Straining Electrode Behavior of Ni Base Alloys in High Temperature Caustic Solution*  

By Kazuo Yamanaka**

The initial repassivation processes of anodic reaction on the newly created surfaces of 75%Ni-0~15%Cr-25~9%Fe alloys were investigated by a rapid straining electrode technique in a 0.4%NaOH solution at 553 and 598 K at constant anodic potentials. The results obtained are as follows:

1. The decrease in current density with time after rapid straining was stopped follows the formula of \(n \approx t^{-n}\) (\(i\): current density, \(t\): time, \(n\): constant) over a time range of about 20~1000 ms.

2. The effects of chromium contents in the range of 0~15 mass\% on the repassivation rate is small at any potentials of \(-0.90\sim-0\) V. This suggests that the influence of chromium depleted zone on the caustic SCC of Alloy 600 should be small.

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Keywords: straining electrode, aqueous solution of sodium hydroxide, high temperature water, chromium depleted zone, nickel-chromium-iron alloys, anodic reaction, caustic stress corrosion cracking

I. Introduction

It has been reported that the intergranular stress corrosion cracking (IGSCC) of Ni-base Alloy 600 occurs in such environments as high temperature caustic solution\(^{(1)-(3)}\), non-deaerated\(^{(6)-(5)}\) and deaerated\(^{(6)}\) high temperature water, and its countermeasure is established. However, the IGSCC mechanism of Alloy 600 in high temperature caustic solution has not been well-defined, and the relation between caustic IGSCC and micro-structure, especially the Cr depleted zone accompanying the precipitation of chromic carboide at the grain boundaries, remains unclear. Namely, it is considered that the IGSCC susceptibility of Alloy 600 in non-deaerated high temperature water is increased by the sensitizing heat treatment and the Cr depleted zone is formed along the grain boundaries as is observed in austenitic stainless steels\(^{(5)-(7)}\). However, there are many reports\(^{(8)-(10)}\) that the IGSCC susceptibility of Alloy 600 in high temperature caustic solution is decreased by the heat treatment at low temperatures between about 873 and 973 K, corresponding to the so-called sensitizing heat treatment, in contrast with austenitic stainless steels. The role of the chromium carboide precipitated at the grain boundaries and the influence of the Cr depleted zone formation accompanied by the precipitation on caustic IGSCC of Alloy 600 have not been well explained. In the present work, the repassivation behavior of 75%Ni alloys varying in chromium content, simulated the alloy compositions of the Cr depleted zone, was investigated to make clear the effect of Cr content on the initial process of anodic behavior on a newly created surface by using a rapid straining electrode technique\(^{(11)}\). This technique can quantitatively analyze a transient anodic dissolution process on the newly created surface.

II. Experimental Method

1. Specimen

The materials used in this study were vacuum-melted 75%Ni-bal.Fe alloys having 0, 5 and 15%Cr. Table 1 shows chemical composi-
Table 1 Chemical composition of alloys (mass%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
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</thead>
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<td>1</td>
<td>0.018</td>
<td>0.11</td>
<td>0.29</td>
<td>0.001</td>
<td>0.001</td>
<td>75.15</td>
<td>15.05</td>
<td>0.21</td>
<td>0.14</td>
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<tr>
<td>2</td>
<td>0.018</td>
<td>0.11</td>
<td>0.29</td>
<td>0.001</td>
<td>0.001</td>
<td>74.55</td>
<td>4.86</td>
<td>0.21</td>
<td>0.13</td>
<td>19.82</td>
</tr>
<tr>
<td>3</td>
<td>0.014</td>
<td>0.13</td>
<td>0.31</td>
<td>0.002</td>
<td>0.001</td>
<td>74.38</td>
<td>0.01</td>
<td>0.20</td>
<td>0.10</td>
<td>25.85</td>
</tr>
</tbody>
</table>

...tion of the alloys. The alloys were forged, hot-rolled and drawn to thin wires of 0.50 mm diameter. The wire specimens were degreased with acetone, annealed in argon atmosphere at 1373 K for 1.8 ks (0.5 h) and then water-quenched. Then, the wires were polished with Emery paper up to No. 1000 and degreased with acetone.

