a deaerated pH 8.5 buffer solution at 30, 50 and 80 °C, respectively. The buffer solution was prepared by mixing H₃BO₃, C₆H₈O₇ for 24 h at the film formation potential (the surface, and then the passive film was grown potentiostatically). According to the PDM, the total current flowing through the solution at a fixed frequency of 1 kHz using an excitation voltage of 10 mV is a function of potential, but the defect structure is “frozen-in” irrespective of the solution temperature. Corrosion rate of Ni at a passive state increased with solution temperature, which was clearly confirmed by the significant increase in the passive current density with an increasing temperature. The passive current density of Ni measured potentiodynamically, however, was not a fixed value, but changed to a steady-state value with passivation time. 

3. Results and discussion

3.1. Potentiodynamic polarization response and potentiostatic current transient

Fig. 2 shows the effects of solution temperature on the potentiodynamic polarization behavior of Ni in deaerated pH 8.5 buffer solution. The corrosion potential (Ecorr) of Ni was measured to be in the range of −0.6 VSCe to −0.68 VSCe at temperatures from 30 to 80 °C. Ni was in the active state from Ecorr to about −0.2 VSCe, and then in the passive state at potentials higher than −0.2 VSCe irrespective of the solution temperature. Corrosion rate of Ni at a passive state increased with solution temperature, which was clearly confirmed by the significant increase in the passive current density with an increasing temperature. The passive current density of Ni measured potentiodynamically, however, was not a fixed value, but changed to a steady-state value with passivation time. According to the PDM, the total current flowing through the passive film, I, can be expressed by Eq. (1) [14,16], considering the fluxes of point defects such as cation vacancies, cation interstitials and oxygen vacancies that are generating or annihilating at the m/f interface and at the i/f interface:

\[
I = F[J^\text{m/f} + (\Gamma - \chi)I^\text{f/f} - \chi J^\text{m/f} - (\Gamma - \chi)I^\text{i/f} - 2J^\text{i/f} + (\Gamma - \chi)c^o C^n_{\text{H}_2}],
\]

where \(J^\text{m/f}\) is the flux of point defects in the film passing through the metal/passive film interface, \(I^\text{f/f}\) is the flux of point defects in the film passing through the film/passive film interface, \(\Gamma\) is the growth rate of passive film, \(\chi\) is the annihilation rate of point defects, \(c^o\) is the concentration of oxygen vacancies, and \(C^n\) is the concentration of cations.

Fig. 3 shows the effects of solution temperature on the current transient of Ni when its potential was stepped to 0.4 VSCe for 24 h. The capacitive behavior of Ni changes from active to passive states. The capacitive behavior of Ni changes from active to passive states.

Fig. 1. The defect generation and annihilation reactions occurring at the interfaces of the barrier layer on a metal in terms of the Point Defect Model. \(V^\text{m/f}\) = cation vacancy, \(M^\text{f/f}\) = cation interstitial, \(V^\text{oxygen/anion}\) = oxygen/anion vacancy, \(M^\text{c/cation}\) = cation in the solution, \(M^\text{c/cation}\) = cation in cation site on the cation sublattice, \(O^\text{oxygen}\) = oxide ion in anion site on the anion sublattice, \(M_{\text{p/f}}\) = stoichiometric passive film.
where $F$ is the Faradaic constant, $\chi$ is the oxidation state of cation vacancy, and $I$ is the oxidation state of metal ion dissolved into solution. The superscripts $m/f$ and $f/s$ designate the metal/film interface and film/solution interface, respectively, and subscripts $c$, $i$ and $o$ designate the cation vacancy, cation interstitial and oxygen vacancy, respectively.

Since the fluxes of point defects described in Eq. (1) are directly related to the rate of interfacial reactions $Q^{m/f} = k_1C^{m/f}_c$, $Q^{i} = k_2$, $J^{m/f} = -k_3C^{m/f}_i$, $J^{o} = -k_4$ and $P^{m/f} = -(\chi/2)k_6C^{m/f}_{21}$, $I$ is expressed as a function of the rate constants of interfacial reactions. Under the steady-state condition $
u^{m/f} = J^{i}$, $J^{m/f} = J^{o}$ and $J^{o} = -(\chi/2)k_7C^{n}_{21}$, $I$ is expressed as Eq. (2):

$$I_{SS} = \frac{RT}{F}[k_4 + k_2 + k_7C^{n}_{21}]$$

where $k_i$ is the rate constant for the reaction (i) and $C_{21}$ is the hydrogen ion concentration in the solution, and $n$ is the kinetic order of the film dissolution reaction with respect to $C_{21}$.

