

Study of the Effect of Acetic Acid and Phosphate on Copper Corrosion by Immersion Tests

Yuna Yamaguchi¹, Kaho Sugiura¹, Toyohiro Arima¹, Fuka Takahashi¹, Itaru Ikeda²,
Yutaka Yamada^{1,3}, Osamu Sakurada^{1*}

¹Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Gifu, Japan

²Dai-Dan Co., Ltd., Saitama, Japan

³Daiwa Techno Co., Ltd., Gifu, Japan

Email: yamaguchi.yuna.t5@s.gifu-u.ac.jp, sugiura.kaho.h9@s.gifu-u.ac.jp, arima.toyohiro.x9@s.gifu-u.ac.jp, takahashi.fuka.k9@s.gifu-u.ac.jp, ikedaitaru@daidan.co.jp, y.yamada@daiwatec.com, *sakurada.osamu.m5@f.gifu-u.ac.jp

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Abstract

It was reported that hemispheric corrosion occurred in copper tubes in an acetic acid environment. When hemispheric corrosion occurred, corrosion could easily progress if water then flowed into the copper pipe, and counter-measures were needed. Therefore, we studied the copper corrosion caused by acetic acid. The present work investigated the relationship between the corrosion form of copper and acetic acid concentration using phosphorous-deoxidized copper, and reported that hemispherical corrosion was observed at acetic acid concentrations of 0.01 to 1 vol.% (0.002 to 0.2 mol·L⁻¹) in the immersion test. In this study, the effects of acetic acid and phosphate on copper corrosion were examined using oxygen-free copper in immersion tests. The results suggested that different concentrations of phosphate in acetic acid solutions and the presence or absence of acetic acid and phosphate affected the corrosion of copper, resulting in different corrosion forms and corrosion progress.

Keywords

Acetic Acid, Phosphate, Oxygen-Free Copper, Hemispherical Corrosion, Ant-Nest Corrosion

1. Introduction

Corrosion by organic acids was a problem. It was reported that organic acid from the paint used for building construction and the operating environment after installation of equipment caused copper corrosion [1]-[11]. The mechanism of corrosion caused by organic acids remained largely unknown. To eluci-

date the mechanism, immersion [8] [9] [10] and wet atmosphere exposure tests [2]-[7] [10] were conducted. These showed that ant-nest corrosion and hemispherical corrosion were the forms of corrosion caused by organic acids and hemispherical corrosion resulted in copper tubes in an acetic acid environment [2] [6] [10]. When hemispheric corrosion occurred, corrosion could easily progress if water then flowed into the copper pipe, and countermeasures were needed. Therefore, we studied the copper corrosion caused by acetic acid. The present work investigated the relationship between the corrosion form of copper and acetic acid concentration using phosphorous-deoxidized copper, and reported that hemispherical corrosion was observed at acetic acid concentrations of 0.01 to 1 vol.% (0.002 to 0.2 mol·L⁻¹), especially at 1 vol.% (0.2 mol·L⁻¹) in the immersion test [12]. In addition to acetic acid ions, phosphate ions due to the dissolution of phosphorus in the phosphorus-deoxidized copper were also inferred as corrosion promoting ions [12]. In this study, we focused on acetic and phosphate ions and reported the effects of acetic acid and phosphate on copper corrosion in immersion tests using oxygen-free copper not containing phosphorus.

2. Experimental Methods

2.1. Test Materials and Test Solution

The test materials were JIS H 3100 C1020 oxygen-free copper sheets 15 mm wide, 0.3 mm thick, and 55 mm long degreased with acetone as pretreatment.

The test solutions consisted of pure water to which acetic acid (CH₃COOH, guaranteed reagent, Nacalai Tesque, Inc., Japan) and potassium dihydrogen phosphate (KH₂PO₄, extra pure reagent, Nacalai Tesque, Inc., Japan) as phosphate were added. The concentration of acetic acid was adjusted to 0.2 mol·L⁻¹, and the concentrations of phosphate were adjusted to various levels. The acetic acid concentration was the same as in the previous report at 1 vol.% [12].

