

Simple Measurement of Carbon Films on Copper Tubes and Their Effects on Corrosion

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Abstract

It has been reported that pitting corrosion in copper tubes occurs due to the effect of a carbon film produced by the influence of undergoing an oil and heat treatment. As a quantitative method for determining the residual carbon amount, it has been reported that the inner surface of a copper tube can be dissolved with a mixed acid to collect and analyze the adhering carbon; however, this method is dangerous and difficult. Therefore, two methods were examined as a simple quantitative method for obtaining the residual carbon amount using copper tubes with known residual carbon amounts. One method utilizes X-ray photoelectron spectroscopy (XPS), and the other method utilizes the potential difference between the carbon film-adhered surface and carbon film-removed surface. In regard to XPS measurement, a linear correlation was found between the spectral intensity of C and the residual carbon amount; therefore, XPS measurements were considered to be effective as a simple measurement method for the carbon film on the inner surface of a copper tube. In the evaluation method by measuring the corrosion potential, a correlation was observed between the potential difference ΔE and the residual carbon amount of the inner surface of the tube and the outer surface of the polished tube. It is considered possible to estimate the residual carbon amount from the prepared calibration curve. Through these studies, it is suggested that the carbon film was non-uniformly present on the surface of the copper tube. Therefore, the galvanic current was measured, and the effect of a non-uniform carbon film on corrosion behavior was investigated. As a result, in the measurement of galvanic current, the current flowed from the copper tube with a large amount of residual carbon (cathode) to the copper tube with

a small amount of residual carbon (anode). In addition, the higher the area ratio of the carbon film was, the larger the galvanic current tended to be.

Keywords

Copper Tube, Residual Carbon, Pitting Corrosion, Cooling Water System, Refrigerator, XPS

1. Introduction

Since copper has high thermal conductivity and is easy to process, it is widely used in the heat exchangers of air conditioning equipment and in sanitary equipment. Additionally, copper is known as a corrosion-resistant material in fresh water [1]; however, it has been reported that type I pitting corrosion is caused by the synergistic effect between the water quality and the carbon film produced by the influence of undergoing an oil and heat treatment [2] [3] [4]. It has also been reported that the occurrence of pitting corrosion is suppressed even in the presence of a carbon film by adding a water treatment agent to the cooling water [5] [6]. In regard to a quantitative method to analyse this carbon film, it has been reported that after degreasing the inside of the tube with an organic solvent, the inside surface of the tube is dissolved with a mixture of nitric and hydrochloric acid to collect and analyze the attached carbon [7]. However, this method is dangerous because it uses a mixed acid. Additionally, since the amount of the carbon film adhered to the inner surface of the tube (hereinafter referred to as “residual carbon amount”) is small; many copper tubes are required for quantification. Since this analysis can be dangerous and difficult, a safe and simple method for measuring the carbon film as the residual carbon amount is desired.

Therefore, in this study, two methods were examined as a simple quantitative method for the residual carbon amount through the use of copper tubes with a known residual carbon amount. One is a method that utilizes X-ray photoelectron spectroscopy (XPS), and the other is a method that uses the potential difference between the carbon film-adhered surface and the carbon film-removed surface. In addition, through these studies, it was suggested that the carbon film was non-uniformly present on the surface of the copper tube; thus, the galvanic current was measured and the effect of a non-uniform carbon film on corrosion behavior was investigated.

2. Method

2.1. Test Materials

JIS H3300 C1220 phosphorus-deoxidized soft copper tubes with 9 different levels of residual carbon amount were used as the test material. **Table 1** shows the residual carbon amount of these test materials, along with the tube dimensions for the corresponding tests. The test material with a residual carbon amount of

Table 1. Description of the test materials.