Eqs. (1) and (2) suggest that the steady-state current density, $I_{SS}$, is associated with the fluxes of point defects and also with the kinetic parameters for the interfacial reactions. Thus, it is expected that we get fundamental understanding on the defects on the corrosion behavior of Ni by examining the defect structure and the kinetic parameters for the passive film on Ni.

### 3.2. Mott–Schottky analysis

Before exploring the temperature influence on the kinetic parameters for the interfacial reactions, we examined the semiconducting properties and defect structure of passive film on Ni using the Mott–Schottky analysis. Mott–Schottky analysis was performed as a function of solution temperature for the passive film on Ni after exposure at 0.4 $V_{SCE}$ for 24 h in deaerated pH 8.5 buffer solution.

For Mott–Schottky analysis, imaginary part of the impedance ($Z''$) was measured as a function of applied potential, and then the interfacial capacitance, $C$, was calculated by $C = -1/\omega Z''$, where $\omega$ is the angular frequency. The interfacial capacitance consists of the space charge capacitance ($C_{SC}$) and Helmholtz layer capacitance ($C_{H}$) by $C = C^{-1} = C_{SC} - C_{H}$, assuming that contribution from surface states can be neglected. The Mott–Schottky relations for p-type and n-type semiconductors are expressed by Eq. (3a) and (3b) by taking account of the contribution of $C_{SC}$ and $C_{H}$.

$$\frac{1}{C^2} = \frac{1}{C_{SC}^2} - \frac{2}{e\varepsilon_0\varepsilon N_A} (V - V_{FB} + \frac{kT}{e}) \quad \text{for p-type semiconductor} (3a)$$

$$\frac{1}{C^2} = \frac{1}{C_{SC}^2} + \frac{2}{e\varepsilon_0\varepsilon N_D} (V - V_{FB} + \frac{kT}{e}) \quad \text{for n-type semiconductor} (3b)$$

where $\varepsilon$ is the dielectric constant of the passive film, $\varepsilon_0$ is the vacuum permittivity ($8.854 \times 10^{-14}$ F/cm), $e$ is the electron charge ($1.602 \times 10^{-19}$ C), $k$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J/K), $V$ is the applied potential, $V_{FB}$ is the flat band potential, $N_A$ is the acceptor density and $N_D$ is the donor density. $C^{-2}$ vs. $V$ plot for p-type semiconductors should be linear with a negative slope that is inversely proportional to the acceptor density, whereas for n-type semiconductor should be linear with positive slope. Apparently, the Mott–Schottky plots in Fig. 4 shows a linear region with a negative slope, indicating that the passive film on Ni exhibits a p-type semiconducting property irrespective of the solution temperature. According to the previous studies [20–24], the cation vacancy ($V_{Ni}^{+}$) acts as an acceptor in NiO, a barrier layer of passive film on Ni. The major effect of solution temperature on the Mott–Schottky plot is an appreciable decrease in the slope of the linear region. Because the slope is inversely proportional to the acceptor density, the decrease in the slope with solution temperature indicates that the concentration of cation vacancy ($V_{Ni}^{+}$) in the passive film increases with an increase in temperature ($C_{V_{Ni}^{+}}(30°C) = 1.33 \times 10^{-21}$ cm$^{-3}$), $C_{V_{Ni}^{+}}(50°C) = 1.97 \times 10^{-21}$ cm$^{-3}$), and $C_{V_{Ni}^{+}}(80°C) = 2.08 \times 10^{-21}$ cm$^{-3}$).

