Effect of Nitrogen Alloying on the Pitting of Type 310 Stainless Steel

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The effect of nitrogen alloying on the pitting behavior of type 310 stainless steel has been investigated through measurements of pitting potential \(E'_{\text{pit}}\) as a function of temperature and concentration of NaCl \(C_{\text{NaCl}}\). Nitrogen was effective to shift \(E'_{\text{pit}}\) to nobler direction especially at temperatures below critical one. The critical pitting temperature was defined as the temperature below which the usual linear relationship between \(E'_{\text{pit}}\) and logarithm of \(C_{\text{NaCl}}\) did not stand. Alloying the stainless steel with nitrogen increased the critical pitting temperature. Below the critical temperature where \(E'_{\text{pit}}\) did not follow the usual dependency on \(C_{\text{NaCl}}\), pitting was retarded most effectively by nitrogen except when \(C_{\text{NaCl}}\) was so high that \(E'_{\text{pit}}\) lay below ca. 400 mV. Although the whole mechanism of nitrogen is not still clear, nitrogen is most likely to suppress acidification of pitting site through formation of ammonium ion. Nitrogen in a metal matrix and nitrate in a solution seemed to have a common feature with respect to the potential dependency of inhibition efficiency. The fact that nobler potentials were more favorable for both nitrogen in metal matrix and nitrate in a solution for inhibition seemed to indicate that oxidation of nitrogen to nitrate might also be involved in the inhibition mechanism.

KEY WORDS: nitrogen; stainless steel; pitting; chloride; nitrate; temperature.

1. Introduction

Among many alloying elements for stainless steel, nitrogen is one of the most attractive one in terms of natural resources, hypersensitivity (substitute for Ni), mechanical property and corrosion resistance.\(^1\)\(^-\)\(^4\) Many authors have investigated corrosion property of nitrogen added stainless steels and recognized that nitrogen improves corrosion resistance especially for localized one.\(^5\)\(^-\)\(^19\) Pitting, the most typical form of localized corrosion, is a crucial issue for passivating materials in practical use.\(^2\) Therefore, to understand the role of nitrogen in pitting is important in design and use of high nitrogen stainless steel. Osozawa et al.\(^6\) reported that the effect of nitrogen addition to 17Cr–16Ni steels on the pitting potential was different from that of other elements such as Mo, Ni, W and Cu. While other elements showed good correlation between pitting potential and critical current density for passivation, nitrogen shifted pitting potential to nobler direction without decreasing the critical current. They suggested that pH buffering due to formation of ammonium ion within a pit is the most probable role of nitrogen. However, there are several other possibilities through which nitrogen inhibits pitting. Enrichment of nitrogen may be taking place within or beneath passive films.\(^7\)\(^,\)\(^10\)\(^,\)\(^12\)\(^,\)\(^13\)\) Nitrogen may not dissolve as fast as substrate metals at nobler potentials, resulting in segregation within a pit.\(^9\) This hypothesis is consistent with the observation that nitrogen added stainless steel sometimes shows significant improvement of pitting resistance when pitting occurs at less noble potentials because of high temperatures or concentrations of chloride. The feature is similar to the case of nitrate addition to a solution.\(^17\)\(^,\)\(^20\) Another possible explanation for inhibitive action of nitrogen especially at nobler potentials is the formation of nitrate ion,\(^15\)\(^,\)\(^24\)\(^,\)\(^25\) which is well known as an inhibitor.\(^20\) In the present study, pitting behavior of nitrogen added stainless steel was investigated through measurement of pitting potential as a function of temperature and concentration of chloride ion. The results will be discussed in terms of analogy between nitrogen in steel and nitrate in a solution.

2. Experimental Procedure

2.1. Materials

Table 1 shows the chemical composition of the stainless steels investigated. They were supplied by Nippon Steel Corporation for a round-robin test organized by ISIJ forum. The base material was type 310 stainless steel and its nitrogen content was changed from 0.023 to 0.325 mass%. They were heat treated at 1 373 K for 15 min and water quenched.

| C   | Si  | Mn  | P   | S   | Ni  | Cr  | Al  | N   | O   |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 310 | 0.048| 0.33| 0.80| 0.024| 0.0010| 19.8 | 25.1 | 0.005| 0.023| 0.0105|
| 310N(1)| 0.048| 0.32| 0.80| 0.024| 0.0009| 19.9 | 25.1 | 0.007| 0.194| 0.0084|
| 310N(2)| 0.048| 0.31| 0.84| 0.024| 0.0010| 20.1 | 25.0 | 0.008| 0.325| 0.0057|
The plates were 3 mm thick and cut into 10×10 mm. The surface was mechanically polished down to 800 grit SiC paper and degreased in acetone and methanol ultrasonically.

