# A New Inhibition Mechanism of SA106 Gr.B Carbon Steel Corrosion by Nitrite in Simulated Closed Cooling Water

Do Haeng Hur <sup>a\*</sup>, Jeoh Han <sup>a</sup>, Soon-Hyeok Jeon <sup>a</sup>, Hee-Sang Shim <sup>a</sup>, Hyuk-Chul Kwon <sup>b</sup> <sup>a</sup> Nuclear Materials Safety Research Division, Korea Atomic Energy Research Institute, Daejeon 34057 <sup>b</sup> Central Research Institute of Korea Hydro & Nuclear Power Co., Ltd, Daejeon 34101 <sup>\*</sup>Corresponding author: <u>dhhur@kaeri.re.kr</u>

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# 1. Introduction

In nuclear power plants, closed cooling water (CCW) systems are used to cool both safety-related and non-safety-related heat exchange equipment such as component cooling systems, emergency generator jackets, enclosure coolers, and lubricant oil coolers [1]. CCW piping consists of carbon steel in many CCW systems. Carbon steel is well known to undergo general corrosion and flow-accelerated corrosion [2]. Therefore, carbon steel corrosion is controlled by adding inorganic inhibitors including nitrite, chromate, molybdate, phosphate, and hydrazine.

Among them, nitrite  $(NO_2^{-})$  has attracted a great deal of attention due to its low cost and relatively good inhibition performance. It has been proposed that nitrite acts as an oxidizing agent and thus promotes conversion of ferrous to ferric resulting in the formation of a robust and stable passive film of iron oxides on the metal surface [3-4]. However, there is still no consensus on the type of nitrite reduction product and iron oxide film during the corrosion inhibition process of carbon steel. In this study, we examine oxide films formed on SA106 Gr.B carbon steel in simulated alkaline CCW water with and without nitrite using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) method. Based on the results, a new corrosion inhibition mechanism is presented.

#### 2. Experimental Methods

# 2.1 Preparation of Specimens and Test Solution

SA106 Gr.B carbon steel was used as a test material. Specimens for electrochemical and immersion corrosion tests were prepared using a wire electric discharge machining method. The surfaces of the specimens were abraded with silicon carbide paper and finished with #1200 grit paper.

Test solution was prepared by adding sodium nitrite into deionized water and its pH was adjusted to  $10\pm0.1$  with ethanolamine.

#### 2.2 Corrosion Tests

Two types of corrosion tests were performed under the conditions listed in Table 1. First, potentiodynamic polarization tests were conducted using a threeelectrode cell. A saturated calomel electrode (SCE) and a coiled platinum wire were used as a reference electrode and a counter electrode, respectively. Each surface-finished specimen was spot-welded to an iron lead wire and then the wire was covered with a heatshrinkable Teflon tube for electrical insulation. A resin was painted around the welded point. This specimen was used as a working electrode.

Second, corrosion coupons were placed in a glass corrosion cell and immersed under the conditions listed in Table 1. To measure the weight change, the coupons were removed from the corrosion cell every 500 h, rinsed in acetone, and dried with compressed air. The weights of the coupons were measured using an analytical balance with a readability of 10  $\mu$ g. After measurement, the coupons were reloaded in the cell filled with fresh solution. The total test duration of the immersion test was 1000 h.

Table I: Test Conditions

Solution	Common
$600 \text{ ppm NO}_2^-$	35 ℃
$50 \text{ ppm NO}_2^-$	pH:10±0.1
Blank (0 ppm NO <sub>2</sub> <sup>-</sup> )	aerated condition

## 2.3 Oxide Characterization

X-ray photoelectron spectroscopy (XPS) experiments were performed on the coupons oxidized in the immersion corrosion solutions at 35 °C for 1000 h. Monochromated Al K $\alpha$  was used as a radiation source. The binding energy scale of the obtained photoelectron spectra was corrected with the reference C 1s peak at 284.6 eV. XRD patterns were also obtained with a scan rate of 1°/min using a high-resolution diffractometer with copper K $\alpha$  radiation

## 3. Results and Discussion

Fig. 1 shows the potentiodynamic polarization curves of SA106 Gr.B carbon steel in the test solutions with different nitrite concentrations. The corrosion potential was relatively low in the blank solution and as the polarization progressed, active dissolution without passivation was observed, resulting in high current density values. However, in the solutions containing nitrite, the corrosion potential increased and spontaneous passivation occurred, resulting in a significant decrease in the anodic current density. This result indicates that nitrite acts as an oxidizing agent to promote the oxidation reaction of forming a passive film on the steel surface. In particular, the change in the cathodic curve by the addition of nitrite was minimal, while the anodic current density values decreased to a few hundredths, confirming that nitrite is an anodic inhibitor.



Fig. 1. Potentiodynamic polarization curves of SA106 Gr.B carbon steel in the solutions containing different nitrite concentrations at 35 °C.