### 3.3. Electrochemical impedance analysis

#### 3.3.1. Electrochemical impedance spectra

Fig. 5 shows the effects of solution temperature on the impedance spectra (Bode plots) for the passive films formed on Ni at 0.4 $V_{SCE}$ for 24 h in pH 8.5 buffer solution. Impedance spectra measured at 30°C shows typical features that are often observed for a passive film grown on Ni at a room temperature [15,20], exhibiting the constant phase behavior in the low frequency region. However, with increasing temperature, phase angle changed drastically in the low frequency region (0.01–0.1 Hz) as well as in the intermediate frequency region (0.1–10 Hz). The intermediate frequency region is associated with the interfacial charge transfer reactions or relaxation in a space charge layer, whereas the low frequency region is related to the transport of point defects [25]. The constant phase behavior of impedance at low frequencies observed at 30°C is a consequence of defect transport in the oxide film being due mainly to migration under the influence of electric field rather than due to diffusion [26]. But, at higher temperature, diffusion probably made an appreciable contribution to the defect transport, consequently leading to an abrupt change in the phase angle. Although the impedance spectra in the low frequency region did not exhibit...
the phase angle of 45° corresponding to the Warburg impedance due to diffusion, it appears that the component was convoluted in the low frequency region of the impedance spectra. Therefore, the diffusion of point defects as well as charge transfer reactions occurring at the interfaces should be considered in analyzing the effects of solution temperature on impedance behavior of the passive film of Ni.

3.3.2. Electrical equivalent circuit

Eq. (4) was used in the present study. The reactions (2), (3a), (3b), (4), (6) and (7) in Fig. 1 is fully described in the previous reports [14, 16]. However, for the impedance considering all the interfacial reactions shown occurring at the m/f and f/s interfaces. The numerical expression was devised by considering the impedance due to the charge transfer reactions occurring at the m/f and f/s interfaces and also that due to the transport of point defects. Total impedance for the system is expressed by Eq. (4):

$$Z = j\omega C + (Z_f+(Z_w^{-1}+R_c^{-1})^{-1}+1)^{-1} + R_s.$$  (4)

where $Z_f$ is the faradic impedance associated with the reactions occurring at the m/f and f/s interfaces. The numerical expression for the impedance considering all the interfacial reactions shown in Fig. 1 is fully described in the previous reports [14, 16]. However, the reduced PDM comprising reactions (1), (3a), (3b), (4), (6) and (7) was used in the present study. The reactions (2) and (5) involving cation interstitial were neglected because cation interstitial is a donor. But reactions involving oxygen vacancy (reactions (3a), (3b), (6) and (7)), which is another type of donor, were considered because they must be present in all barrier layers that has a finite dissolution rate (regardless of the electronic type) [15]. $Z_w$ is the Warburg impedance associated with the transport of cation vacancy, and expressed by Eq. (5) [16, 27]:

$$Z_w = \sigma_{M0}^{-1/2} - j\omega\sigma_{M0}^{-1/2}.$$  (5)

Since the transport (diffusion and migration) of cation vacancy is influenced by temperature, $Z_w$ is considered to be an important factor in exploring the temperature effects on the total impedance response. $R_s$ is the resistance due to the transport of electronic defects such as electrons or holes, and $R_s$ is the solution resistance. $C$ is the total capacitance for the Ni/NiO/solution system, comprising contributions from a geometric capacitance ($C_p$), capacitance of the space charge region ($C_{Sc}$), and that of Helmholtz layer ($C_H$) by the relationship of $C^{-1} = (C_{Sc}+C_H^{-1})^{-1} + C_{Hi}^{-1}$.