2. Experimental equipment

A schematic drawing of the rapid straining electrode equipment used in this investigation is shown in Fig. 1. The autoclave with the volume of about 0.18 m$^3$ is made of Alloy 600. The wire specimen is attached to the chucks made of Hastelloy C, and zirconia coated zirconium plates is inserted between the chuck and the specimen in order to electrically isolate the specimen from the autoclave. One side (upper part) of the specimen holding chuck is connected to a pull rod made of Hastelloy C, and the pull rod passes through the autoclave head plate with water-cooled pressure balanced fitting seal and is connected to a piston in a cylinder. When high pressure argon gas is led into the cylinder, the piston is pulled up rapidly and the pull rod is moved up, and then the wire specimen is elongated. A constant amount of strain is given by a stopper set in the cylinder, the amount of strain is measured by a transducer mounted on the top of a piston. A 0.4%NaOH (pH=13 at a room temperature) solution was used as a testing solution, and test temperatures were 553 and 598 K. Reference electrodes are an internal Ag/AgCl reference electrode (a liquid inside an electrode: 0.1 kmol·m$^{-3}$ KCl) for the measurement at 553 K and a platinum-black electrode for that at 598 K. The transient anodic current and the output of the strain transducer are recorded in a 2-channel digital memory recorder (Kawasaki Electronica, Type TMR-10).

3. Straining electrode testing method

The wire specimen was mounted on the specimen holding chuck, filled with a testing solution, and the solution was deaerated by high purity argon gas. Then the autoclave was heated to a desired temperature. At the desired elevated temperature, the straining electrode test was carried out several times by applying a constant potential. When a rapid strain is applied to the specimen, the surface film is ruptured and transient current is observed due to the appearance of a newly created surface. And then the current decays immediately after stopping elongation. The current density on the newly created surface, $i$, is defined by the following equation:

![Fig. 1 Schematic drawing of the strain electrode equipment in high temperature aqueous solutions.](image-url)
\[ i = \frac{\Delta i(t)}{\Delta S} \]  

(1)

Here, \( \Delta i(t) \) is calculated by reducing the residual current that is measured just before straining from the transient current measured. \( \Delta S \) is a small amount of increase of the specimen surface. Assuming that the volume is a constant, \( \Delta S \) is calculated by the following equation:\(^{(1)}\):

\[ \frac{\Delta S}{S_0} = \frac{1}{2} \frac{\Delta l}{l_0} \]  

(2)

where \( S_0 \) is the initial surface area, \( \Delta l \) is a small amount of elongation, and \( l_0 \) is initial length.

In the present work, as \( l_0 = 25 \text{ mm} \), \( S_0 = 3.9 \times 10^{-5} \text{ m}^2 \) and \( \Delta l = 0.40 \text{ mm} \) were adopted, \( \Delta S \) calculated by an eq. (2) is \( 3.1 \times 10^{-7} \text{ m}^2 \). Since an elongation of 0.40 mm required about 7 ms, the strain rate was about 2.3 s\(^{-1}\) which was a little slower than that by the equipment of Shibata et al.\(^{(13)}\). Furthermore, for the purpose of making clear the effect of Cr content on the caustic corrosion, the corrosion test was also carried out in 4%NaOH solution.

### III. Experimental Results

1. Anodic polarization curves

Anodic polarization curves for 75%Ni-0-15%Cr-25-9%Fe alloys in 0.4%NaOH solution at 553 K is shown in Fig. 2. The curves in Fig. 2 exhibit the presence of the active peak, the first passive state and the second passive state near −0.95 V (vs Ag/AgCl), in the range from about −0.85 to −0.5 V and from about −0.2 to +0.1 V, respectively. As the Cr content was lowered from 5 to 0%, the current density of the active peak was increased and the current density in the potential range from about −0.4 to 0.1 V lowered. The presence of the current density peak in the potential range from −0.4 to 0.1 V in 75%Ni-15%Cr-9%Fe alloy was considered to be due to chromium dissolution. Straining electrode tests at the temperature of 553 K were carried out by applying the fixed potential of −0.90 V (vs Ag/AgCl) (a in Fig. 2) corresponding to the range of active/passive state transitions, −0.85 V (b), −0.65 V (c) and −0.50 V (d) in the first passive state, and 0 V (e) in the second passive state. The tests at 598 K were carried out at the same potential as above at the equivalent potential with a Ag/AgCl reference electrode using a platinum-black reference electrode.

2. Straining electrode behavior

Figure 3 shows changes in transient current density with time at various potentials of 75%Ni-15%Cr-9%Fe alloy in a 0.4%NaOH solution at 553 K after the longation. At the potential of −0.90 V, corresponding to the range of the active/passive state transitions, it can be seen that the change in the transient current density with time after the elongation was small and showed a large current density of about 10\(^3\) A/m\(^2\) even after 1000 ms.