2.2. Immersion Test

Figure 1 shows a schematic illustration of the immersion test and image of the test specimen before the test. As in our previous report [12], test specimens were placed in 100 mL lidded polypropylene containers containing 20 mL of the test solution, and the bottom 2 cm of the specimens were immersed in the test solution. The following heat cycle was conducted 5 days/week. After the upper volume inside the containers was replaced with oxygen gas at 25 L·min⁻¹ for 5 s, the containers were placed in a constant temperature and humidity apparatus (SANYO Electric Co.: MTH-4400) and kept at a temperature of 60°C for 1 hour. The containers were then removed from the apparatus and kept at room temperature for 23 hours. For 2 days/week they were kept at room temperature. The test period was 3 weeks.

The immersion tests were conducted under the following three conditions.

1) Effect of changes in phosphate concentration on copper corrosion in acetic acid solution

To investigate the effect of changes in phosphate concentration on copper

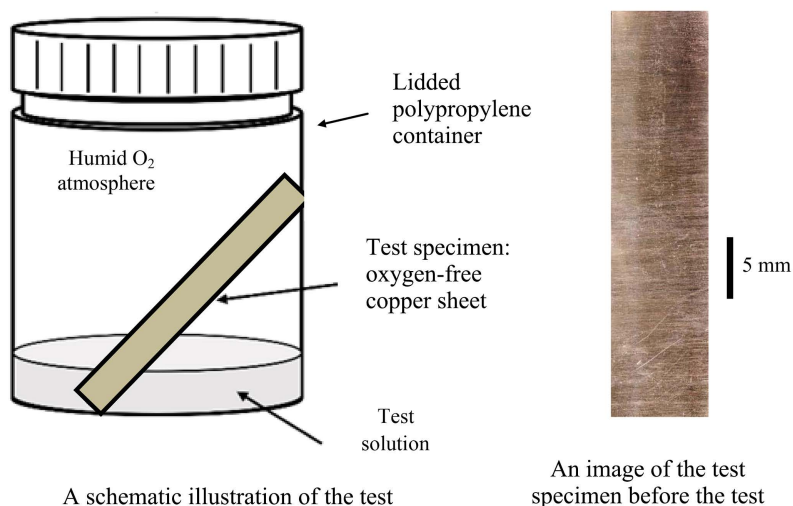


Figure 1. A schematic illustration of immersion test and an image of the test specimen before the test.

corrosion in acetic acid solution, immersion tests were conducted using mixed solutions of $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid and various concentrations of phosphate.

2) Respective effects of acetic acid and phosphate on copper corrosion

To investigate the respective effects of acetic acid and phosphate on copper corrosion, immersion tests were conducted in three different test waters: mixed solution of $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid and $0.02 \text{ mol}\cdot\text{L}^{-1}$ phosphate, $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid only, and $0.02 \text{ mol}\cdot\text{L}^{-1}$ phosphate only.

3) Effect of adding of acetic acid and phosphate on copper corrosion

To investigate the effects of adding acetic acid and phosphate on copper corrosion, immersion tests were conducted under the following two test conditions.

a) The specimens were immersed in $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid for 1 week, then phosphate was added to the test water, and the specimens were immersed in the mixed solution of $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid and $0.02 \text{ mol}\cdot\text{L}^{-1}$ phosphate for 2 weeks.

b) The specimens were immersed in $0.02 \text{ mol}\cdot\text{L}^{-1}$ phosphate for 1 week, then acetic acid was added to the test water, and the specimens were immersed in the mixed solution of $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid and $0.02 \text{ mol}\cdot\text{L}^{-1}$ phosphate for 2 weeks.

After the tests, the specimens were evaluated by surface and cross-section observations. A digital microscope (Keyence Corp.: VHX-5000) was used for these observations. The composition of corrosion products after the test was analyzed by X-ray diffraction (Rigaku: Miniflex 600, Cu- $K\alpha$ ray, tube voltage 40 kV, tube current 10 mA).