Since the total impedance $Z$ incorporates impedance associated with the charge transfer reactions occurring at the m/f and f/s interfaces and that for the transport of point defects, it should be a function of kinetic parameters for interfacial reactions and diffusion of cation vacancy. By optimizing the reduced PDM on the measured impedance data, the kinetic parameters for the interfacial reactions as well as those for the transport of ionic defects were extracted, and the results are presented in Table 1.
the passive film on Ni exhibits the p-type semiconducting property, which means the flux of oxygen vacancy/cation interstitial is negligible compared to that of cation vacancy. The current density should be most significantly controlled by the interfacial reactions involving cation reactions involving cation vacancy, i.e. reactions (1) and (4). Under the steady-state condition ($J_{\text{Ni}}' = J_{\text{Ni}}''$), the rate constant for the cation vacancy generation reaction, $k_6$, increased abruptly with increasing solution temperature, confirming that the formation of cation vacancy at the f/s interface was facilitated by raising the solution temperature, and hence $J_{\text{Ni}}'$ increased with temperature. As mentioned above, oxygen vacancies are minority defects in the passive film on Ni and make little contribution to the total current density. However, it plays an important role in increasing the concentration and flux of cation vacancy. Considering the Schottky-pair reaction at the f/s interface in the local equilibrium, cation vacancy flux is a function of oxygen vacancy concentration at the f/s interface ($J_{\text{Ni}}'' = J_{\text{Ni}}' [C_{V_{\text{Ni}}''}]^{1/2}$), where $J' = \chi k_6 \rho_{\text{Ni}} [N_{\text{V}}/\Omega]^{1/2} \exp(-\Delta G_{\text{V}}/(RT))$, $N_{\text{V}}$ is the Avogadro’s number, $\Omega$ is the molecular volume per cation, and $\Delta G_{\text{V}}$ is the change in Gibbs energy for the Schottky-pair reaction) [9]. When $C_{V_{\text{Ni}}''}$ decreases due to the occupation of anion (e.g. Cl$^-$) into $V_{\text{Ni}}''$, $J_{\text{Ni}}''$ should be enhanced. Although Cl$^-$ was not added to the test solution in this study, adsorption of H$_2$O or anions such as BO$_3^{3-}$ and PO$_4^{3-}$ to the oxygen vacancy may be facilitated by increasing solution temperature. Oxygen vacancy annihilation (reaction (6)) will be enhanced by the adsorption of H$_2$O, thereby decreasing the $C_{V_{\text{Ni}}''}$. Additionally, the adsorption of BO$_3^{3-}$ and PO$_4^{3-}$ may decrease the activity of oxygen vacancy ($\alpha_{V_{\text{Ni}}''}$) although such large anions themselves cannot occupy the oxygen vacancy. Thus, Schottky-pair reaction would be facilitated to compensate the decreasing $C_{V_{\text{Ni}}''}$ and $\alpha_{V_{\text{Ni}}''}$, and to meet the local electroneutrality condition at the f/s interface. Consequently, the concentration and flux of the cation vacancy increase at the f/s interface.

According to the PDM, the cation vacancies generated at the f/s interface move toward the m/f interface. The driving force for the transport of the cation vacancy is the electric field ($\varepsilon$) and the concentration gradient ($\partial C_{V_{\text{Ni}}''}/\partial x$) across the passive film. Diffusivity of cation vacancy has a significant effect on the migration due to electric field as well as on the diffusion due to concentration gradient. The diffusivity of $V_{\text{Ni}}''$ calculated according to Eq. (7) [16,27,28] was presented in Table 2.

$$D_{V_{\text{Ni}}''} = 2\sigma^2(1 - \varepsilon^2) J_{\text{SS}}^2 e^2$$

$D_{V_{\text{Ni}}''}$ increased significantly with raising the solution temperature, and accordingly the flux of cation vacancy moving through the passive film ($J_{\text{transport}}''$) increased with solution temperature. The calculated $D_{V_{\text{Ni}}''}$ was presented as a function of temperature with the previously reported diffusivity values [29–31] in Fig. 9. Lesage et al. [30] and Atkinson and Taylor [31] reported that the activation energy ($E_a$) for the diffusion of cation vacancy in the single crystalline NiO was 154 kJ/mol (1.6 eV/atom) and 58 kcal/mol

### Table 1: Extracted parameters by optimization of PDM on the experimental impedance data.

<table>
<thead>
<tr>
<th>Properties</th>
<th>30 ºC</th>
<th>50 ºC</th>
<th>80 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric field strength ($\varepsilon$)</td>
<td>1.5×10$^6$</td>
<td>1.6×10$^9$</td>
<td>1.5×10$^{10}$</td>
</tr>
<tr>
<td>Polarizability</td>
<td>0.325</td>
<td>0.275</td>
<td>0.252</td>
</tr>
<tr>
<td>Base rate constant for reaction (1) in Fig. 1</td>
<td>$k_1$ (cm s$^{-1}$)</td>
<td>5.37×10$^{-11}$</td>
<td>6.82×10$^{-12}$</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>1.62×10$^{-13}$</td>
<td>3.54×10$^{-14}$</td>
</tr>
<tr>
<td></td>
<td>$k_3$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>3.32×10$^{-14}$</td>
<td>7.69×10$^{-14}$</td>
</tr>
<tr>
<td></td>
<td>$k_4$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>3.25×10$^{-14}$</td>
<td>7.69×10$^{-14}$</td>
</tr>
<tr>
<td>Transfer coefficient ($\alpha$)</td>
<td>0.40</td>
<td>0.34</td>
<td>0.32</td>
</tr>
<tr>
<td>Warburg coefficient ($\sigma$)</td>
<td>5.87×10$^3$</td>
<td>5.27×10$^3$</td>
<td>1.45×10$^3$</td>
</tr>
</tbody>
</table>

