Repassivation Behavior of Newly Created Surface of Pure Nickel in High Temperature and High Pressure Neutral Solution

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A rapid straining electrode technique has been applied to investigation of the initial process of anodic behavior on a newly created surface of pure nickel in high temperature and high pressure borate buffer solution up to 553 K. The analysis of the relation between the current density and the charge density shows that the repassivation process is divided into early and later stages. At the early stage, the newly created surface is covered with a monolayer of oxide film. The rate of this process follows a direct logarithmic law, showing neither potential nor temperature dependence. The mechanism of this stage is explained by the mutually-blocking pore model. At the later stage, the passive film grows following a parabolic law with the rate constant depending not only on temperature but also on potential. The rate of this process is determined by migration and diffusion of Ni$^{2+}$ ions in the liquid phase under the potential and the concentration gradient through pores and other defects contained in the passive film.

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I. Introduction

Nickel base alloys, such as Alloy 600, 690 and 800, are extensively used in a nuclear power generator, which comprises high temperature and high pressure water environments(1)-(3). A considerable number of researches have been performed on nickel base alloys with respect to SCC(4), crevice corrosion and IGA(5) in this environment. Since the electrochemical dissolution and film formation play an important role in causing these failures, it is required to understand the basic electrochemical process of pure nickel or high nickel alloys in high temperature and high pressure water. A large amount of work has been performed on the kinetics of active dissolution and film growth on nickel in acidic and neutral solutions at room temperature(6)-(9). Little work, however, has been performed on the basic electrochemical process of the high nickel alloys or pure nickel in the high temperature and high pressure water environment(10). In a previous work(11)(12), the authors have investigated a rapid straining electrode behavior of pure nickel in high temperature and high pressure aqueous solution containing sulphate ions. It is revealed that the passive film of nickel is locally broken down due to an aggressive action of sulphate ions in a specific temperature range. In the present work, the initial process of anodic behavior of a newly created surface of pure nickel is examined by means of a rapid straining electrode technique in neutral borate buffer solution which is known not to cause any localized corrosion at all(12).

II. Experimental

The specimen used in the present work was a nickel wire (0.35 mm in dia.) of commercial purity, the chemical composition of which was: 0.028 C, 0.0032 P, 0.0037 S, 0.06 Si, 0.38 Mn, 0.29 Co, 0.09 Fe, 0.007 Cu, 0.001 Cr (mass%), and balance Ni. The wire was degreased in acetone and then subjected to annealing in a vacuum at 1073 K for 900 s, follow-
ed by water quenching. The specimen surface was neither polished nor given any further treatments. The electrolyte used was borate buffer solution of 0.15 kmol·m⁻³ H₃BO₃ + 0.0375 kmol·m⁻³ Na₂B₄O₇ (pH=8.5 at room temperature), prepared with reagent grade chemicals and distilled water.

The straining electrode technique has been described in previous publications(11)-(13). It consists of an autoclave system with a device for rapid elongation. A static type autoclave with a volume of 1570 cm⁻³ was used, and it was equipped with a pair of checks for holding the wire specimen. The upper part of the chuck is connected to a pull rod. Furthermore, the pull rod is connected to the gas pressure activated rapid elongation device, which is outside the autoclave. The strain rate was approximately 0.5 s⁻¹. A straining electrode test was conducted several times for one specimen, each strain being about 1.5% for every elongation. The initial length of the specimen exposed to test solution was 30 mm. An internal Ag/AgCl/0.01 M KCl reference electrode, a Pt counterelectrode and an C-A thermocouple were also equipped in the autoclave. The EMF of the reference electrode was calculated on the basis of data reported by Greely, et al.(14)(15), and was converted to the SHE scale at a test temperature. The test solution was deaerated by high purity N₂ gas at room temperature before heating. Soon after a desired temperature was reached, the potential of specimen was polarized rapidly from a corrosion potential to a noble potential and kept for about 1000 s, in order to obtain a steady passive surface. The increase in the anodic current during strain and its decay with time after reaching a constant strain were recorded by a digital memory scope and a digital voltmeter that were controlled with a microcomputer, and the data processing was conducted automatically and instantaneously by the microcomputer.