3. Results and Discussion of the Immersion Tests of Copper Corrosion Form and Progress

3.1. Effect of Changes in Phosphate Concentration on Copper Corrosion in Acetic Acid Solution

Figure 2 shows the results of surface and cross-section observations after immersion tests in mixed solutions of $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid and various

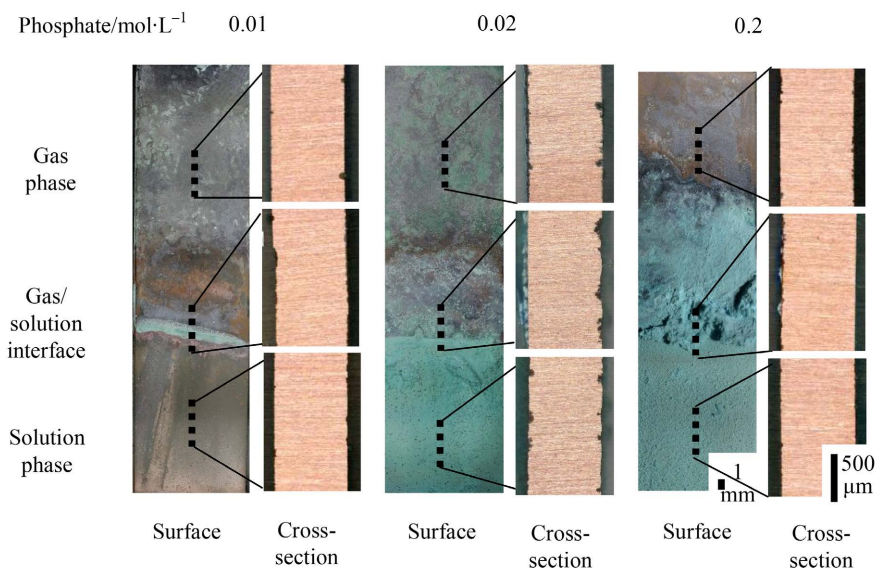


Figure 2. Images of surface and cross-section observations of copper plates after immersion tests in mixed solutions of 0.2 mol·L⁻¹ acetic acid and 0.01, 0.02, and 0.2 mol·L⁻¹ phosphate.

concentrations of phosphate. The surface observations showed that at 0.01 mol·L⁻¹ phosphate, blackish brown discoloration was observed throughout the specimen, and a small amount of greenish blue corrosion products were observed at the gas/solution interface and gas phase. At 0.02 mol·L⁻¹ phosphate, blackish brown discoloration was observed at the gas/solution interface and gas phase, and greenish blue corrosion products were formed throughout. In particular, the solution phase was covered with the corrosion products. At 0.2 mol·L⁻¹ phosphate, blackish brown discoloration was observed at the gas phase, and was covered with greenish blue corrosion products at the solution phase and gas/solution interface. **Figure 3** shows the results of X-ray diffraction of the corrosion products at the gas/solution interface at 0.2 mol·L⁻¹ phosphate, where the greenish blue corrosion products were most abundant. As a result, the peak of Cu₃(PO₄)₂·3H₂O (PCPDF #00-022-0548) was detected in the greenish blue corrosion products. Therefore, it was inferred that the greenish blue corrosion products on the copper were hydrates of copper phosphate.

Figure 4 shows a summary of the cross-section observations in **Figure 2**. At 0.01 mol·L⁻¹ phosphate, light corrosion was observed throughout. At 0.02 mol·L⁻¹ phosphate, hemispherical corrosion was observed. At 0.2 mol·L⁻¹ phosphate, light corrosion was observed throughout. From the results, it was inferred that oxygen-free copper corrosion progressed differently in 0.2 mol·L⁻¹ acetic acid depending on the phosphate concentration, and hemispherical corrosion progressed the most at 0.02 mol·L⁻¹ phosphate.

