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Effect of Rust Inhibitor in Brine on Corrosion Properties of Copper

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Abstract

In this study, the effects of rust inhibitors in brine on corrosion behaviors of copper were investigated by measurement of cathode and anode polarization curves and an immersion test. For rust inhibitors, benzotriazole, sodium benzoate and sodium nitrite were prepared. From measurement results of cathode and anode polarization curves, it was found that the corrosion rate of copper in the benzotriazole solution is low and a stable passive film with excellent corrosion resistance generates on the surface of copper in the solution. In the case of the sodium benzoate solution, the corrosion resistance of the passive film was inferior to that in the benzotriazole solution although the passive film generated on the surface of copper. In contrast, the passive film scarcely generated on the surface of copper in the sodium nitrite solution. The result shows that the rust preventive effect of the solution to copper is weak. Furthermore, the immersion test revealed that the benzotriazole solution has the rust preventive effect to copper. In contrast, the effect of the sodium benzoate solution is weak and that of the sodium nitrite solution is scarcely expected.

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Keywords: Brine; Rust inhibitor; Corrosion; Copper; Polarization curve

1. Introduction

Equipment such as a home floor heating adjusts the temperature by flowing brine in pipes made of copper or copper alloys. Generally, brine is composed of propylene glycol as a solvent and several rust inhibitors [1]. Since

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brine is used in a wide range of temperature such as -20 ^{o}C to 80 ^{o}C, it is worn out and decreases during use. To investigate the corrosion behaviors of copper in brine, the immersion tests and electrochemical measurements have been conducted [1-5]. Although many studies have been conducted to investigate various factors on the corrosion of copper, the evaluation for the effect of various rust inhibitors on piping materials is not enough. In particular, the effect of degradation of an individual inhibitor on corrosion of metals used for pipes has not been clarified yet. Under such a background, the aim of this study is to investigate the effects of rust inhibitors in brine on corrosion behaviors of copper. The measurement of cathode and anode polarization curves and an immersion test were conducted using solutions with rust inhibitors.

2. Experimental procedure

Benzotriazole ($C_6H_5N_3$), sodium benzoate ($C_7H_5NaO_2$) and sodium nitrite ($NaNO_2$) were prepared as rust inhibitors. Table 1 shows chemical compositions of solution investigated in this study. Each inhibitor was added in propylene glycol ($C_3H_8O_2$) and ion exchanged water was used as diluting liquid.

For polarization experiments, a Cu plate with 150 x 10 x 1 mm^3 size was prepared. Except for the area of 10 x 10 mm^2 of the tip of the Cu plate and the electrode part of the other end, the surface of the Cu plate was coated by resin. The polarization experiments were carried out using the potentio/galvano stat (Hokutodenko HAB-151) as a polarization device. Platinum and silver/silver chloride (SSE) in saturated potassium chloride solution were used as a counter electrode and as a reference electrode, respectively. The polarization curve measurement was conducted at a scan rate of 20 mV/min at three temperatures of 25 ^{o}C, 60 ^{o}C and 80 ^{o}C. The cathodic polarization measurement was conducted in the atmosphere. The scanning potential range was from spontaneous-potential after the immersion of the specimen in the solution for 10 min to -1.5 V. When the current value was less than -1000 μA, the measurement was finished even if the potential was larger than -1.5 V. One specimen was measured under each test condition. The anodic polarization measurement was conducted while ventilating nitrogen. The ventilating nitrogen in the solution was conducted for 30 min at a flow rate of 40 ml/min before the measurement. The flow rate of nitrogen in the solution was 20 ml/min in the measurement. The scanning potential range was from -0.6 V to 1.2 V. When the current value was more than 1000 μA, the measurement was finished even if the potential was lower than 1.2 V. Three specimens were measured under each test condition. The spontaneous-potential measurement was also conducted at 25 ^{o}C for 10 days.