The current density on a newly created surface, \( i \), is defined by

\[
i(t) = \frac{(I(t) - I_r)}{\Delta S} = \frac{\Delta I(t)}{\Delta S},
\]

where \( I(t) \) is the transient current at time \( t \) and \( I_r \) the residual current measured just before straining. \( \Delta S \) is a small amount of increase in the specimen surface, and is calculated by

\[
\Delta S = \frac{(S_0/2)(\Delta l/l_0)},
\]

where \( l_0 \) is the initial length of the specimen (=30 mm), \( S_0 \) is the initially exposed area (=3.3 \times 10⁻⁵ m²) and \( \Delta l \) is a small amount of elongation.

III. Results

1. Polarization behavior

Polarization curves of pure nickel in the borate buffer solution at several temperatures are shown in Fig. 1. Pure nickel shows a wide and steady passive region. At any temperature, there always exists the stable passive potential region contrasted to that reported previously for solutions containing \( \text{SO}_4^- \) ion, in which a temperature region showing no stable passiva-

\[
\text{tion}^{(11)(12)} \text{ is observed.}
\]

The straining electrode test was conducted at potentials in the passive region observed in these polarization curves.

![Fig. 1 Anodic polarization curves of pure nickel in borate buffer solution (0.15 kmol·m⁻³ H₃BO₃ + 0.0375 kmol·m⁻³ Na₂B₄O₇, pH=8.5 at room temperature).](image-url)
2. Straining electrode behavior

Typical changes in anodic current with time measured by the straining electrode test are shown in Fig. 2. The current density on the newly created surface decays following a power law:

\[ i = at^{-n}. \]  (3)

The value \( n \) in this equation ranges from 0.5 to 0.8. In most cases, the relation described by eq. (3) is observed from the time lapse of about 0.1 s for 3 decades. The value of \( n \) shows no considerable dependence upon temperature and also upon potential.

In order to discuss the repassivation behavior on the newly created surface, it is necessary to estimate the accumulated charge density that has passed through the newly created surface, because the anodic current is suppressed by the formation and thickening of the passive film. In the literature\(^{16}\), the behavior of the passive film formation and growth are described by several kinetics; a logarithmic rate law, an inverse logarithmic rate law, a parabolic rate law, a power law and others. The first three kinetics are expressed by the following equations as a functional relation between current density, \( i \), and accumulated charge density as film, \( Q_{\text{film}} \), which is proportional to the thickness of passive film:

- logarithmic: \( i = A \exp(bE - cQ_{\text{film}}) \),  (4)
- inv. logarithmic: \( i = i_0 \exp(aE/Q_{\text{film}}) \)  (5)
- parabolic: \( i = k/Q_{\text{film}} \),  (6)

where \( E \) is an applied potential and \( i_0, a, b, c \) and \( A \) are constants.

The current passed through the newly created surface is the sum of two currents:

\[ i = i_{\text{dis}} + i_{\text{film}}, \]  (7)

where \( i_{\text{dis}} \) is the dissolution current and \( i_{\text{film}} \) is the film formation current. Thus, the observed charge density, \( Q \), is also the sum of two charges, corresponding to the above two currents:

\[ Q = Q_{\text{dis}} + Q_{\text{film}}. \]  (8)

At present, however, there is no decisive method to separate experimentally these two charge densities. Since a part of \( Q \) precipitates as film, it may be assumed that the thickness of film is proportional to the observed charge density, \( Q \). Thus the relation between the total charge density, \( Q \), in stead of \( Q_{\text{film}} \), and the current density, \( i \), as a function of time is analyzed below.

The charge density that passes through the newly created surface generated by the rapid elongation was estimated by

\[ Q(t) = (q_0 + \int_0^t \Delta J(t) \, dt) / \Delta S, \]  (9)

where \( t \) is the time lapse after the straining is stopped and \( q_0 \) is the charge passed during elongation. The integration of this equation was performed by a summation of \( i \) vs \( t \) curves measured in the experiment.