With an increase of the applied potential, the change in transient current density with time becomes larger. At the potentials of −0.65 and −0.50 V in the first passive state, the initial current density of about 3 × 10\(^4\) A/m\(^2\) immediately after the elongation was stop-
ped was lowered to near 10 A/m² after 1000 ms. Although the anodic current decreased rapidly even at the potential of 0 V in the second passive state as in the case of the potentials of -0.65 and -0.50 V in the first passive state, the current density showed a slightly higher value than in the case of the latter potentials. Typical changes in transient current density with time at several potentials are shown in Fig. 3. After the elongation, the distinct regions in the current decay with time were observed. Namely, the current density exponentially decreased with time in the initial region before about 20 ms, and decreased in power rate with time in the second region after about 20 ms. This suggests that a film repassivation process at least consists of two stages. Details concerning this will be described in Chapter IV.

Although the behavior similar to the case at 553 K, was seen even in 0.4%NaOH at 598 K, the changes in transient current density with time were generally about one order higher at any potentials than the case at 553 K. The concentrations of both Ni and Cr ions dissolved from 75%Ni-15%Cr-9%Fe alloy were analyzed by using ICP after the straining electrode test, and those at 598 K were $4.8 \times 10^{-1}$ and $1.0 \times 10^{-1}$ mol/m³, respectively. The effects of Cr content on the anodic current attenuation curves caused by a repassivation phenomenon after the elongation at the potentials of -0.90 and -0.65 V are shown in Fig. 4 and Fig. 5, respectively. In both figures, all of the three alloys varying in Cr content showed nearly a similar current decay behavior in the concentration range of 0-15% Cr. This can also be seen from Fig. 6 at 553 K and Fig. 7 at 598 K, in which the maximum current density $i_{\text{max}}$ immediately after rapid straining and the current densities $i_{10 \text{ ms}}$ at 10 ms, $i_{100 \text{ ms}}$ at 100 ms and $i_{1000 \text{ ms}}$ at 1000 ms after the elongation, Fig. 3, are plotted against the applied potential. From these figures, it can be seen that at both temperatures $i_{\text{max}}$ of 75%Ni-15%Cr-9%Fe alloy, which has the highest Cr content among the three alloys, showed a slightly larger value than that of other two alloys less in Cr con-

![Fig. 3 Change in transient current density with time at various potentials of 75%Ni-15%Cr-9%Fe alloy in 0.4%NaOH at 553 K.](image1)

![Fig. 4 Effect of Cr content on anodic current decay curves in 0.4%NaOH at 553 K under applied potential of -0.90 V (vs Ag/AgCl).](image2)
Fig. 5 Effect of Cr content on anodic current decay curves in 0.4% NaOH at 553 K under the applied potential of −0.65 V (vs Ag/AgCl).

Fig. 6 Effect of potential of $i_{\text{max}}$, $i_{10\text{ms}}$, $i_{100\text{ms}}$, and $i_{1000\text{ms}}$ of 75%Ni–0–15%Cr–25–9%Fe alloys in 0.4% NaOH at 553 K.

Fig. 7 Effect of potential on $i_{\text{max}}$, $i_{10\text{ms}}$, $i_{100\text{ms}}$, and $i_{1000\text{ms}}$ of 75%Ni–0–15%Cr–25–9%Fe alloys in 0.4% NaOH at 598 K. On the other hand, in regard to $i_{10\text{ms}}$, $i_{100\text{ms}}$, and $i_{1000\text{ms}}$, 75%Ni–15%Cr–9%Fe alloy showed, in contrast with the above, a little smaller value than the other two alloys.

3. Caustic corrosion

In order to making clear the caustic corrosion behavior of both the matrix and the Cr depleted zone of Ni base Alloy 600, the corrosion test was carried out in a 4% NaOH solution at −0.90 V corresponding to the potential in the active/passive transition region where the occurrence of caustic SCC is reported. The reason why a 4% NaOH solution was used for the corrosion test was due to the corrosion rate being very small in a 0.4% NaOH solution. The results are shown in Fig. 8. In the concentration range of 0–15% Cr, the corrosion rates were within the range of $9.7 \times 10^{-4} \sim 1.4 \times 10^{-3}$ g/m²·sin all the alloys, with little effect of Cr content on the corrosion rate.
Fig. 8 Effect of Cr content on the corrosion rate of 75%Ni-X%Cr-bal. Fe alloys in 4%NaOH at 553 K under applied potential of $-0.90$ V (vs Ag/AgCl).