For an immersion test, a Cu plate with 50 x 10 x 1 mm^3 size was prepared. The immersion test was conducted for 15 days at three temperatures of 25 ^{o}C, 60 ^{o}C and 80 ^{o}C using a centrifuge tube. After the test, deposit on the Cu plate was removed with a nylon brush and subsequently the Cu plate was immersed in the solution including hydrochloric acid and ion exchanged water at 1:1. Afterwards, the mass of the specimen was measured and the penetration rate was evaluated using expressions (1) and (2). The general view of the specimens after the test was observed with a digital camera.

Table 1. Chemical compositions of solution investigated (mass ratio).

Solution	$C_3H_8O_2$	$C_6H_5N_3$	$C_7H_5NaO_2$	$NaNO_2$	H_2O
benzotriazole solution	37	0.2	—	—	63
sodium benzoate solution	37	—	1.5	—	63
sodium nitrite solution	37	—	—	0.2	63

$$W = \frac{W_1 - W_2}{S \times T} \tag{1}$$

W: Corrosion degree (mdd), W_1: Weight of specimen before immersion test (mg),
W_2: Weight of specimen after immersion test (mg), S: Surface area of specimen before immersion test (dm^2),
T: Immersion time (day)

$$P = W \times \frac{365 \times 10^{-4}}{d} \tag{2}$$

P: Penetration rate (mm/y), W: Corrosion degree (mdd), d: Density of specimen (g/cm^3)

3. Results and discussion

3.1. Polarization curves

3.1.1. Benzotriazole solution

Fig. 1 shows typical potentiodynamic polarization curves of copper in the benzotriazole solution. Corrosion potential (E_{corr}) was approximately -0.2 V (vs. SSE) regardless of the temperature. In this study, the corrosion current density (I_{corr}) was investigated as a point of intersection of the anode polarization curve and the cathode polarization curve. I_{corr} were evaluated to be 0.5, 0.53 and 0.17 μA/cm^2 for 25, 60 and 80 ^{o}C, respectively. Since low I_{corr} means a low corrosion rate, it was confirmed that the benzotriazole solution has a rust preventive effect for copper. The passivity electric potential area was approximately 0.75 V (vs. SSE) regardless of temperature. This relative large value means that the stable passive film generated on the surface of copper. The current density in the passivity electric potential area is relatively low although the value increased with increasing the temperature. The low current density in the passivity electric potential area indicates that the corrosion resistance of the passive film is excellent.

3.1.2. Sodium benzoate solution

Fig. 2 shows typical potentiodynamic polarization curves of copper in the sodium benzoate solution. E_{corr} was obtained to be from -0.1 V to -0.2 V (vs. SSE) regardless of the temperature. The obtained values were similar to those of copper in the benzotriazole solution. I_{corr} were evaluated to be 2.5, 3.3 and 4.3 μA/cm^2 for 25, 60 and 80 ^{o}C, respectively. Those values were higher than those of copper in the benzotriazole solution. Since high I_{corr} means a high corrosion rate, the corrosion resistance of the passive film generated on the surface of copper is inferior. In particular, I_{corr} remarkably increased at high temperatures of 60 ^{o}C and 80 ^{o}C and thus the corrosion resistance of the passive film seems to degrade at high temperatures. The passivity electric potential area was approximately 0.4 V (vs. SSE) regardless of the temperature, and the value is small compared with that in the benzotriazole solution. Moreover, the current density in the passivity electric potential area is higher than those in other solutions. The results indicate that corrosion reaction is active although the passive film generates.