Residual Carbon Amount [mg/m ²]	0	0.5	1.0	2.1	5.3	6.1	6.6	13.0	23.0
Diameter φ [mm]	15.2	15.2	15.9	15.9	15.9	15.9	15.9	15.9	15.9
Thickness t [mm]	0.4	0.4	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Test I	•	•	-	•	•	•	•	•	•
Test II	-	-	•	-	-	-	•	•	-
Test III	•	-	-	-	-	-	-	-	•

0 mg/m² was prepared by immersing 0.5 mg/m² test material in 3.0 mass% sulfuric acid for 10 s and then thoroughly rinsing with water. In a test that evaluated the relationship between the peak intensity of C and the residual carbon amount using XPS (hereinafter referred to as “Test I”), a copper tube was cut in half, opened like a plate, and then washed with acetone for 10 s. In the test in which the relationship between the corrosion potential difference between the carbon film-adhered surface (inner surface of the tube) and the carbon film-removed surface (outer surface of the tube) was measured to determine the residual carbon amount (hereinafter referred to as “Test II”), the length of the test material was 50 mm. The inner surface of the tube was only degreased with acetone, and the outer surface of the tube was polished 5 times with 400# emery polishing paper in the axial direction of the tube and then degreased with acetone. In addition, after coating the cut surface of the tube end, one of the tube ends was closed with a silicon plug and used for the test. In a test in which the correlation between the carbon film and corrosion was investigated by measuring the galvanic current while short-circuiting the test materials with residual carbon amounts of 0 and 23.0 mg/m² and different area ratios (hereinafter referred to as “Test III”), the test material was halved and degreased with acetone; then, the other parts were coated so that the exposed inner surface of the tube was 1, 2 and 4 cm².

2.2. Test Equipment

A Quantera SXM instrument (ULVAC-PHI) was used for the XPS measurement in Test I. **Figure 1** shows the measurement points with a residual carbon amount of 6.6 mg/m² as an example. Moreover, the plate-shaped test material was fixed to a holder with carbon tape, as shown in **Figure 1**, and there were 10 measurement points with 3 mm intervals on each test material. The photoelectron spectra of C 1s, Cu 2p_{3/2}, and O1s were measured at a pass energy of 55.0 eV using an Al K α radiation source ($h\nu = 1486.6$ eV) with a beam diameter of 100 μ m, an acceleration voltage of 15 kV, and an output of 25 W. The calibration of the binding energy of each data point was performed with the C 1s peak at 285.0 eV.

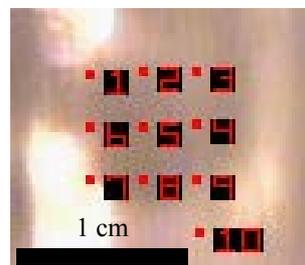


Figure 1. Schematic showing the measurement points for XPS.

Figure 2 shows a schematic diagram of the test equipment for Test II. The test water used was a pH 6 aqueous solution in which KCl was dissolved in pure water; the KCl concentrations were adjusted to 0.1, 0.5, 1.0, 2.0 and 3.3 M. The test material was placed in a 100 mL beaker, and 80 mL of test water was poured into the beaker to measure the corrosion potential on the outer surface of the tube. Then, 4 mL of test water was poured into the tube to measure the corrosion potential on the inner surface of the tube. A potentiostat (Hokuto Denko: HZ-5000) was used to measure the corrosion potential, and an Ag/AgCl electrode was used as the reference electrode. The measurement time was set to 150 s, and the potential was measured at $n = 5$.

Figure 3 shows a schematic diagram of the test equipment for Test III. A 0.5 M KCl aqueous solution was used as the test water, and the test was conducted at room temperature under open-air conditions and stirred at 300 rpm. Briefly, 200 mL of test water was placed in a 200 mL beaker. The area ratio was adjusted to residual carbon amounts of 0 and 23.0 mg/m² test specimens; additionally, a distance of approximately 2 cm was set between the electrodes, and a non-resistance ammeter (Hokuto Denko HM-103A) was used. The current was measured at $n = 3$. The current density was calculated by converting the measured current value per unit area.

3. Results and Discussion

3.1. Test I Evaluation by XPS Analysis

Figure 4 shows the XPS spectra of C 1s, Cu 2p_{3/2}, and O 1s at residual carbon amounts of 0, 6.6, and 23.0 mg/m². The C 1s peak tended to increase as the residual carbon amount increased. At a residual carbon amount of 23.0 mg/m², a shoulder was recognized at approximately 286 eV. It is thought that this was due to the carbon film. On the other hand, in the spectrum of Cu 2p_{3/2}, the peak tended to decrease as the residual carbon amount increased, and it is thought that the exposed area of copper decreased due to the carbon film. The O 1s peak also tended to decrease as the residual carbon amount increased.