IV. Discussion

1. Effect of Cr content on straining electrode behavior

Figure 9 shows a schematic representation of the anodic current decay behavior obtained by the measurement of 75%Ni-0~15%Cr-25~9%Fe alloys in a high temperature 0.4%NaOH aqueous solution after rapid straining. That is, the current decay consists of two stages: the current density in a short period (within around 20 ms) immediately after rapid straining decays to the formula of $i \propto \exp(-t^n)$ (1: current density, t: time, n: constant) (named stage I), and then the density at least up to 1000 ms decays to the formula of $i \propto t^{-n}$ (stage II). The fact that the current density follows the formula of $i \propto t^{-n}$ was already obtained by Shibata et al.$^{(23)}$ in high temperature Na$_2$SO$_4$ and H$_3$BO$_3$+Na$_2$B$_4$O$_7$ aqueous solutions. Typical examples of the formula of change in anodic current density with time for stage I and stage II obtained in this experiment are shown in Table 2.

The results that the current density followed the formula of $i \propto \exp(-t^n)$ in stage I and $i \propto t^{-n}$ in stage II have been reported by Diegle and Vermilyea$^{(14)}$, and Ford$^{(15)}$, using pure iron and carbon steel in NaOH solutions at an atmospheric pressure. They explained that the monolayer of an oxide film (Fe$_2$O$_3$) initially forms in stage I and then the growth of the oxide film in thickness occurs in stage II. Surmising from the current decay curves obtained, it is considered that the repassivation behavior of both a carbon steel and a Ni base alloy is similar to some extent, although the compositions of oxide film formed on a Ni base alloy in a high temperature caustic solution are different from that on a carbon steel. The corrosion depth caused by the one-time straining electrode test and the effect of Cr content thereon were studied by using the following equations. According to Faraday's law, the

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Current density (A/m$^2$)</th>
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<tbody>
<tr>
<td></td>
<td>Stage I ($t&lt;20$ ms)</td>
</tr>
<tr>
<td>75%Ni-15%Cr-9%Fe</td>
<td>$3.5 \times 10^9 \exp(-23.35 t^{0.406})$</td>
</tr>
<tr>
<td>75%Ni-5%Cr-20%Fe</td>
<td>$3.2 \times 10^9 \exp(-23.30 t^{0.421})$</td>
</tr>
<tr>
<td>75%Ni-0%Cr-25%Fe</td>
<td>$3.1 \times 10^9 \exp(-36.59 t^{0.518})$</td>
</tr>
</tbody>
</table>
relation between corrosion depth $d_t$ and charge $Qt$ is given by

$$d_t = \frac{M}{N \rho F} Qt$$  \hspace{1cm} (3)

where $Qt$: charge, $M$: atomic weight, $\rho$: density, $F$: Faraday’s constant (96500 coulomb).

In the case of Alloy 600, $M = 57.4$ g/mol, $\rho = 8.45 \times 10^3$ kg/m$^3$ and $N = 2$, assuming that the NiO oxide film is formed. Substituting these values for eq. (3), eq. (4) is obtained:

$$d_t = 3.52 \times 10^{-8} Qt(m)$$ \hspace{1cm} (4)

Charge $Qt$ in eq. (4) is expressed by the accumulation of charge $Q_{\text{stage I}}$ in stage I and charge $Q_{\text{stage II}}$ in stage II as given by

$$Qt = Q_{\text{stage I}} + Q_{\text{stage II}}$$ \hspace{1cm} (5)

$$Q_{\text{stage I}} = \int_0^t i_0 \exp (-At^n) dt$$ \hspace{1cm} (6)

($t = 0$ means the time just after the elongation)

$$Q_{\text{stage II}} = \int_{t_1}^t i_i t^{-n} dt$$ \hspace{1cm} (7)

Where $i_0$: current density at $t = 0$, $i_i$: current density at $t = t_1$, $A$: constant.

Using eqs. (4)–(7), $d_t$ was calculated in the case of $t_1 = 20$ ms and $t = 1000$ ms. The change in corrosion depth with time as a function of potential of 75%Ni–0%Cr–25%Fe alloy in a 0.4%NaOH solution at 553 and 598 K is shown in Fig. 10. And the change in corrosion depth with time as a function of potential and Cr content of 75%Ni–X%Cr-bal.Fe alloys in a 0.4%NaOH solution at 553 K is shown in Fig. 11. It is known from these figures that though the effects of both potential and temperature on the corrosion depth are large, the effect of Cr content on the depth is small in the concentration range of 0–15%Cr. In particular, concerning the effect of potential on the corrosion depth, the corrosion depth is extremely small at the potentials of $-0.65$ and $-0.50$ V in the first passivation state. This suggests that the repassivation rate may be larger than the corrosion rate on the newly created surface, so that the anodic localized corrosion necessary for the SCC initiation may be hard to occur at these potentials. On the other hand, the corrosion depth at the potential of $-0.90$ V corresponding to the transition range of active/passive state is considerably large. Therefore, this implies that the repassivation rate on a

Fig. 10 Change in corrosion depth with time as a function of potential of 75%Ni–0%Cr–25%Fe alloy in 0.4%NaOH.
newly created surface may be almost the same as or smaller than the corrosion rate, resulting in the condition that the localized corrosion may be easy to occur in these potential range.