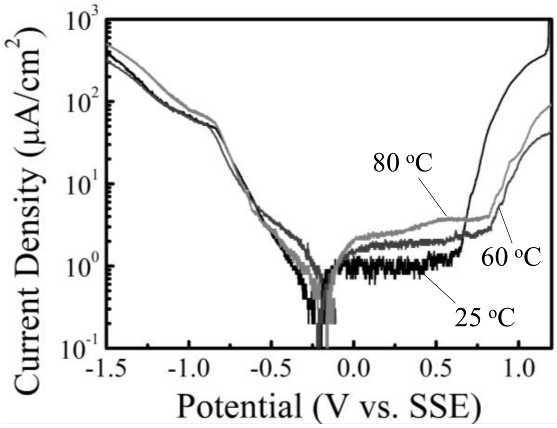

Fig. 1. Potentiodynamic polarization curves of copper in benzotriazole solution.

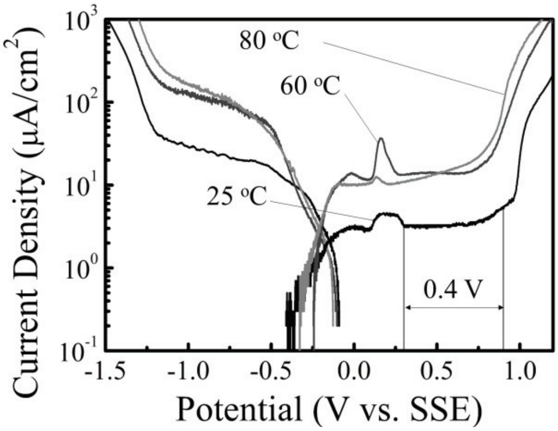

Fig. 2. Potentiodynamic polarization curves of copper in sodium benzoate solution.

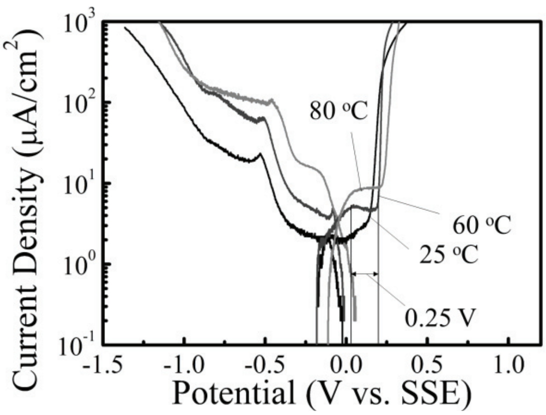

Fig. 3. Potentiodynamic polarization curves of copper in sodium nitrite solution.

3.1.3. Sodium nitrite solution

Fig. 3 shows typical potentiodynamic polarization curves of copper in the sodium nitrite solution. E_{corr} was approximately -0.1 V (vs. SSE) regardless of the temperature, and was similar to those of copper in other solutions. I_{corr} were evaluated to be 1.9, 3.7 and 4.0 μA/cm^2 for 25, 60 and 80 ^{o}C, respectively. The values were higher than those of copper in the benzotriazole solution and similar to those of copper in the sodium benzoate solution. Similar to the sodium benzoate solution, it seems that the corrosion resistance of the passive film generated on the surface of copper is inferior and degrades at high temperatures. The passivity electric potential area was not almost seen at 25 ^{o}C. This indicates that the passive film does not generate and the corrosion occurred immediately with increasing potential. The passivity electric potential area was approximately 0.25 V (vs. SSE) at 60 ^{o}C and 80 ^{o}C. Since the value is small compared with those in other solutions, the passive film scarcely generates. Furthermore, the current density drastically increased in the passivity electric potential area. The result revealed that the rust preventive effect of the sodium nitrite solution to copper is weak.

