

Relationship between Corrosion Form and Elution Behavior of Copper Tubes Surfaces with Different Residual Carbon Amounts

Yuma Kano¹, Itaru Ikeda², Takashi Iyasu³, Yuna Yamaguchi¹, Yutaka Yamada^{1,4}, Osamu Sakurada^{1*}

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

²Dai-Dan Co., Ltd., Saitama, Japan

³Kurita Water Industries Ltd., Tokyo, Japan

⁴Daiwa Techno Co., Ltd., Gifu, Japan

Email: a4524025@edu.gifu-u.ac.jp, ikedaitaru@daidan.co.jp, t.iyasu78@kurita-water.com, b4524083@edu.gifu-u.ac.jp, y.yamada@daiwatec.com, *sakurada@gifu-u.ac.jp

How to cite this paper: Kano, Y., Ikeda, I., Iyasu, T., Yamaguchi, Y., Yamada, Y. and Sakurada, O. (2022) Relationship between Corrosion Form and Elution Behavior of Copper Tubes Surfaces with Different Residual Carbon Amounts. *Materials Sciences and Applications*, 13, 595-602.
<https://doi.org/10.4236/msa.2022.1312037>

Received: November 2, 2022

Accepted: December 13, 2022

Published: December 16, 2022

Copyright © 2022 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

It was well known that residual carbon on the inner surface of copper tubes was a cause of pitting corrosion, and copper tube surfaces with different residual carbon amount were different corrosion forms. In this study, the relationship between corrosion form and elution of copper in immersion tests by accelerated corrosion test solutions was examined. Generally, pitting corrosion that occurs in actual machines was reported to observe chloride ion at the bottom of the pitting corrosion of copper tubes. Energy dispersive X-ray (EDX) mapping analysis indicated that chlorine was concentrated in the upper layer of the samples where copper was not detected under conditions of low residual carbon amount, while chlorine was concentrated under part of the micromounds (including the bottom of the pits) under conditions of high residual carbon amount. It was also suggested that the amount of copper eluted was related to the amount of residual carbon.

Keywords

Carbon Film, Residual Carbon Amount, Pitting Corrosion, Corrosive Anion, The Pitting Corrosion Resistance Test

1. Introduction

Leakage of water due to pitting corrosion was a problem in heat-transfer copper tubes for air handling units used in building facilities. The pitting corrosion process of copper was affected by the amount of residual carbon on the inner surface of

the material [1] [2] [3]. Environmental factors, such as water quality, pH [4] [5] [6], chloride ions [7] [8] [9] [10], sulfate ions [11] [12], and dissolved oxygen [13], also had effects on this process. It was reported that pitting corrosion tended to occur when the amount of residual carbon (hereafter referred to as “residual carbon amount”) was 2 mg/m² or higher [14] [15], but no standardized test method for pitting corrosion resistance of copper tubes had been established, and electrochemical tests and water flow tests were generally used [16] [17] [18] [19] [20]. However, these tests were difficult to apply for quality analysis because it took time to obtain the results of pitting corrosion. Therefore, we evaluated pitting corrosion resistance of copper tubes by a 1 h filling test with a test solution consisting of a mixture of corrosion promoting factors (hydrogen peroxide, chloride ions, sulfate ions) and a corrosion inhibiting factor (benzotriazole). As a result, the optimal solution concentration for the test and the measurement range of micromounds were reported. A relationship between the number of micromounds and the amount of residual carbon was observed, and it was concluded that this rapid test would be useful to evaluate the pitting corrosion resistance of copper tubes [21]. In this study, immersion tests were conducted using a rapid evaluation test solution to approximate the actual environment. The relationship between the corrosion form of copper tubes and the amount of copper eluted was examined by cross-sectional observation of corrosion products.

2. Experimental Methods

2.1. Test Materials

Unfortunately, it was not possible to produce copper tubes with a determined amount of residual carbon. Therefore, JIS H3300 C1220 phosphorus-deoxidized soft copper tubes with 5 different levels of residual carbon amount in the market were used as the test material. Residual carbon amount on the inner surfaces of 0.5 mg/m² (hereafter referred to as “C 0.5”), 2.5 mg/m² (hereafter referred to as “C 2.5”), 5.3 mg/m² (hereafter referred to as “C 5.3”), 6.6 mg/m² (hereafter referred to as “C 6.6”), and 13 mg/m² (hereafter referred to as “C 13”). The C 0.5 specimen had an outer diameter of 15.2 mm and a wall thickness of 0.4 mm, and the C 2.5, C 5.3, C 6.6, and C 13 specimens had an outer diameter of 15.88 mm and a wall thickness of 0.8 mm. The residual carbon amount of this test material was measured by the conventional method [15]. The specimens were cut to a length of 10 cm, and each test material was cut in half. The amount of residual carbon was determined by the conventional method. The test material was coated with silicone resin except for a 3 cm² test area on the inner surface and to ensure testing under the same conditions as experienced in actual machines, no treatments, such as degreasing, were performed.