3.2. Respective Effects of Acetic Acid and Phosphate on Copper Corrosion

Figure 5 shows the results of surface and cross-section observations after

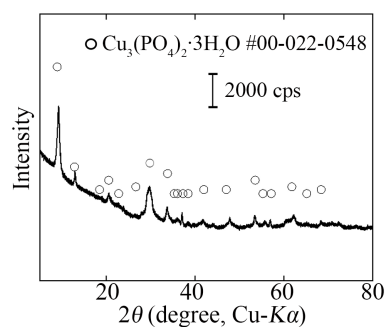


Figure 3. The X-ray diffraction profile of the greenish blue corrosion products at the gas/solution interface at mixed solutions of $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid and $0.2 \text{ mol}\cdot\text{L}^{-1}$ phosphate.

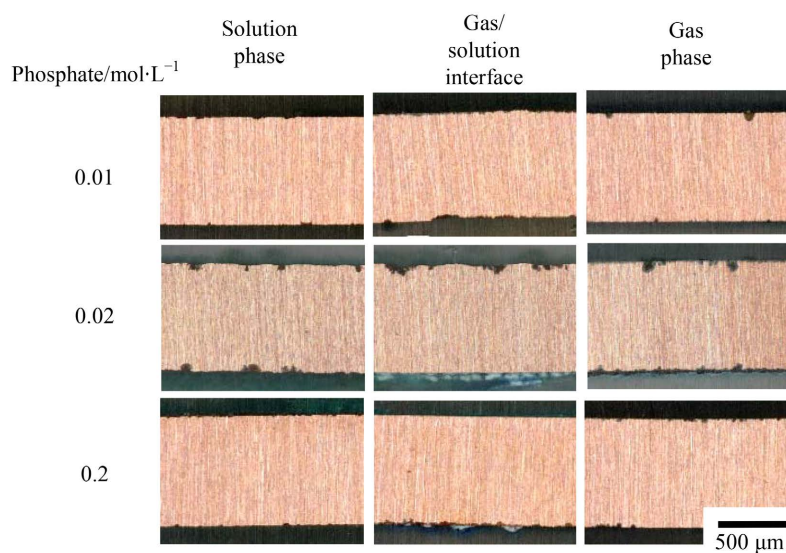


Figure 4. A summary of the cross-section observations in Figure 2.

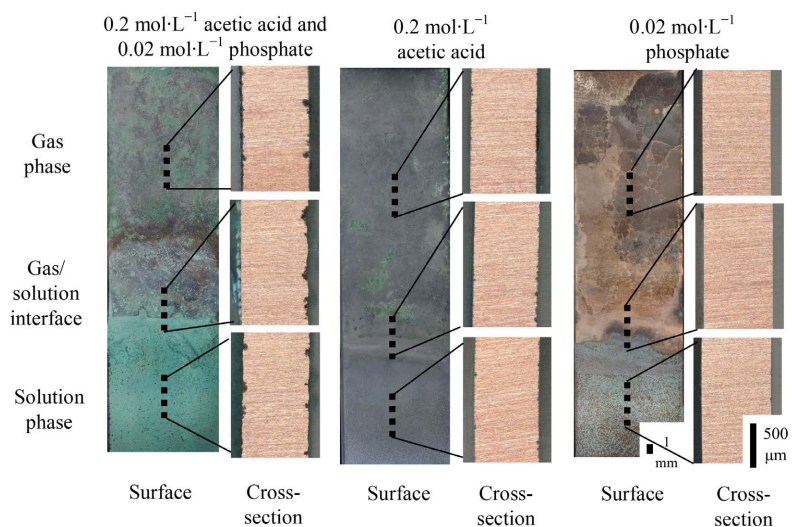


Figure 5. Images of surface and cross-section observations of copper plates after immersion tests in the mixed solution of $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid and $0.02 \text{ mol}\cdot\text{L}^{-1}$ phosphate, $0.2 \text{ mol}\cdot\text{L}^{-1}$ acetic acid only, and $0.02 \text{ mol}\cdot\text{L}^{-1}$ phosphate only.