3.2. Spontaneous−potential of copper in each solution

Fig. 4 shows spontaneous−potential measurement results for each solution at 25 ^{o}C. After ten days, spontaneous−potentials of copper were 0.026, 0.075 and 0.08 V (vs. SSE) in benzotriazole, sodium benzoate and sodium nitrite solutions, respectively. Compared with potentiodynamic polarization curves shown in Figs. 1-3 and spontaneous−

potential evaluated from Fig. 4, the following was clarified. In the benzotriazole solution, spontaneous−potential of copper existed in the passivity electric potential area so that the passive film is formed on the surface of copper. In the sodium benzoate solution, spontaneous−potential of copper was located in the point before the peak in the passivity electric potential area shown in Fig. 2. This indicates that the passive film begins to be formed on the surface of copper. Moreover, in the sodium nitrite solution, spontaneous−potential of copper was located in the short passivity electric potential area. Spontaneous−potential of copper was in the passivity electric potential area so that the passive film is formed on the surface of copper. However, since the passivity electric potential area is short as shown in Fig. 3, the corrosion of copper could progress rapidly with a little increase of potential.

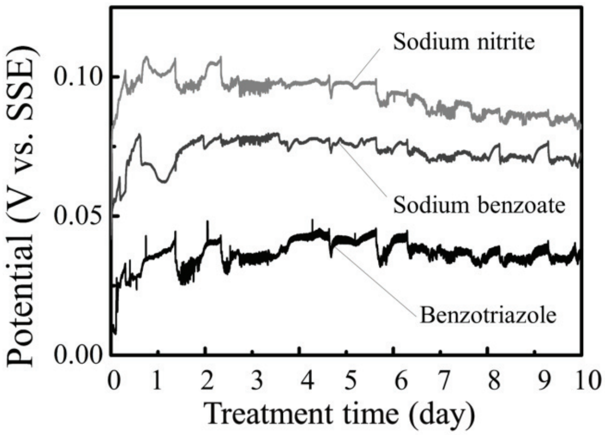

Fig. 4. Results of spontaneous−potential measurement at 25 °C.

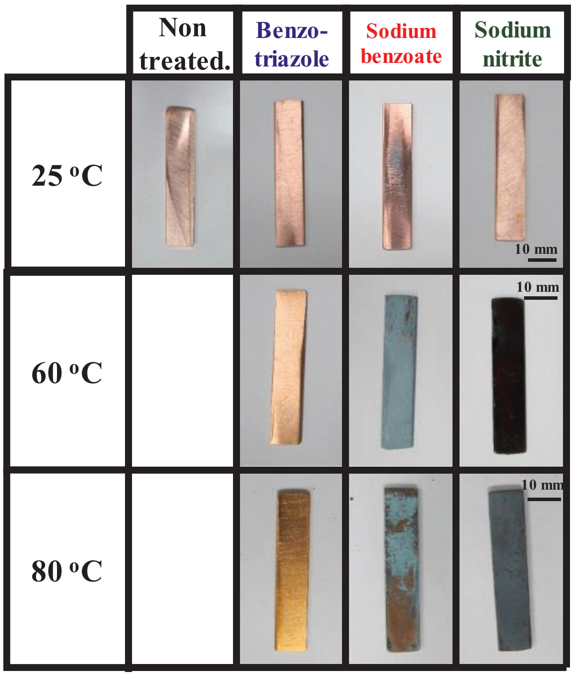

Fig. 5. General views of specimens after immersion test for 15 days

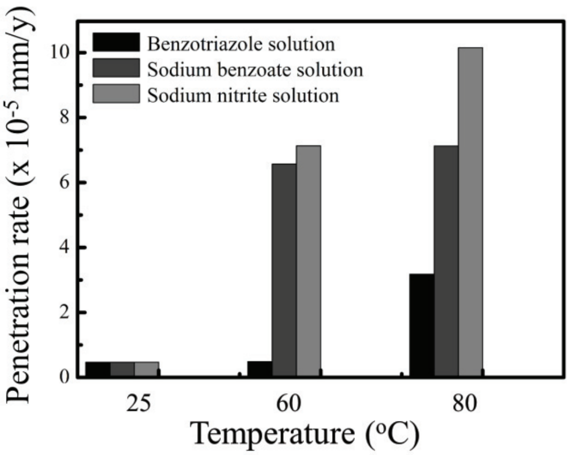

Fig. 6. Comparison of penetration rate (*P*) of copper in each solution.