2.2. Test Solutions

The test solutions used consisted of pure water to which hydrogen peroxide (H₂O₂: special grade reagent; Santoku Chemical Industries Co., Ltd., Tokyo, Japan),

chloride ions (Cl^-), sulfate ions (SO_4^{2-}), and benzotriazole (BTA: special grade reagent; Kanto Chemical Co., Inc. Tokyo, Japan) had been added. The concentrations of H_2O_2 and BTA were adjusted to 10 mg/L, while Cl^- and SO_4^{2-} were adjusted to 100 mg/L. For Cl^- and SO_4^{2-} , sodium salts (special grade reagent; Kanto Chemical Co., Inc. Tokyo, Japan) were used.

2.3. Immersion Tests

The test specimens were immersed in 1 L of test solutions for 30 days, after which the appearance of the specimen was observed. In addition, the amount of copper eluted and pH was measured every 7 days after the start of the test. The tests were conducted at room temperature, with the specimens open to the atmosphere and the solution stirred at 300 rpm with a magnetic stirrer. Copper elution was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (ULTIMA2; Horiba Jovin Yvon, Ltd., Kyoto, Japan) at a wavelength of 324.75 nm. Measurements were made for C 0.5, C 6.6, and C 13, and the results of copper elution analysis are shown as maximum, minimum, and average values. The results of copper dissolution analysis are shown as the maximum, minimum, and average values. After the immersion test, the surface of the test specimen was observed with a digital microscope (DMV5000; Leica Microsystems, Wetzlar, Germany) and by scanning electron microscopy (SEM) (S-4300; Hitachi High-Technologies Co., Tokyo, Japan) equipped with energy dispersive X-ray analysis (EDX) (EX-220; Horiba, Ltd., Kyoto, Japan) performed under high-vacuum conditions with an acceleration voltage of 15 kV.

3. Results and Discussion

3.1. Progressive Observation of Copper Corrosion Form

Figure 1 shows the results of corrosion after immersion tests. The surfaces of the test specimens after the immersion test are shown in the upper row of **Figure 1**. Corrosion products were observed throughout the specimens regardless of the residual carbon amount. Cross-sectional observations at the locations where corrosion products were detected are shown in the second row of **Figure 1**. C 0.5 and C 2.5 showed corrosion with a wide front, while C 5.3, C 6.6, and C 13 showed corrosion with a narrow front that progressed in the depth direction. In SEM observation of the cross-sections shown in the third row of **Figure 1**, differences in the form of corrosion products were observed according to the residual carbon amount, similar to the cross-section observations shown in the second row. In addition, EDX mapping analysis of copper and chlorine (hereafter referred to as Cu and Cl) shown in the fourth and fifth rows of **Figure 1** indicated that Cl was concentrated in the upper layer of the sample where Cu was not detected at C 0.5 and C 2.5, while Cl was concentrated under part of the micro-mounds (including the bottom of the pits) in C 5.3, C 6.6, and C 13. From the above results, it was inferred that the form of the corrosion products and the progression of corrosion were affected by differences in residual carbon amount.

Figure 2 shows the area per corrosion product. At C 0.5, the area of corrosion products is approximately 200,000 μm^2 . As the residual carbon amount increases, the area becomes smaller, and the area per corrosion product is about 50,000 μm^2 . It seems that the relationship between the width of the frontage and the corrosion form, as shown in the cross-section observation in **Figure 1**, is related to the area per corrosion product.