immersion tests in the mixed solution of 0.2 mol·L⁻¹ acetic acid and 0.02 mol·L⁻¹ phosphate, 0.2 mol·L⁻¹ acetic acid only, and 0.02 mol·L⁻¹ phosphate only. The surface observations showed that in the mixed solution of 0.2 mol·L⁻¹ acetic acid and 0.02 mol·L⁻¹ phosphate, blackish brown discoloration was observed at the gas/solution interface and gas phase, and greenish blue corrosion products were formed throughout. In particular, the solution phase was covered with corrosion products. At 0.2 mol·L⁻¹ acetic acid only, blackish brown discoloration was observed throughout, and a small amount of greenish blue corrosion products were observed at the gas phase. At 0.02 mol·L⁻¹ phosphate only, dark brown discoloration was partially observed at the gas/solution interface and gas phase, and greenish blue corrosion products were observed at the solution phase and gas/solution interface.

Figure 6 shows a summary of the cross-section observations in **Figure 5**. In mixed solution of 0.2 mol·L⁻¹ acetic acid and 0.02 mol·L⁻¹ phosphate, hemispherical corrosion was observed throughout. At 0.2 mol·L⁻¹ acetic acid only, light corrosion was observed throughout. At 0.02 mol·L⁻¹ phosphate only, light corrosion was observed at the solution phase, and almost no corrosion was observed at the gas/solution interface and gas phase. From the results, it was inferred that hemispherical corrosion progressed more in the presence of both acetic acid and phosphate than in the presence of only one of them.

3.3. Effect of Adding of Acetic Acid and Phosphate on Copper Corrosion

Figure 7 shows the results of surface and cross-section observations after immersion tests under the following test conditions: a) the specimens were immersed in 0.2 mol·L⁻¹ acetic acid for 1 week, then phosphate was added to the test water, and the specimen was immersed in the mixed solution of 0.2 mol·L⁻¹ acetic acid and 0.02 mol·L⁻¹ phosphate for 2 weeks, and; b) the specimens were immersed in 0.02 mol·L⁻¹ phosphate for 1 week, then acetic acid was added to the test water, and the specimen was immersed in the mixed solution of 0.2 mol·L⁻¹ acetic acid and 0.02 mol·L⁻¹ phosphate for 2 weeks. The surface observations showed that for a), blackish brown discoloration was observed at the gas/solution interface and gas phase, and greenish blue corrosion products were observed throughout. The corrosion products were especially observed at the solution phase. For b), blackish brown discoloration was observed throughout. Green corrosion products were observed at the solution phase. Greenish blue corrosion products were observed at the gas/solution interface and gas phase, especially at the gas/solution interface.

Figure 8 shows a summary of the cross-section observations in **Figure 7**. For a), near ant-nest corrosion was observed at the solution phase. At the gas/solution interface, light corrosion was observed. At the gas phase, hemispherical corrosion was observed. The corrosion forms differed depending on the phases. For b), light corrosion was observed throughout. From the results, it was inferred that the corrosion forms and corrosion progress of oxygen-free copper were affected by the test water at the initial stage of immersion.