2.2. Experimental Method

The specimen was mounted on a PTFE holder and covered with vinyl chloride adhesive tape leaving test area of Φ6 mm. The specimen was set into a conventional three electrodes system cell containing about 130 cm$^3$ of solution. The reference electrode was Ag/AgCl/KCl (2 mol dm$^{-3}$) maintained at the same temperature as the cell. Potentials will be indicated as measured referring this electrode. The counter electrode was a Pt plate with area of about 5.5 cm$^2$. NaCl solutions with variety of concentrations were used without deaeration. The cell was heated in a water bath that was controlled to the constant temperature (±0.1 K). After the test temperature was reached and the corrosion potential became stable, the specimen was polarized from the corrosion potential to −300 mV at 1 mV s$^{-1}$ and then the scan was reversed to anodic direction until pitting occurred. When anodic current density reached 100 μA cm$^{-2}$ and continued to increase, the potential was determined as the pitting potential ($E_{\text{pit}}$).

Qualitative analysis was carried out to check if ammonium or oxoacid (nitrate or nitrite) ions formed in 3 mol dm$^{-3}$ NaCl solution after pits were grown on 310N(1) steel. The polarization was continued until the amount of electricity reached about 56 C so that the concentration of the dissolved nitrogen species (0.2 ppm-N) was expected to be in a detectable level for a colorimetric method. The coloring reagents were sodium salicylate for ammonium (indophenol method) and N-(1-naphtyl)ethylenediamine for nitrite and nitrate (after reduction by zinc). The detection limits are 0.1 ppm-N for ammonium ion, 0.1 ppm-N for nitrate and 0.01 ppm-N for nitrite, respectively. The dissolved metals were removed previously to avoid the interference.

3. Results

3.1. Effect of Temperature

Anodic polarization curves for three steels were obtained typically in 3 mol dm$^{-3}$ NaCl solution as a function of temperature since the steels had rather high resistance against pitting. Figures 1 and 2 show typical anodic polarization curves measured at 323 and 353 K, respectively. $E_{\text{pit}}$ for 310 steel which contains almost no nitrogen, was always the least noble at every temperature tested. 310N(2) steel, which contains the highest nitrogen, suffered from no pitting throughout extensive anodic polarization at 323 K but pitting occurred readily at 353 K at potential as low as 240 mV. The amplitude of oscillation of current observed for 310N(2) steel at 323 K became largest at around 400 mV but tended to fade at nobler potentials. The difference in $E_{\text{pit}}$ due to nitrogen content among three steels was large at 323 K, while it became less pronounced at 353 K. The feature was also observed for type 304 based stainless steels alloyed with nitrogen.17)

In Fig. 3, $E_{\text{pit}}$ in 3 mol dm$^{-3}$ NaCl solution was plotted as a function of temperature. $E_{\text{pit}}$ became less noble with increase of temperature gradually for 310 steel, while $E_{\text{pit}}$ for 310N(1) steel showed a sharp fall at 323 K. 310N(2)
steel was the most resistant to pitting at every temperature but the differences in \( E_{\text{pit}} / H_11032 \) pit among three steels became smaller above certain temperature. It is worth noting that \( E_{\text{pit}} \) for nitrogen added steels lay below ca. 400 mV when their advantage became less prominent.

3.2. Effect of Nitrate

In our earlier report, \(^{17}\) the effect of nitrogen and molybdenum in type 304 stainless steel matrix on the pitting behavior was compared with nitrate and molybdate in a solution. As known widely, \(^{20}\) nitrate retards pitting effectively but the mechanism is not clear enough in terms of potential dependency for inhibition. \(^{21,22}\) In Fig. 4, anodic polarization curves for 310 steel in 3 mol dm\(^{-3}\) NaCl solution containing 0.3 mol dm\(^{-3}\) \(\text{NaNO}_3\) are shown as a function of temperature. It is characteristic for nitrate that the current oscillates most intensively at around 300 mV and calms down at nobler potential. However, pitting starts before those nobler potentials are reached at higher temperature (323 K in this case). Thus, pitting potential changes sharply between 318 and 323 K. The critical temperature is not characteristic at all for this steel or nitrate but varies depending the ratio of chloride and nitrate. The important point is that pitting is inhibited effectively by nitrate except when the environment is so severe that passive films can not withstand against chloride attack up to 400 mV. The feature seems similar to the case of nitrogen added steel in Fig. 3.