Fig. 2 shows the surface photographs of corrosion coupons immersed in the test solutions at 35 °C for 1000 h. Corrosion did not occur enough to maintain metal gloss under the conditions of 50 and 600 ppm nitrite. However, it can be seen that severe corrosion occurred over almost the entire surface of the coupon to form a thick oxide. The oxide was easily crumbled, and the outmost surface of the oxide was a dark orange color, while the inside was black. Based on weight loss and 1000 h test time, the corrosion rate was calculated to be 0.0004  $\mu$ g/cm<sup>2</sup>h for both 50 and 600 ppm nitrite solutions and 10.94  $\mu$ g/cm<sup>2</sup>h for the blank solution.



Fig. 2. Surface photographs of corrosion coupons immersed in the test solutions at 35  $\,^\circ\!\!C$  for 1000 h.

Fig. 3 depicts the core-level XPS spectra obtained from the coupon immersed in 600 ppm nitrite solution for 1000 h. The deconvolution of the Fe 2p peak revealed that the spectra consisted of  $Fe^{0}$ ,  $Fe^{2+}$ , and  $Fe^{3+}$ peaks. Satellites of  $Fe^{2+}$  and  $Fe^{3+}$  were also observed. This indicates that the surface is covered with an iron oxide consisted of both  $Fe^{2+}$  and  $Fe^{3+}$  ions. Considering the penetration depth of XPS beam, the detection of the metallic  $Fe^0$  peak suggests that the thickness of the oxide film is less than 10 nm. The N 1s peak was also detected, which was composed of a single NH<sub>4</sub><sup>+</sup> chemical state at a binding energy of 399.8 eV. This indicates that nitrite is not adsorbed and the reduction product of nitrite is NH<sub>4</sub><sup>+</sup>. Similar results were observed in 50 ppm nitrite solution, except that the intensity of the N 1s peak was reduced by half.



Fig. 3. High resolution XPS spectra of Fe 2p, O 1s and N 1s core-levels from the oxide films formed on SA106 Gr.B carbon steel in the 600 ppm nitrite solution at 35 °C.

It has been proposed that the stable passive film of maghemite is formed on the metal surface by nitrite as the following reaction [5,6].

$$2Fe^{2+} + 2OH^{-} + 2NO_2^{-} \rightarrow 2NO + \gamma - Fe_2O_3 + H_2O \quad (1)$$

Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) is an iron oxide composed of only Fe<sup>3+</sup> ions, which is different from the XPS results. In addition, nitrite and nitrogen oxide were not detected and only ammonium ions were consistently detected. Therefore, based on the results of this study, it is suggested that the inhibition mechanism of carbon steel corrosion by nitrite follows the reaction equations below:

$$NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$$
 (2)

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{3}$$

$$3Fe + NO_2^- + 2H_2O + 8H^+ + 6e^-$$

$$\rightarrow \mathrm{Fe}_{3}\mathrm{O}_{4} + \mathrm{NH}_{4}^{+} + 4\mathrm{H}_{2} \tag{4}$$

where Eq. (2) is the reduction reaction of nitrite ( $\Delta G_{35^{\circ}C} = -519.0 \text{ kJ/mol}$ ), Eq. (3) is the oxidation reaction of iron metal ( $\Delta G_{35^{\circ}C} = -66.8 \text{ kJ/mol}$ ), and Eq. (4) is the overall reaction ( $\Delta G_{35^{\circ}C} = -585.8 \text{ kJ/mol}$ ). Here,  $\Delta G_{35^{\circ}C}$  in Eq. (4) demonstrates that it occurs spontaneously.

In summary, the reduction reaction of added nitrite promotes the formation reaction of a Fe<sub>3</sub>O<sub>4</sub> protective film on the surface of carbon steel, thereby suppressing material corrosion. NO<sub>2</sub><sup>-</sup> added during this process is not adsorbed, while NH<sub>4</sub><sup>+</sup>, a reduction product of NO<sub>2</sub><sup>-</sup>, is adsorbed to the outermost layer. In alkaline aqueous solutions, the zeta potentials of most oxide particles, oxide films and material surfaces have a negative value [7,8]. Therefore, adsorption of NO<sub>2</sub><sup>-</sup> is difficult because a repulsive force acts between both the negatively charged NO<sub>2</sub><sup>-</sup> and the metal surface. On the other hand, adsorption of NH<sub>4</sub><sup>+</sup> is favored since an attractive force acts between the positively charged  $NH_{4^+}$  and the negatively charged metal surface. Therefore, the detection of  $NH_{4^+}$  ions in the outermost layer can also be explained in terms of the zeta potential.

On the other hand, thick oxides formed in the blank solution were analyzed using XRD. As shown in Fig. 4, all XRD diffraction angles of the oxides exactly matched those of cubic  $Fe_3O_4$  and orthorhombic  $\gamma$ -FeO(OH). Considering the diffraction intensity and peak area,  $Fe_3O_4$  is identified as the main component of the oxide



Fig. 4. XRD spectra from oxides formed on SA106 Gr.B carbon steel in the blank solution at  $35 \,^{\circ}$ C.

## 4. Conclusions

Nitrite promotes the formation of a protective  $Fe_3O_4$  film on the carbon steel surface through the reduction reaction of nitrite. The overall reaction is presented as follows, which is confirmed to occur spontaneously by thermodynamic calculation:

 $3Fe + NO_2^- + 2H_2O + 8H^+ + 6e^- \rightarrow Fe_3O_4 + NH_4^+ + 4H_2$ 

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