By examining the experimental data in \( \log i \) vs \( Q \), \( \log i \) vs \( 1/Q \) and \( 1/i \) vs \( Q \) plots, which are discussed before, the proper relation can be determined.

Examples of plots in \( \log i \) vs \( Q \) and in \( 1/i \) vs \( Q \) using the same experimental data are shown in Figs. 3(a) and (b), respectively. As can be seen in these figures, it is revealed that the experimental data obtained in the present work can not be described as a single kinetics. Most of data, however, fit a logarithmic rate law at
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The initial stage and a parabolic rate law at the later stage. This behavior is likely to correspond to the two stage process as discussed later. The linear region of curves in Fig. 3(a) do not intersect y-axis (Q=0), because some charge less than 10 C·cm⁻² flows through the newly created surface during the elongation. Thus the maximum current density observed just after the straining is stopped is not the true current density on the newly created surface, because the film formation already occurs during the elongation. But if the logarithmic rate law is applied to the initial stage of the film growth, the value of current density at Q=0 is estimated by extrapolation of the linear portion of curves in Fig. 3(a) to y-axis. The value given above is called the estimated current density on the bare surface, \( i_{Q=0} \). The values of \( i_{Q=0} \) are shown in Fig. 4 as a function of potential at various temperatures. The value of \( i_{Q=0} \) increases with increasing potential in a less noble potential region, and then exhibits a plateau in the noble potential region. A similar plateau region is also observed in other metal/environment systems\(^1\)\(^2\)\(^3\). As shown in this figure, \( i_{Q=0} \) in the plateau region increases with increasing temperature, although some scatter is observed.

IV. Discussion

1. Early stage of behavior on newly created surface

As seen in Figs. 3(a) and (b), two distinct stages are observed in the repassivation process. In this section, the early stage is discussed.

As shown in Fig. 4, the estimated maximum current density, \( i_{Q=0} \), shows the plateau or the potential independent region at potentials
The temperature dependence of $i_{Q=0}$ in the plateau region is demonstrated as a function of $1/T$ in Fig. 5. A linear relation between $i_{Q=0}$ and $1/T$ is recognized, even though the values show some scatter. From this figure, the apparent activation energy, $\Delta H_a$, is estimated to be 32 kJ/mol, which is of the same order as that of the activation energy for diffusion in aqueous solution\(^{17}\).

Thus, the reaction rate just after the bare surface is exposed can be explained by the diffusion of dissolved species from the bare surface to the bulk solution. Following this initial process, the film formation is initiated immediately.

As shown in Fig. 3(a), a linear relation between $\log i$ and $Q$ is observed at the early stage of repassivation, or the film formation. Thus the decay of current density is described in a logarithmic rate law:

$$i = i_0 \exp\left(-\frac{Q}{C}\right),$$

(10)

where, $i_0$ is the current density at $Q=0$. The decay parameter, $C$, is shown in Fig. 6 as a function of potential at various temperatures. The value of $C$ shows neither potential dependence nor temperature dependence. The change in the kinetics from the logarithmic to the parabolic, as stated before, is observed at a critical amount of charge density, $Q_c$. The value of $Q_c$ can be determined by comparing Figs. 3(a) with (b). The value of $Q_c$ is actually estimated by the extrapolation of the linear portion of parabolic plots in Fig. 3(b) toward $1/i=0$. The value of $Q_c$ thus estimated increases with increasing temperature, but does not depend on the applied potential, being almost in the range of 5 to 25 C·m\(^{-2}\). If the passive film is assumed to be NiO, the density of which is 7.55 g/cm\(^2\), the anodic charge density required for the monolayer oxide formation is calculated to be about 5 C·m\(^{-2}\). Therefore, the measured value of $Q_c$ corresponds to 1-5 layers of oxide film. As stated before, the dissolution current is included in $Q$, so that $Q_c$ estimated above also contains a contribution by the dissolution. In addition, the roughness of the newly created surface has not been considered. If these two factors are taken into consideration, the exact amount of the accumulated charge corresponding to the change in the kinetics is roughly equivalent to the monolayer oxide formation. Therefore, it can be concluded that the accumulation of charge at the early stage is controlled by the logarithmic rate law until the bare surface is covered with a monolayer of oxide film.