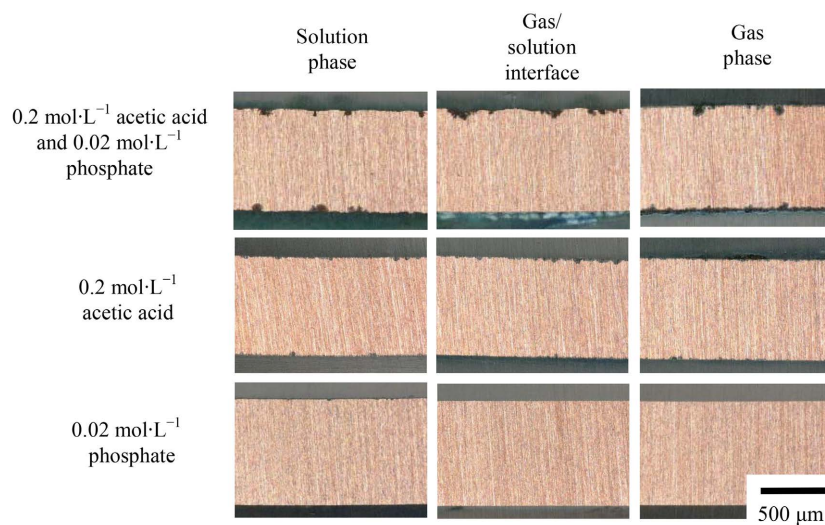


Figure 6. A summary of the cross-section observations in **Figure 5**.

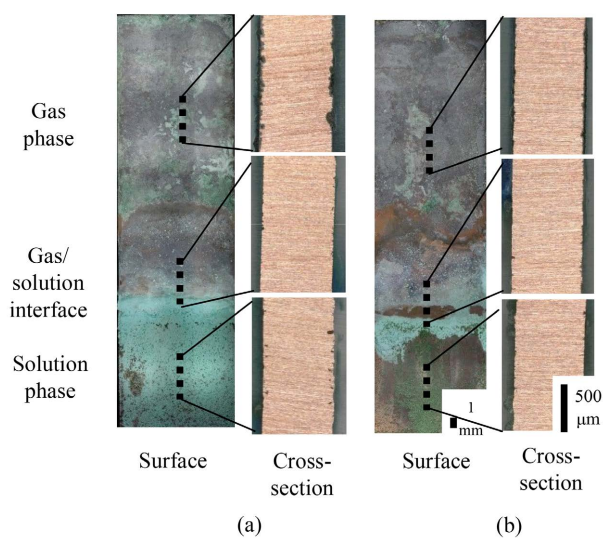


Figure 7. Images of surface and cross-section observations of copper plates after immersion tests under the test conditions (a) and (b).

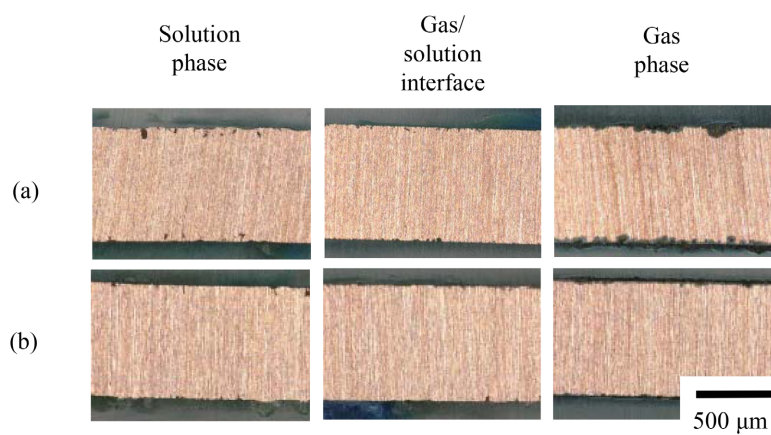


Figure 8. A summary of the cross-section observations in **Figure 7**.

From the above results, it was assumed that copper corrosion was affected by the difference in phosphate concentration in acetic acid, and the presence or absence of acetic acid and phosphate, resulting in differences in corrosion forms and corrosion progress.

4. Conclusion

This study showed that oxygen-free copper corrosion progressed differently in 0.2 mol·L⁻¹ acetic acid depending on the phosphate concentration, and hemispherical corrosion progressed the most at 0.02 mol·L⁻¹ phosphate. The hemispherical corrosion was assumed to progress more in the presence of both acetic acid and phosphate than in the presence of only one of them. It was inferred that the corrosion forms and corrosion progress of oxygen-free copper were affected by the test water at the initial stage of immersion. From the above results, it was assumed that copper corrosion was affected by the difference in phosphate concentration in acetic acid, and the presence or absence of acetic acid and phosphate, resulting in differences in corrosion forms and corrosion progress.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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