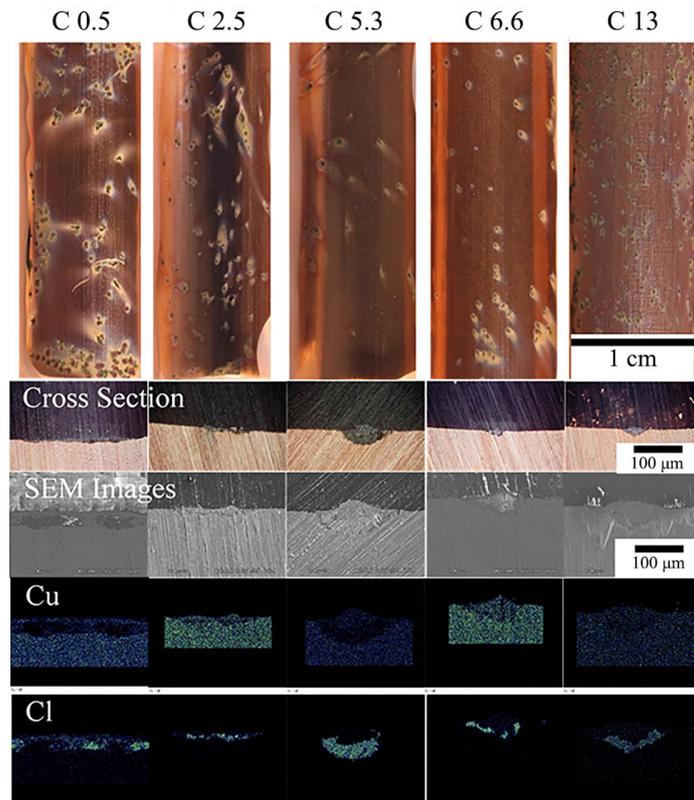


Figure 1. Observations of the inner surfaces and results of EDX analysis for the cross sections of the copper tubes.

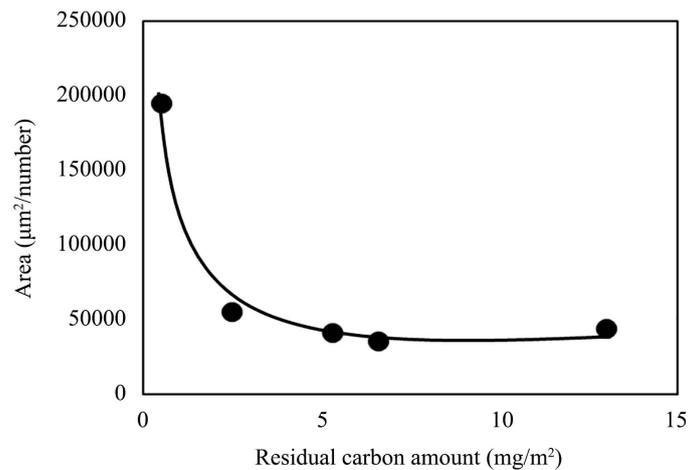


Figure 2. Relationship between area of corrosion products and amount of residual carbon.

3.2. Evaluation of Corrosion Resistance

The upper panel of **Figure 3** shows the amount of copper eluted every 7 days in three types of specimens: C 0.5 with low residual carbon amount, C 6.6 with intermediate residual carbon amount, and C 13 with high residual carbon amount. C 0.5 showed copper elution of 0.42 mg/L after 7 days and 0.64 mg/L after 1 month. C 6.6 showed copper elution of 0.51 mg/L after 7 days and 0.87 mg/L after 1 month. C 13 showed copper elution of 0.50 mg/L after 7 days and 0.86 mg/L after 1 month. The increase in amount of copper eluted from 7 days to 1 month was 0.22 mg/L for C 0.5, while it was 0.36 mg/L for C 6.6 and C 13. It was inferred that the difference in the amount of elution was related to the amount of carbon film that acts as an accelerator of the anodic reaction. Therefore, it was considered that copper tubes with high residual carbon amount would have a pitting corrosion form due to the localized anodic reaction, resulting in an increase in the amount of copper elution. The variation of pH with time is shown in the lower panel of **Figure 3**. C 0.5 showed an increase in pH after 14 days, and was around pH 7 after 1 month. C 6.6 transitioned near pH 5.7 from the start of the test to 21 days, and was close to pH 6.5 after 1 month. C 13 tended to transition between pH 5.5 and pH 6.0 from the start of the test to 1 month later. The above results showed that copper forms a stable film at pH 6.5 or higher [22] [23], and only C 0.5 shown in the lower part of **Figure 3** reached the neutral region above pH 6.5, suggesting that corrosion was less likely to progress under