Figure 5 shows the average and standard deviation of the integrated intensities of the C 1s and Cu 2p_{3/2} peaks for each residual carbon amount at 10 measurement positions. It was observed that the integrated intensity of the C 1s peak increased linearly with the residual carbon amount and that Cu 2p_{3/2} decreased

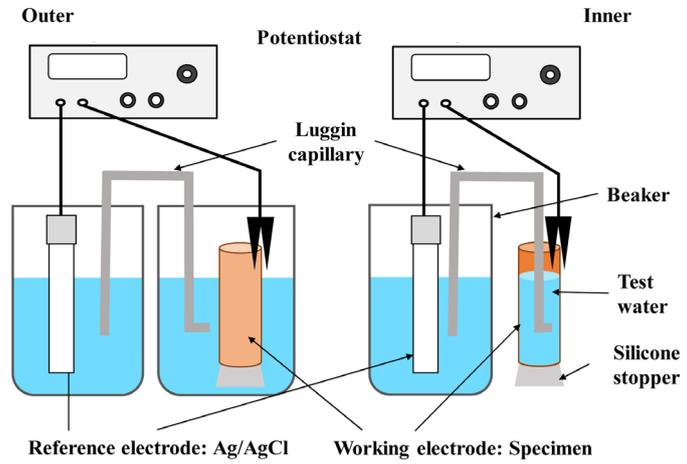


Figure 2. Schematic diagram showing the corrosion potential measurement device.

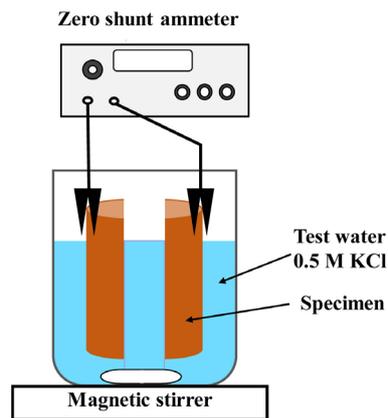


Figure 3. Schematic diagram the experimental galvanic current measurement.

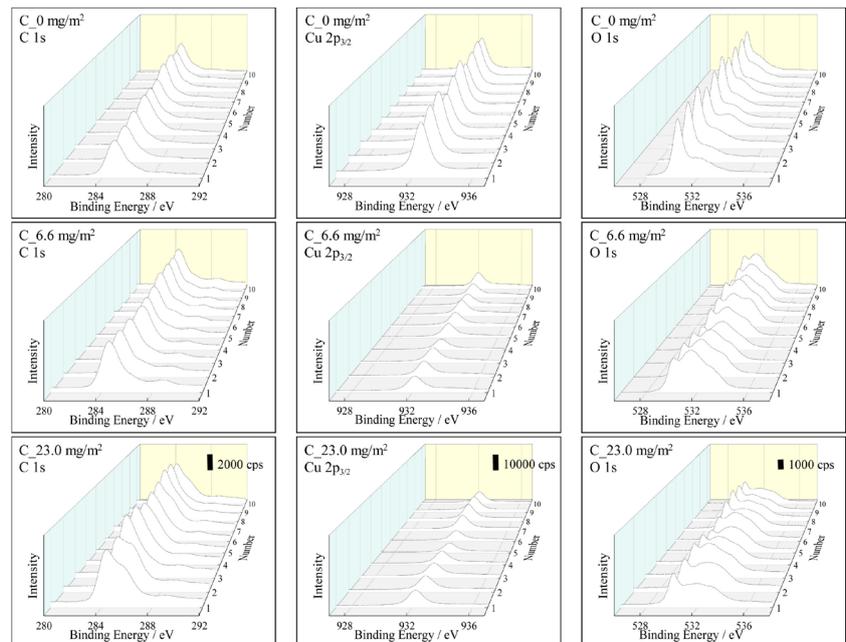


Figure 4. XPS measurement results (residual carbon amount 0, 6.6 and 23.0 mg/m²).