3.3. Effect of Concentration of Chloride

Figures 5 and 6 show the relationship between \( E_{\text{pit}} \) and concentration of NaCl (\( C_{\text{NaCl}} \)) at 323 and 353 K, respectively. At 323 K, 310 steel followed the usual relation between \( E_{\text{pit}} \) and logarithm of \( C_{\text{NaCl}} \):

\[
E_{\text{pit}} = a - b \log C_{\text{NaCl}} \tag{1}
\]

From Fig. 5, \( a = 260 \) (mV) and \( b = 200 \) (mV/decade) were obtained for 310 steel. \( E_{\text{pit}} \) for 310N(1) steel did not follow the relation but showed a steep change between 1 and 3 mol dm\(^{-3}\). The feature is again similar to Fig. 3. At 353 K, on the other hand, \( E_{\text{pit}} \) for 310N(1) steel, as well as for 310 steel, showed the usual linear relationship with logarithm of \( C_{\text{NaCl}} \). The values of \( a \) and \( b \) were: \( a = 200 \) and \( b = 180 \) for 310 steel and \( a = 290 \) and \( b = 210 \) for 310N(1) steel. The relation did not stand for 310N(2) steel even at 353 K. It seems that the linear relation between \( E_{\text{pit}} \) and logarithm of \( C_{\text{NaCl}} \) stands when solution temperature exceeds a critical value for each steel, while \( E_{\text{pit}} \) shows a jump in the course of concentration change at temperatures below it. At the very critical temperature, \( E_{\text{pit}} \) showed a strong scatter.

Figure 7 shows the case for 310N(1) where \( E_{\text{pit}} \) could not be determined within a reasonable distribution at 333 K. The usual linear relation stood above 338 K regardless of the value of \( E_{\text{pit}} \) being higher or lower than 400 mV.

3.4. Solution Analysis

Table 2 summarizes the detected species in a solution after about 56 C of electricity was passed through the 310N(1) steel at each potential. Only ammonium ion was detected at 260 mV. Ammonium ion was also detected at
potential as noble as 550 mV. Nitrate ion was detected above 350 mV. Nitrite ion was also detected above 350 mV but was not regarded as a major species.

4. Discussion

4.1. Effect of Nitrogen on Critical Pitting Temperature

Figure 8 summarizes $E_{\text{pit}}$ as a function of temperature and $C_{\text{NaCl}}$ for the three steels. Iso-pitting potential lines were drawn every 100 mV. It is clearly seen that nitrogen alloying widens no pitting area. But the shapes of the iso-pitting potential lines for the steels seem unusual. Iso-pitting lines usually lean toward high concentration or high temperature because $E_{\text{pit}}$ becomes less noble with increase of them. Figure 8 indicates that these steels have critical temperature, around which $E_{\text{pit}}$ is very sensitive to temperature but not to $C_{\text{NaCl}}$. Above the critical temperature, the iso-pitting potential lines show the usual relation. As mentioned earlier, the linear relationship between $E_{\text{pit}}$ and logarithm of $C_{\text{NaCl}}$ stands above this temperature, while $E_{\text{pit}}$ shows a steep fall down below 400 mV above a certain value of $C_{\text{NaCl}}$. The values of critical temperature are ca. 313 K for 310 steel and ca. 333 K for 310N(1) steel. $E_{\text{pit}}$ strongly scattered at 333 K for 310N(1) steel at NaCl concentrations between 0.1 to 1 mol dm$^{-3}$. This is attributed to the fact that the temperature corresponded to the critical temperature. The critical temperature for 310N(2) steel is not clear form Fig. 8 but seems to be around 353 K. Several authors have reported that nitrogen is benefit for increasing critical pitting temperature. The present study also supports that nitrogen enhances critical pitting temperature. However, Fig. 8 indicates that pitting can be caused even under critical pitting temperature when the $C_{\text{NaCl}}$ is very high. Critical pitting temperature can not be defined as the highest temperature below which pitting never generates. We define it as the temperature above which the usual linear relation between $E_{\text{pit}}$ and logarithm of $C_{\text{NaCl}}$ stands, while pitting is inhibited extensively under the condition of $C_{\text{NaCl}}$ not being too high to cause a steep drop in $E_{\text{pit}}$.

4.2. Role of Nitrogen

The most probable mechanism of nitrogen for suppression of pitting is the formation of ammonium ion with simultaneous consumption of hydrogen ion within a pit. The steel was polarized to each potential in 3 mol dm$^{-3}$ NaCl solution until 36 C of electricity was reached at 298 K.