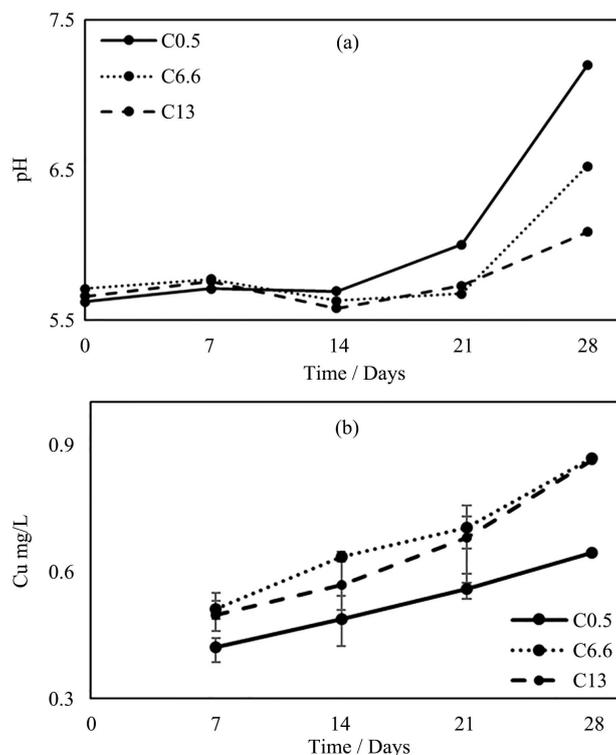


Figure 3. Copper concentration eluted from copper tube and pH conditions of immersion time.

these conditions. Therefore, it was inferred that C 0.5 with low residual carbon amount, in which Cl was concentrated in the upper layer of the specimen, had good corrosion resistance.

4. Conclusions

The results of this study can be summarized as follows.

1) Cross-sections at the location where corrosion products occurred showed full corrosion for C 0.5 and C 2.5, while C 5.3, C 6.6, and C 13 showed pitting corrosion.

2) Cross-sectional EDX mapping analysis showed that Cl was concentrated in the upper layers of C 0.5 and C 2.5, and Cl was concentrated under part of the micromounds (including the bottom of the pits) in C 5.3, C 6.6, and C 13.

3) We speculated that the difference in the corrosion form of copper tubes was related to the amount of carbon film that acts as an accelerator of the anodic reaction, and we considered the amount of leaching elution with the pitting corrosion form.

Acknowledgements

This research was supported by a 2019 research grant from the Japan Institute of Copper. We are grateful to Dr. H. Tamagawa (UACJ Copper Co., Toyokawa-shi, Aichi, Japan) who provided specimens for the test. In addition, we are grateful to Mr. K. Kawano (UACJ Co., Chiyoda-ku, Tokyo, Japan) for assistance with the experiments.

Conflicts of Interest

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

References

- [1] Cornwell, F.J., Wildsmith, G. and Gilbert, P.T. (1976) Pitting Corrosion in Copper Tubes in Cold Water Service. *American Society of Testing Materials*, **576**, 155-179. <https://doi.org/10.1520/STP41404S>
- [2] Smith, S. and Francis, R. (1990) The Use of Electrochemical Noise to Detect Initiation of Pitting Conditions on Copper Tubes. *British Corrosion Journal*, **25**, 285-291. <https://doi.org/10.1179/000705990799156364>
- [3] Seri, O., Jimbo, Y. and Sakai, M. (2006) Effects of Debris and Residual Carbon Film in Circulated Water Containing a Corrosion Inhibiter on Pitting Attack of Copper Tubes for Air Conditioning System. *Zairyo-to-Kankyo*, **55**, 505-510. <https://doi.org/10.3323/jcorr.55.505>
- [4] Thomas, J.G. and Tiller, A.K. (1972) Formation and Breakdown of Surface Films on Copper in Sodium Hydrogen Carbonate and Sodium Chloride Solutions: II. Effects of Temperature and pH. *British Corrosion Journal*, **7**, 263-267. <https://doi.org/10.1179/000705972798322702>
- [5] Cohen, A. and Myers, J.R. (1987) Mitigating Copper Pitting through Water Treatment. *Journal American Water Works Association*, **79**, 58-61.