### Table 2: Calculated values using the extracted parameters based on the PDM.

<table>
<thead>
<tr>
<th>Properties</th>
<th>30 ºC</th>
<th>50 ºC</th>
<th>80 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard rate constant for reaction (i) in Fig. 1</td>
<td>$k_0$ (cm s$^{-1}$)</td>
<td>2.84×10$^{-11}$</td>
<td>4.32×10$^{-11}$</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>2.07×10$^{-10}$</td>
<td>4.47×10$^{-10}$</td>
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<td></td>
<td>$k_3$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>1.98×10$^{-10}$</td>
<td>7.59×10$^{-10}$</td>
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<td></td>
<td>$k_4$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>1.50×10$^{-13}$</td>
<td>1.82×10$^{-13}$</td>
</tr>
<tr>
<td>Rate constant for reaction (i)</td>
<td>$k_1$ (cm s$^{-1}$)</td>
<td>1.68×10$^{-4}$</td>
<td>9.74×10$^{-10}$</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>8.44×10$^{-13}$</td>
<td>1.02×10$^{-13}$</td>
</tr>
<tr>
<td></td>
<td>$k_3$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>2.02×10$^{-13}$</td>
<td>1.64×10$^{-12}$</td>
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<tr>
<td></td>
<td>$k_4$ (mol cm$^{-2}$ s$^{-1}$)</td>
<td>1.50×10$^{-13}$</td>
<td>1.82×10$^{-13}$</td>
</tr>
<tr>
<td>Cation vacancy concentration at the m/f interface</td>
<td>$C_{V_{\text{Ni}}''}$ (cm$^{-3}$)</td>
<td>7.24×10$^{18}$</td>
<td>1.01×10$^{20}$</td>
</tr>
<tr>
<td>Steady state current density</td>
<td>$I_{\text{SS}}$ (A cm$^{-2}$)</td>
<td>3.89×10$^{-4}$</td>
<td>3.16×10$^{-7}$</td>
</tr>
<tr>
<td>Steady state film thickness</td>
<td>$L_{\text{SS}}$ (nm)</td>
<td>1.90</td>
<td>2.33</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$D$ (cm$^2$ s$^{-1}$)</td>
<td>4.51×10$^{-20}$</td>
<td>1.14×10$^{-18}$</td>
</tr>
</tbody>
</table>
Fig. 8. Bode plots for the passive film on Ni formed at 0.4 V_{SCE} in pH 8.5 buffer solution at 30, 50 and 80°C.

Fig. 9. Comparison of Diffusivity of cation vacancy in the passive film on Ni.

Fig. 10. Measured and calculated $I_{ss}$ for Ni passivated at 0.4 V_{SCE} for 24h in pH 8.5 buffer solution at 30, 50 and 80°C, respectively.

Fig. 11. Calculated $L_{ss}$ for Ni passivated at 0.4 V_{SCE} for 24h in pH 8.5 buffer solution with previously reported film thickness values [33] for Ni measured in 0.1 M Na$_2$HPO$_4$ solution (pH 9.1).
As solution temperature increases, the more cation vacancies generated at the f/s interface, the generated cation vacancies moved toward the m/f interface more rapidly, and the cation vacancy concentration was remained higher at the m/f interface. Those factors increased the flux of the cation vacancies in the film, and hence increased the steady-state current density of Ni. The $I_{SS}$ calculated using kinetic parameters by Eq. (6) and the measured $I_{SS}$ from the potentiostatic test (Fig. 3) are compared in Fig. 10. The steady-state film thickness ($L_{SS}$) was calculated using the kinetic parameters by Eq. (8) [14] and was presented as a function of solution temperature in Fig. 11. According to Eq. (8), $L_{SS}$ is a function of $\epsilon$, $\alpha$, $V$, $n$, $\alpha_3$, $\gamma$, pH, $k_3^0$ and $k_7^0$. Among those variables, $\alpha$, $\beta$, $k_3^0$ and $k_7^0$ were sensitive to solution temperature (Tables 1 and 2), but $L_{SS}$ was most significantly affected by the change in $k_3^0$ rather than $\alpha$, $\gamma$, and $k_7^0$. Thus, the increase of the film thickness with increasing temperature is probably due to that film formation reaction (reaction (3a), (3b)) is facilitated with increasing solution temperature. Previously reported film thickness values for Ni, which were measured in 0.1 M Na$_2$HPO$_4$ solution (pH 9.1), similar pH with the solution employed in this study, using ellipsometric technique [33], were also presented in Fig. 11. Calculated $I_{SS}$ and $L_{SS}$ were consistent with the experimental values overall.