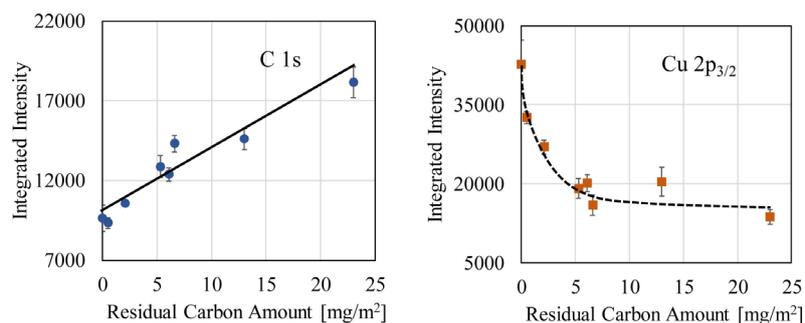


Figure 5. Relationship between the residual carbon amount and integrated intensity of C 1s and Cu 2p_{3/2}. Error bars indicate the SD (n = 10).

exponentially. Since the residual carbon amount and the integrated intensity of the peak at C 1s showed a linear response, it is considered possible to quantify the residual carbon amount on the inner surface of the tube by measuring the C 1s peak by XPS.

Based on the above results, it is considered that XPS measurements were effective as a simple quantitative method for measuring the residual carbon amount. However, as a more versatile quantification method, an evaluation method by potential measurements was examined.

3.2. Test II Evaluation by Potential Difference

3.2.1. Corrosion Potential Measurement

Figure 6 shows an example of the corrosion potential measurement results on the inner and outer surfaces of the test material with a residual carbon amount of 6.6 mg/m² in 0.5 M KCl. The corrosion potential on the outer surface was almost constant immediately after immersion approximately -0.18 V vs. Ag/AgCl, and the corrosion potential on the inner surface was -0.08 V vs. Ag/AgCl immediately after immersion, and then gradually decreased with time. Similar tendencies were observed in test water with other KCl concentrations. The gradual decrease in the inner surface potential was considered to be due to the carbon film. Hereafter, the values after 30 s of immersion were used in this report.

3.2.2. Examination of the KCl Concentration and Internal Observation Results

Figure 7 shows the relationship between the residual carbon amount and the potential difference ΔE 30 s after the start of immersion at each KCl concentration. In comparison with 0.5 M KCl, which showed a linear correlation between the residual carbon amount and ΔE , ΔE showed a large value from 0.07 to 0.09 V vs. Ag/AgCl with 0.1 M KCl, and no correlation was observed. On the other hand, with 1.0 M KCl or higher, the ΔE of 1.0 M KCl showed a large value that was similar to that with 0.5 M KCl at a residual carbon amount of 1.0 mg/m². In contrast, ΔE values of 2.0 and 3.3 M KCl were similar, showing small values of approximately 0.02 to 0.04 V vs. Ag/AgCl, regardless of the residual carbon amount. No clear correlation was found between the residual carbon amount and ΔE

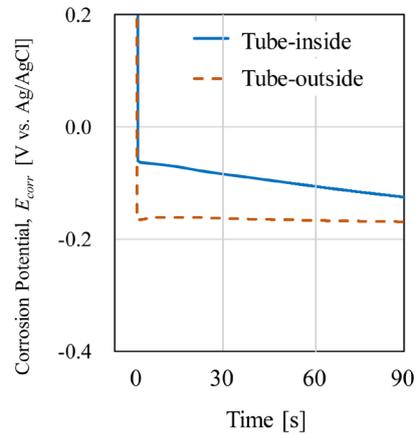


Figure 6. Potential measurement results (0.5 M KCl test solution, residual carbon amount 6.6 mg/m²).