2. **Effect of the Cr depleted zone on caustic IGSCC**

The effect of Cr depleted zone along the grain boundaries on caustic IGSCC of Ni base Alloy 600 was considered. It is generally considered that SCC, proceeded by APC (active path corrosion), occurs in such a condition that both the anodic dissolution rate and the repassivation rate are almost the same rate and competed with each other at the crack tip in the potential range where the surface passive film is unstable. Straining electrode test results obtained in this work (Figs. 6 and 7) show that the effect of Cr content on the repassivation rate is small in the concentration range of 0\(\sim\)15\%Cr.

This fact suggest that even if the Cr concentration is greatly lowered along the grain boundaries, caused byformation of the Cr depleted zone accompanied by the intergranular precipitation of chromium carbides, its influence on the initiation and propagation of caustic IGSCC may be very small. This fact agrees with the results of Fig. 8 which, in a high temperature NaOH solution, the corrosion rates of 75\%Ni\(-\)15\%Cr\(-\)9\%Fe alloy and 75\%Ni\(-\)0\sim\)5\%Cr\(-\)25\sim\)20\%Fe alloys simulated the Cr depleted zone are almost the same degree, and thus the possibility of selective active corrosion in the Cr depleted zone is small. Besides, as can be seen from the pH-Potential diagrams at high temperatures (Fig. 12), it is important to note that the stable potential range of chromium oxide (Cr\(_2\)O\(_3\)) exists in neutral and acidic environments, but the chromium oxide is hard to exist in a stable state under the caustic environment above pH 8 over the range of potentials containing

Fig. 11 Change in corrosion depth with time as function of potential and Cr content of 75\%Ni\(-\)X\%Cr\(-\)bal.\(\)Fe alloys in 0.4\%NaOH at 553 K.
the active/passive transition region where the occurrence of caustic IGSCC has been reported\(^{12}\). Here, the thermodynamic calculation for constructing the pH-potential diagrams in Fig. 12 was carried out by using Gibbs’ free energy equation in case of the ion concentration of \(10^{-1} \text{ mol/m}^3\) in the same manner as Hirano et al.\(^{19}\).

Furthermore, it seems to be also supported by the fact that there are many reports\(^{3,9,12,16}\) for Ni-base Alloy 600, that the caustic IGSCC resistance is not influenced or, on the contrary, improved even if so-called severe sensitizing heat treatment is performed. Theus et al.\(^{12}\) have demonstrated that, in the Streicher test, the relationship between the intergranular corrosion susceptibility and the caustic IGSCC susceptibility are completely contrary to each other, and the caustic IGSCC resistance is improved by heat treatments in which intergranular corrosion severely occurs. Therefore, it is thought that the Cr depletion would not be the main material factor of the caustic IGSCC of Ni-base Alloy 600.

**V. Conclusion**

Using a rapid straining electrode technique, the initial repassivation processes on newly created surface of 75\%Ni–0–15\%Cr–25–9\% Fe alloys in a high temperature 0.4\%NaOH aqueous solution at 553 and 598 K were investigated by applying constant anodic potentials in the range of \(-0.90 \sim 0\) V (vs Ag/AgCl), and the following results were obtained.

(1) The decrease in current density with time after rapid straining follows the formula of \(i \propto t^{-n}\) (\(i: \text{ current density, } t: \text{ time, } n: \text{ constant}\) over the time range of \(20 \sim 1000\) ms.

(2) The effect of potential on the change in the anodic current attenuation with time (repassivation rate) was large. It was observed that the repassivation rate was comparatively small at potentials in the range of active/first passive stage transitions, but it was large at the potentials of the first passivation and the second passivation state.

(3) The effect of Cr contents in the range of 0–15 mass\% Cr on the repassivation rate was small at any potential between 0.90 and 0 V.

(4) This suggests that the influence of the Cr depleted zone on the caustic IGSCC of Alloy 600 should be small.

**REFERENCES**