$$L_{SS} = \frac{1}{\epsilon} [1 - \alpha V + \frac{1}{\epsilon} \frac{2.303n}{\alpha_3 Y'} - \beta] \text{pH} + \frac{1}{\alpha_3 \gamma K} \ln \left( \frac{k_3^0}{k_7^0} \right)$$  \hspace{1cm} (8)

It has also been reported frequently that the film breakdown of Ni and Ni-based alloys occurs at lower potential at higher temperature [4–6], although this phenomenon was not observed explicitly in the present study due to being conducted in Cl$^-$-free buffer solution. According to the PDM [12], when cation vacancies arriving at the m/f interface cannot be annihilated by reaction (1) in Fig. 1, the excess vacancies condense at the interface and the film is detached locally from the metal. Due to separation of the film from the metal, the film growth by reaction (3a), (3b) ceases. However, because the dissolution of passive film by reaction (7) continues, the film thins locally and results in the rupture of the film (film breakdown). It is worth mentioning again that the cation vacancy concentration at the m/f interface ($C_{m/f}^{m/f}$) calculated using kinetic parameters increased drastically with solution temperature. Therefore, it is suggested that the possibility of formation of “vacancy condensate” increases with temperature and accordingly, the susceptibility to film breakdown increases with solution temperature. The principal features discussed in Section 3.4 are summarized in Fig. 12.

4. Conclusions

The effects of temperature on the corrosion behavior of Ni were examined by analyzing the kinetic parameters for the interfacial reactions at the m/f and f/s interfaces and diffusivity of cation vacancy based on the PDM.

- Corrosion rate of passivated Ni increased with solution temperature, as confirmed by the increase in the passive current density and also in the steady-state current density with temperature.
- Mott–Schottky analysis revealed that the passive film formed on Ni in pH 8.5 buffer solution exhibits a p-type semiconducting property irrespective of the solution temperature, indicating that the majority defect in the passive film on Ni is cation vacancy. The slope of linear region of Mott–Schottky plot decreased appreciably with increasing temperature, which demonstrates the concentration of cation vacancy ($V_{m/f}^\prime$) in the passive film increases with an increase in temperature.
- By optimizing the reduced PDM for p-type passive film on the experimental impedance data for passive nickel measured as a function of solution temperature, base rate constant and transfer coefficients for the charge transfer reactions occurring at the m/f interface.

![Fig. 12. Summary of the effects of solution temperature on the corrosion behavior of Ni.](image)
and f/s interfaces were extracted and the Warburg coefficient for the cation vacancy transport was also determined. The calculated $I_{ss}$ using kinetic parameters was consistent with the measured $I_{ss}$ from the potentiostatic tests, and the calculated cation vacancy diffusivities were also in agreement with the trend of previously reported diffusivity values with temperature.

- The mechanism of the increase in $I_{ss}$ was explained according to the calculated kinetic parameters (rate constants for the interfacial reactions, diffusivity of cation vacancy, etc.) based on the PDM. Under the steady-state condition, the current density is associated with cation vacancy flux ($I_{SS} = FJ_{V''_{Ni}}$) in the passive film. With increasing temperature, the cation vacancy generation rate at the f/s interface increased significantly, thereby increasing the cation vacancy flux at the f/s interface ($J_{f/s}V''_{Ni}$). Because diffusivity of cation vacancy was significantly enhanced by solution temperature, the cation vacancy generated at the f/s interface moved to the m/f interfaces more rapidly. While the annihilation rate of cation vacancy decreased by solution temperature, the cation vacancy concentration at the m/f interface ($C_{m/f}V''_{Ni}$) increased abruptly, thereby increasing the cation vacancy flux at the m/f interface ($J_{m/f}V''_{Ni}$). The increase in cation vacancy flux in the passive film resulted in the increase of $I_{ss}$.

- According to the PDM, film breakdown is closely associated with cation vacancy condensation at the m/f interface. The cation vacancy concentration at the m/f interface increased drastically with solution temperature. Therefore, it is suggested that the possibility of formation of “vacancy condensate” increases with temperature and accordingly, the susceptibility to film breakdown increases with solution temperature.

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References