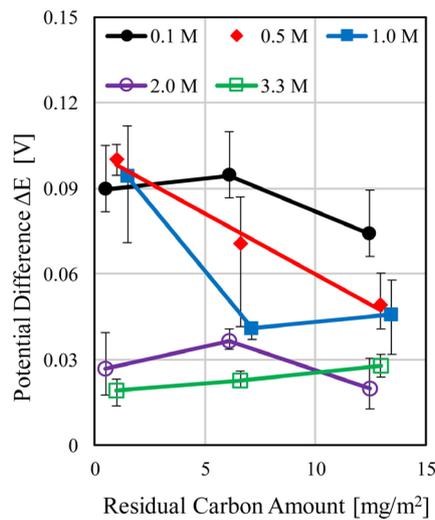


Figure 7. Relationship between the residual carbon amount with several concentrations of KCl and the potential difference 30 s after the start of immersion.

with 1.0 M KCl or higher. The reason why ΔE became small with high KCl concentrations is that in this test, copper ions were concentrated near the surface over time because there was no flow velocity under static conditions; thus, it is considered that the higher the KCl concentration is, the faster the elution and concentration of the copper ions.

Figure 8 shows the observation results of the inner surface after the test with a solution of 2.0 M KCl as an example. At 1.0 mg/m² of residual carbon, the entire inner surface was reddish brown, at 6.6 mg/m² of residual carbon, a mixed reddish brown surface with metallic luster was observed, and at 13.0 mg/m² of residual carbon, most of the inner surface had a metallic luster. The reddish brown was considered to be a copper oxide, and the metallic luster was considered to be a carbon film. Therefore, it was presumed that when the residual carbon amount was approximately 6.0 mg/m², the presence or absence of the carbon film varied widely, and the carbon film adhered unevenly.

Residual Carbon Amount	Inner Surfaces
1.0 mg/m ²	
6.6 mg/m ²	
13.0 mg/m ²	

Figure 8. Observations of the inner surfaces (2.0 M KCl test solution).

From the above results, the relationship between the residual carbon amount and ΔE was linear after 30 s from the start of immersion in the 0.5 M KCl solution at pH 6. Therefore, it was judged that this condition was suitable for obtaining a calibration curve for evaluating the amount of carbon film adhered to the inner surface of the copper tube.

3.2.3. Verification by Market Products

Figure 9 shows the approximate formula of the residual carbon amount and ΔE obtained by adding the result of the residual carbon amount of 6.1 mg/m² to the previous results (pH 6, 0.5 M KCl and 30 s after the start of immersion), and the measurement results of the market products (commercially available products and actual heat transfer tube for refrigerators). In the approximate formula, it was confirmed that the error of ΔE was larger than the others when the residual carbon amount was approximately 6.0 mg/m². The inner surface observation results in **Figure 8** were considered to be due to the uneven adhesion of the carbon film. In the verification of market products, the commercial product (b) with a residual carbon amount 23.0 mg/m² and the actual heat transfer tube with a residual carbon amount of 5.0 mg/m² generally followed a linear approximation. The commercial product (a) with a residual carbon amount of 9.7 mg/m² exhibited a value that deviated from the linear approximation, but it was considered to be within the variation range of industrial products. Since the standard deviation of ΔE was large for copper tubes with a residual carbon amount of approximately 6.0 mg/m², we would like to improve the accuracy of the approximation by increasing the number of samples in the future.

3.3. Test III Galvanic Current Measurement

Figure 10 shows the changes over time in the measured values of the galvanic current at each area ratio. The galvanic current flowed so that the test specimen with a residual carbon amount of 0 mg/m² became the anode and the test specimen with 23.0 mg/m² became the cathode, which was the same as previous reports [8] [9]. The current density was stable 30 s from the start of measurement

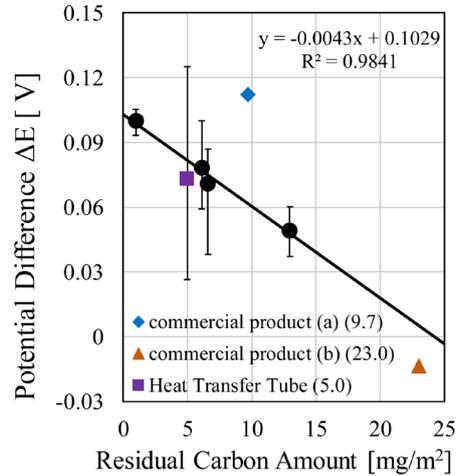


Figure 9. Verification results with actual tubes and heat transfer tubes.