Several mechanisms to explain the logarithmic rate law are proposed for the formation of the first monolayer of oxide\(^{(18)-(20)}\), the process of which involves the nucleation and the two dimensional extension. In the case of the straining electrode, a newly created surface emerges as slip steps which break down a preformed oxide. Thus, the newly created sur-
face is surrounded by the oxide layer already formed. Therefore, the early stage on the newly created surface is supposed to be the process of filling the emergent slip steps with oxide, which comes from dissolved Ni\textsuperscript{2+} ions and OH\textsuperscript{-} ions. Consequently, the rate of film growth is supposed to be determined by the number of slip steps emerging at the straining and also the rate of decrease in the number of slip steps. This behavior was able to be properly explained by the mutual-blockage model proposed by Evans\textsuperscript{(21)}.

When the rate of accumulation of oxide is assumed to be proportional to the number of slip steps produced by the straining, the following equation is introduced:

\[
\frac{dQ}{dt} = k_1 N, \quad (11)
\]

where \(N\) is the number of steps at time \(t\). According to the mutually-blocking pores mechanism, the accumulation process of oxide in a step affects also the decreasing rate of neighboring steps, and then a chance of decrease of the steps, \(-dN\), is formulated as follows.

\[
-dN = k_2 N \frac{dQ}{dt} \quad (12)
\]

The integration of eq. (12) in the condition of \(N = N_0\) at \(Q = 0\), gives

\[
\ln \left( \frac{N}{N_0} \right) = -k_2 Q, \quad (13)
\]

or

\[
N = N_0 \exp(-k_2 Q). \quad (14)
\]

From eqs. (11) and (14), the rate of accumulation of oxide is expressed as

\[
\frac{dQ}{dt} = k_1 N_0 \exp(-k_2 Q). \quad (15)
\]

This equation is equivalent to eq. (10), which is exactly observed at the early stage of repassivation behavior on the newly created surface.

2. Steady state growth

As shown in \(1/i\) vs \(Q\) plot of Fig. 3(b), the anodic current at the later stage after the formation of first monolayer oxide decays following the parabolic rate law. The parabolic law thus observed suggests that the film growth rate is determined by diffusion and/or migration of reaction species through reaction products. As stated before, the parabolic rate law is described in the following equation:

\[
i = \frac{k}{Q}. \quad (16)
\]

The rate constant \(k\) obtained by the experiment is shown in Fig. 7 as a function of potential at various temperatures. The rate constant \(k\) shows positive dependence not only on temperature but also on potential. This fact suggests that the movement of reaction species through the film is due partly to a migration of charged ions under a potential gradient in addition to diffusion under a concentration gradient.

The flux, \(J\), of ions under both the concentration gradient, \(dC/dx\), and the potential gradient, \(dE/dx\), is generally described by

\[
J = D \frac{dC}{dx} + ZF \omega \frac{dE}{dx}, \quad (17)
\]

where \(D\) and \(\omega\) is the diffusion constant and the mobility of moving species, respectively, and \(Z\) is the valency of charged ion and \(F\) is Faraday's constant. When the length of mass transfer path is small, \(dC/dx\) and \(dE/dx\) are expressed approximately as \(\Delta C/\Delta x\) and \(\Delta E/\Delta x\), respectively, where \(\Delta C\) and \(\Delta E\) are differences in concentration and potential between two sides of mass transfer path, and the thickness of the path is \(\Delta x\). Thus, eq. (17) is modified to

\[
J = D \frac{\Delta C}{\Delta x} + ZF \omega C_i \frac{\Delta E}{\Delta x}, \quad (18)
\]

where \(C_i\) and \(C_0\) are the concentrations of ions...
at interfaces of metal/film and film/solution. Since the concentration of ions on the solution side in this experiment is almost zero, $C_0$ can be neglected. Thus eq. (19) is reduced to

$$J = (D + ZF\omega E)C_i/\Delta x. \quad (20)$$

This equation is equivalent to eq. (16), because $\Delta x$ is proportional to $Q$. By comparing eq. (16) with eq. (20), $k$ in eq. (16) can be equated as follows:

$$k \propto (D + ZF\omega E). \quad (21)$$

That is, the rate constant $k$ in the parabolic law includes two factors corresponding to diffusion and migration.