- <https://doi.org/10.1002/j.1551-8833.1987.tb02799.x>
- [6] Edwards, M. and Ferguson, J.F. (1993) Accelerated Testing of Copper Corrosion. *Journal American Water Works Association*, **85**, 105-113.
<https://doi.org/10.1002/j.1551-8833.1993.tb06085.x>
- [7] Adeloju, S.B. and Hughes, H.C. (1986) The Corrosion of Copper Pipes in High Chloride Low Carbonate Mains Water. *Corrosion Science*, **26**, 851-870.
[https://doi.org/10.1016/0010-938X\(86\)90068-5](https://doi.org/10.1016/0010-938X(86)90068-5)
- [8] Lucey, V.F. (1972) Developments Leading to the Present Understanding of the Mechanism of Pitting Corrosion of Copper. *British Corrosion Journal*, **7**, 36-41.
<https://doi.org/10.1179/000705972798323332>
- [9] Drogowska, M., Brossard, L. and Menard, H. (1987) Anodic Copper Dissolution in the Presence of Cl⁻ Ions at pH 12. *Corrosion*, **43**, 549-552.
<https://doi.org/10.5006/1.3583899>
- [10] Daikuhara, T., Gomi, Y., Nakazato, N. and Sakai, M. (2020) Copper Tube Pitting Corrosion Product and Evaluation of Influence of Chloride Ion Concentration in Hot Water Environment. *Zairyo-to-Kankyo*, **69**, 83-89.
<https://doi.org/10.3323/jcorr.69.83>
- [11] Mattsson, E. (1980) Corrosion of Copper and Brass: Practical Experience in Relation to Basic Data. *British Corrosion Journal*, **15**, 6-13.
<https://doi.org/10.1179/000705980798318708>
- [12] Hamamoto, T., Kumagai, M., Kawano, K. and Yamauchi, S. (1987) Effect of Water Compositions on the Pitting Corrosion of Copper Tubes in Hot Water Service. *Journal of the Japan Copper and Brass Research Association*, **26**, 81-86.
- [13] Hirano, A. and Nakamichi, H. (2016) Corrosion Inhibition Performance for Copper Tubes of Heat Source Machines by Oxygen Reducing Treatment Using Sealing Materials for a Water Surface in an Open Heat Storage Water System, Based on Analyzing Eddy-Current Inspection Results. *Zairyo-to-Kankyo*, **65**, 515-519.
<https://doi.org/10.3323/jcorr.65.515>
- [14] Yamada, Y. (2019) Development of Corrosion Protection Research for Copper Tube in Recent Years and Future Prospects. *Refrigeration*, **94**, 73-77.
- [15] Yamada, Y., Mori, A., Hatanaka, R., Atsumi, T. and Nakao, N. (1998) Pitting Corrosion of Copper Coiled Tubes in the Air Conditioning System Having the Open Heat Storage Water Tank. *Zairyo-to-Kankyo*, **47**, 723-728.
<https://doi.org/10.3323/jcorr1991.47.723>
- [16] Isobe, G., Kyo, Y., Tameda, H., Kousaka, Y. and Tsuru, M. (2019) Corrosion Resistant Metal Materials, Corrosion Resistance Testing in Corrosion Protection Methods. Copper (Wrought Copper). *Rust Prevention & Control Japan*, **63**, 460-469.
- [17] Akkaya, M. and Ambrose, J.R. (1985) The Effect of Ammonium Chloride and Fluid Velocity on the Corrosion Behavior of Copper in Sodium Bicarbonate Solutions. *Corrosion*, **41**, 707-714. <https://doi.org/10.5006/1.3583007>
- [18] Reiber, S.H. (1989) Copper Plumbing Surfaces: An Electrochemical Study. *Journal American Water Works Association*, **81**, 114-122.
<https://doi.org/10.1002/j.1551-8833.1989.tb03246.x>
- [19] Rushing, J.C. and Edwards, M. (2004) Effect of Aluminium Solids and Chlorine on Cold Water Pitting of Copper. *Corrosion Science*, **46**, 3069-3088.
<https://doi.org/10.1016/j.corsci.2004.05.021>
- [20] Hanaki, S., Kawabata, A., Uchida, H., Nakayama, T., Hosogi, T. and Ishibashi, A. (2009) On Occurrence of Type I Pitting Corrosion of Copper Tube by Accelerated Immersion Test. *Journal of Japan Institute of Copper*, **48**, 159-164.

- [21] Kano, Y., Ikeda, I., Iyasu, T., Kuratani, M., Yamada, Y. and Sakurada, O. (2022) Relationship between the Occurrence of Pitting Corrosion and Amount of Residual Carbon by Accelerated Testing of Carbon Tubes. *Journal of Japan Institute of Copper*, **61**, 159-162. https://doi.org/10.34562/jic.61.1_159
- [22] Corrosion Protection Association of Japan, ed. (1988) Metal Corrosion and Corrosion Protection Q&A: Corrosion 110, Maruzen, 8.
- [23] Yamada, Y., Ito, J., Atumi, T. and Nagata, K. (1995) Performance of Tin Coated Copper Tube against Cuprosolvency Problem “Blue Water” in the East of Hokkaido. *Journal of Japan Institute of Copper*, **34**, 107-112.