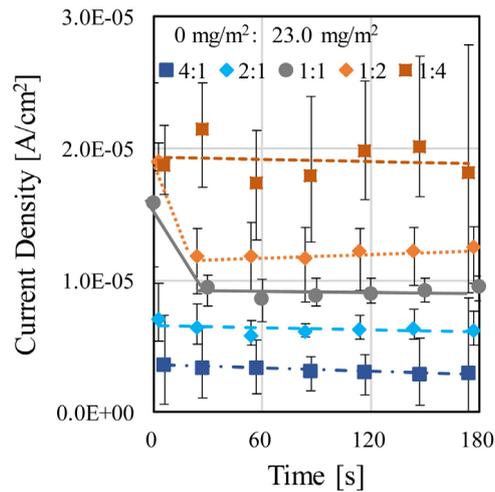


Figure 10. Galvanic current measurement results at several area ratios.

regardless of the area ratio. In addition, the larger the area ratio with 23.0 mg/m² residual carbon is, that is, the larger the area ratio of the carbon film, the higher the current density tended to be.

The area ratios 4:1, 2:1, 1:1, 1:2 and 1:4 were represented by the carbon film occupancy, and the relationships between the carbon film occupancy and the current density immediately after the start of measurement, after 30 s and after 180 s are shown in Figure 11. Immediately after the start of the measurement, the current density increased sharply from approximately 33% of carbon film occupancy to approximately 66%, this behavior was almost constant regardless of the carbon film occupancy. After 30 and 180 s, the current density increased linearly with increasing carbon film occupancy, and after approximately 66%, it tended to increase more rapidly. The relationship between the carbon film occupancy and the current density shown in Figure 11 suggested that the carbon film occupancy was significantly related to corrosion. It was also considered that the higher the carbon film occupancy is, the larger the galvanic current flowing

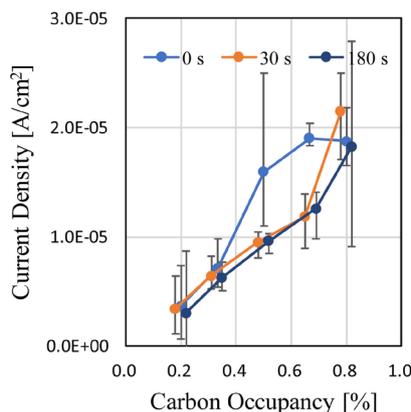


Figure 11. Relationship between the carbon occupancy and current density.

through the local new surface of copper, which makes pitting corrosion more likely to occur.

4. Conclusions

As a simple quantitative analysis of the residual carbon amount, we examined the surface by an XPS analysis and by evaluating the corrosion potential measurement using a copper tube with a known residual carbon amount. We also investigated the effect of a non-uniform carbon film on the copper tube surface on the corrosion behavior and obtained the following results.

1) In the XPS measurements, the spectral intensity of C 1s tended to increase, and the spectral intensity of Cu 2p tended to decrease as the residual carbon amount increased.

2) In regard to the C 1s spectra, a linear correlation was found between the spectral intensity and the residual carbon amount; thus, the XPS analysis was considered to be effective as a simple measurement method for the carbon film on the inner surface of the copper tube. It is considered that the residual carbon amount could be estimated from the calibration curve by XPS analysis.

3) In the evaluation method by measuring the corrosion potential, a correlation was observed between the potential difference ΔE and the residual carbon amount of the inner surface (with a carbon film) of the tube and the outer surface (without a carbon film) of the polished tube 30 s after the start of immersion at room temperature and using 0.5 M KCl at a pH of 6. Therefore, it is considered possible to estimate the residual carbon amount from the prepared calibration curve.

4) When the average residual carbon amount was approximately 6.0 mg/m^2 , the error range was considered to be wide due to the non-uniformity of the carbon film.

5) In the measurement of galvanic current, it was found that the higher the carbon film occupancy is, the larger the galvanic current tended to be.

6) It is considered that the higher the carbon film occupancy is, the larger the galvanic current on the local new surface and the more likely it is that pitting

corrosion will occur.

7) In the future, we would like to increase the number of samples and improve the accuracy of the XPS measurement and corrosion potential measurement methods.

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Conflicts of Interest

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

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