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Table 2. Nitrogen species detected after polarization of 310N(1) steel.

| Potential (V) | NH$_4^+$ | NO$_2^-$ | NO$_3^-$ |
|--------------|---------|----------|----------|
| 0.26         | ○       | ×        | ×        |
| 0.35         | ○       | △        | ○        |
| 0.55         | ○       | △        | ○        |

○: clearly detected, △: detected with less clarity, ×: not detected.

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Fig. 7. Effect of temperature on the relation between $E_{\text{pit}}$ and log $C_{\text{NaCl}}$ for 310N(1) steel.

Fig. 8. $E_{\text{pit}}$ as a function of $C_{\text{NaCl}}$ and temperature. Iso-pitting potential lines are drawn every 100 mV (a: 100, b: 200, c: 300, d: 400, e: 500, f: 600, g: 700, h: 800, i: 900, j: 1 000 mV).
Ammonium ion has been detected by many researchers in a solution after growth of pits for nitrogen added stainless steels. We also detected it after anodic polarization tests in the present study. It should be also mentioned that electrons for reaction (1) is supplied by metal matrix:

$$N + 4H^+ + 3e^- \rightarrow NH_4^+ \quad \text{(1)}$$

Equation (4) indicates that metal oxides can be formed without acidification of the anode site. Because the molar ratio of nitrogen to chromium in 310N(2) steel matrix is about 0.03, the amount of nitrogen seems to be insufficient even to neutralize the hydrogen ions formed by the hydrolysis of dissolved chromium(III) ion. An account might be given for it supposing a slow rate of hydrolysis of metal ions at lower temperatures. As temperature increases above a certain value, the hydrolysis becomes so fast that nitrogen is not able to neutralize all the hydrogen ion formed. Thus, the inhibitive effect could be lost suddenly. Another account is related to enrichment of nitrogen at solution/metal interface. The enrichment might become more important for nitrogen at nobler potentials because nitrogen may not be oxidized to dissolve as fast as metal matrix. The enriched nitrogen may make up for the relative deficiency for the pH buffering.

We have described that nobler potentials were advanta-gous for both nitrogen in a metal matrix or nitrate in a solution for inhibition of pitting. Some authors detected nitrate ion in a solution after extensive electrolysis of nitrogen added stainless steels, though a negative result is also reported. In our preliminary analysis, nitrate ion, together with ammonium ion, was detected after the nitrogen added stainless steels were polarized at 550 mV while only ammonium ion was detected at 260 mV. It seems that the potential of the bottom of a pit should not be noble enough to form nitrate in an acidified solution even when the passivated surface is polarized to a nobler potential in a neutral solution. Since addition of ammonium ion to a solution does not cause any change in $E'_{pc}$ nor passive current density, it is not likely to happen either that ammonium ion is oxidized to nitrate ion on a passivated surface of stainless steel. Nitrogen could be oxidized to nitrate around pit edge where the surface is not fully covered with oxide and the potential is noble enough. Because nitrate is expected to inhibit pitting by means of adsorption, only small amount is needed to cover the pitting surface. For example, when 1 ng of stainless steel dissolves, the pit volume and surface is roughly $10^{-10}$ cm$^3$ and $10^{-8}$ cm$^2$, respectively. To cover this surface with nitrate ion whose ionic radius is ca. 1.2 $\times$ 10$^{-8}$ cm, only 5 $\times$ 10$^{-2}$ ng of nitrogen is needed. Thus, 0.2% of nitrogen content can be much enough in contrast with the case of neutralization mechanism. Although the oxidation of nitrogen to nitrate is possible using a potentiostat, it is not likely to happen under the usual open circuit conditions. Therefore, it does not seem very practical that nitrogen shifts relatively noble pitting potentials to further nobler values through formation of nitrate. The weaker effect of nitrogen at relatively less noble potential region as appeared at high temperatures could be made up for by the addition of molybdenum. Because the effect of molybdenum becomes more pronounced at higher temperatures, the combination of nitrogen and molybdenum would provide a desirable pitting resistivity over a wide range of potential and temperature.

5. Conclusions

(1) Pitting is suppressed by nitrogen addition to stainless steel remarkably when temperature is lower than the critical value.

(2) The critical pitting temperature was defined as the temperature above which the usual linear relation between pitting potential and logarithm of concentration of NaCl stands, while it does not stand below it. Nitrogen addition is effective to increase the critical pitting temperature.

(3) Nitrogen in a metal matrix and nitrate ion in a solution have a common feature in terms of potential dependency of pitting inhibition.

(4) Alloying stainless steels with nitrogen does not give a remarkable effect to enhance the pitting resistance under every condition as is the case at high temperature but the weak point of nitrogen could be made up for by additional alloying with molybdenum.

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