It is difficult to separate above two factors from the observed rate constant. Thus the temperature dependence of diffusion constant, $D$, can not be calculated. However, the temperature dependence of mobility, $\omega$, can be estimated by plotting $\partial k/\partial E$ against $1/T$, because $\partial k/\partial E = ZF\omega$. As shown in Fig. 8, the temperature dependence of $\partial k/\partial E$ shows that the activation energy of mobility, $\omega$, is $27$ kJ/mol. This value lies in the range of generally accepted values of ion's mobility in aqueous solution$^{(22)}$. Therefore, it is concluded that the observed parabolic growth is controlled by diffusion and migration in aqueous liquid under the concentration gradient and the potential gradient. It is difficult to estimate which factor of diffusion and migration is more dominant. But, the distinct potential dependence of $k$ in Fig. 7 suggests that the migration under potential gradient has a larger contribution.

It is reported that the growth of passive film in neutral solutions at room temperature takes place by the field assisted ion conduction$^{(23)(24)}$ or the place exchange mechanism$^{(25)}$, which follows the inverse logarithmic or the direct logarithmic rate law. Namely, both processes occur in a thin oxide film under a high electric field in the solid state. However, the film growth of pure nickel in a high temperature water environment as observed in this experiment is determined by the parabolic law which is different from that observed at room temperature.

The logarithmic law observed at the early stage and the parabolic rate growth at the later stage observed in the present work suggest the following repassivation mechanism schematically shown in Fig. 9. The metal is covered uniformly with a passive film before the elongation (Fig. 9(a)). When a strain is given, the

Fig. 8 Temperature dependence of $\partial k/\partial E$. $k$ is the rate constant of the parabolic growth law shown in Fig. 7. The temperature dependence of $\partial k/\partial E$ shows that of mobility, $\omega$, of ions, because $\partial k/\partial E = ZF\omega$.

Fig. 9 A schematic model of repassivation process of pure nickel on the newly created surface which emerges due to elongation.
repassivated surface is broken by emergence of many slip steps. The newly created surface, namely, the slip step, is surrounded by preformed passive film, and the nucleation of oxide film starts at the edge of preformed film (Fig. 9(b)). Then, the logarithmic rate law is observed during two-dimensional extension of oxide film until the newly created surface is covered with a monolayer of the film. The metal surface is covered with a mixture of preformed thick passive film and newly formed thin film, so that the surface film has a heterogeneous structure. Thus, there are many pores and other defects, which contain the liquid phase and give paths for transportation of ions. The Ni^{2+} ions dissolved into pore and/or other defects at the metal/film interface transfer outward through these paths, and then Ni^{2+} ions deposit as oxide on the outer surface of the passive film (Fig. 9(c)). This process corresponds to the parabolic growth observed at the later stage. Then, the rate is determined by diffusion and migration through the liquid phase in defects in the passive film not only under the concentration gradient but also under the potential gradient.

It should be emphasized that the specific condition given by the rapid straining provides the heterogeneity of passive film. In addition, it is supposed that the structure of passive film formed at high temperature is quite different from that formed at room temperature.

V. Conclusion

(1) The repassivation process of pure nickel in the high temperature and high pressure borate buffer solution at temperatures up to 553 K was investigated by means of the rapid straining electrode technique.

(2) The current density on the newly created surface decayed following a power law, \( i = at^{-n} \) with \( n \) ranging from 0.5 to 0.8.

(3) The repassivation process is divided into two stages: the early stage and the later stage.

(4) During the early stage, the newly created surface is covered with a monolayer of oxide film following a logarithmic rate law, which is explained by the mutual-blockage model proposed by Evans.

(5) At the later stage, the passive film grows following a parabolic law with the rate determined by diffusion and migration of Ni^{2+} ions under both the concentration and the potential gradient through the liquid phase contained in many pores and other defects in the passive film.

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