3.3. Immersion test

Fig. 5 shows general views of specimens after immersion in each solution for 15 days. In the benzotriazole solution, no change was observed on the surfaces of copper at all temperatures. On the other hand, in the sodium benzoate solution, the formation of deposit on the surfaces of copper was observed and the formed deposit increased at high temperatures of 60 °C and 80 °C. Moreover, in the sodium nitrite solution, the discoloration area was seen partially on the surface of copper at 25 °C. The whole of the surface of copper changed in black at 60 °C, and the formation of deposit on the surface was observed at 80 °C. Further experiment is required to identify the deposit and the discoloration area on the surfaces.

Fig. 6 shows the penetration rate (*P*) of copper in each solution evaluated from the expression (2). At 25 °C, the difference in *P* is negligible among three solutions investigated. At 60 °C, *P* in both sodium benzoate and sodium nitrite solutions significantly increased although *P* in the benzotriazole solution slightly increased. The change corresponds to the change of the surfaces of copper shown in Fig. 5. *P* in the sodium nitrite solution is a little higher than that in the sodium benzoate. At 80 °C, the value of *P* increased in all solutions. The order of *P* in each solution became such as benzotriazole < sodium benzoate < sodium nitrite.

From the above-described results, it was clarified that the benzotriazole solution has the rust preventive effect to copper. In contrast, the effect of the sodium benzoate solution is weak and that of the sodium nitrite solution is hardly expected.

4. Conclusions

In this study, the effects of rust inhibitors in brine on corrosion behaviors of copper was investigated. The measurement of cathode and anode polarization curves and an immersion test were conducted using three types of solutions with benzotriazole, sodium benzoate and sodium nitrite. The obtained results are summarized as follows.

(1) In the benzotriazole solution, the corrosion current densities (I_{corr}) were evaluated to be 0.5, 0.53 and 0.17 μA/cm^2 at 25, 60 and 80 °C, respectively. Such low I_{corr} means a low corrosion rate and thus it was confirmed that the benzotriazole solution has a rust preventive effect for copper. The passivity electric potential area was approximately 0.75 V (vs. SSE) regardless of the temperature. This relative large value means the generation of the stable passive film. The current density in the passivity electric potential area was relatively low. The result shows that the corrosion resistance of the passive film is excellent.

(2) In the sodium benzoate solution, I_{corr} were evaluated to be 2.5, 3.3 and 4.3 μA/cm^2 for 25, 60 and 80 ^{o}C, respectively. Such high I_{corr} indicates that the corrosion resistance of the passive film is inferior to that in the benzotriazole solution. The passivity electric potential area was approximately 0.4 V (vs. SSE) regardless of the temperature and the current density in the area is higher than those in other solutions. The results indicate that corrosion reaction is active although the passive film generates.
(3) In the sodium nitrite solution, I_{corr} were evaluated to be 1.9, 3.7 and 4.0 μA/cm^2 for 25, 60 and 80 ^{o}C, respectively. The values were similar to those in the sodium benzoate solution. The passivity electric potential area was not almost seen at 25 ^{o}C and was approximately 0.25 V (vs. SSE) at 60 ^{o}C and 80 ^{o}C. Such small value means that the passive film scarcely generates. Furthermore, the current density drastically increased in the passivity electric potential area. The result revealed that the rust preventive effect of the solution to copper is weak.
(4) In the immersion test at 25 ^{o}C, the difference in the penetration rate (P) was negligible among three solutions investigated. At 60 ^{o}C, P in both sodium benzoate and sodium nitrite solutions significantly increased although that in the benzotriazole solution slightly increased. At 80 ^{o}C, the value of P increased in all solutions and the order of P in each solution became such as benzotriazole < sodium benzoate < sodium nitrite.

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