Materials Sciences and Applications, 2023, 14, 45-52
https://www.scirp.org/journal/msa
ISSN Online: 2153-1188
ISSN Print: 2153-117X

Evaluation of Expansion Process to Improve Corrosion Resistance of Copper Tubes with High Residual Carbon on the Inner Surface

Yuma Kano[1], Itaru Ikeda[2], Takashi Iyasu[3], Yuna Yamaguchi[1], Yutaka Yamada[1,4], Osamu Sakurada[1*]

[1]Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Gifu, Japan
[2]Dai-Dan Co., Ltd., Saitama, Japan
[3]Kurita Water Industries Ltd., Tokyo, Japan
[4]Daiwa 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. (2023) Evaluation of Expansion Process to Improve Corrosion Resistance of Copper Tubes with High Residual Carbon on the Inner Surface. *Materials Sciences and Applications*, **14**, 45-52.
https://doi.org/10.4236/msa.2023.142003

Received: December 27, 2022
Accepted: February 5, 2023
Published: February 8, 2023

Abstract

Residual carbon on the inner surface of copper tubes is known to be a cause of pitting corrosion. We showed previously that the rapid filling test was useful to evaluate the pitting corrosion resistance of copper tubes. Immersion tests using the rapid evaluation test solution showed that corrosion occurs on the entire surface of copper tubes with low residual carbon amounts, while those with high residual carbon amounts show pitting corrosion. Therefore, it is necessary to improve the corrosion resistance of copper tubes with high residual carbon amount, which are expected to undergo pitting corrosion. As pitting corrosion occurs when anodes are locally concentrated on part of the metal surface, it has been suggested that anodes be dispersed over the entire surface by the processing of the metal surface. Metal processing methods have various purposes, including changing the shape and properties of metals, and in this case, leading to desirable surface properties (such as expansion and drawing processes). Here, we focused on the expansion process and its effects on corrosion resistance of copper tubes. The results showed that hydraulic expansion has a significant effect on the inner copper surface by improving corrosion resistance as the anode area increases.

Keywords

Expansion Process, Carbon Film, Pitting Corrosion, Corrosive Anion, the Pitting Corrosion Resistance Test

1. Introduction

Leakage of water due to pitting corrosion is a problem for heat transfer copper tubes used in air handling units used in building facilities. Pitting corrosions of copper tubes were affected by the amount of residual carbon on the inner surface of the material [1] [2]. Environmental factors, such as water quality, pH [3] [4], chloride ions [5] [6], and sulfate ions [7] [8], also affect this process. We have been studying the corrosion resistance of copper tubes based on the amount of residual carbon, defined as the amount of carbon film on the inner surface, and the number of micromounds present at the start of corrosion. We reported the optimal solution concentration for testing and the measurement range of micromounds [9]. We expected that it would be possible to evaluate pitting corrosion resistance from the relationship between the number of micromounds and the amount of residual carbon [9]. Some studies [9] [10] have shown that it is possible to evaluate the pitting corrosion resistance from the relationship between the number of micro-mounts and the amount of residual carbon. Analysis of cross-sections of the corroded region after the immersion test using the rapid evaluation test solution suggested that copper tubes with low residual carbon amount showed corrosion over the entire surface, while those with high residual carbon amount showed pitting corrosion [10]. Such pitting corrosion is usually quick and could require equipment shutdown due to a leak. As pitting corrosion occurs when anodes are locally concentrated on part of the metal surface, it has been suggested that anodes be dispersed over the entire surface by the processing of the metal surface [11] [12]. Metal processing methods have various purposes, including changing the shape and properties of metals, and in this case, processing methods capable of affecting the surface (such as expansion and drawing processes) are desirable. As the amount of residual carbon cannot be adjusted in production of copper tubes, we considered that the copper film could be destroyed by machining during copper tube production [11]. We report on the effect of pitting corrosion on the corrosion resistance of copper tubes for the purpose of destroying the carbon film caused by the expanding process performed during the manufacture of heat exchangers for air conditioning.

2. Experimental Methods

2.1. Test Materials

Unfortunately, it was not possible to produce copper tubes with specified residual carbon amount. Copper tubes with high residual carbon amount were therefore selected from various copper tubes purchased from commercial sources and analyzed for residual carbon amount. Copper tubes with an outer diameter of 9.53 mm and wall thickness of 0.35 mm were used in this study. The residual carbon amount of the commercial copper tubes measured by XPS [13] was 20 mg/m^2. Copper tubes were expanded by the hydraulic expansion method with an expansion ratio of approximately 0.1% to 6.5% by controlling the water pressure. Copper tubes subjected to the expansion process were referred to as "expanded copper tubes" and untreated copper tubes were referred to as "as received copper tubes."

2.2. Test Solutions

The test solutions used consisted of pure water to which had been added hydrogen peroxide (H_2O_2, special reagent grade; Santoku Chemical Industries Co., Ltd., Tokyo, Japan), chloride ions (Cl^-), sulfate ions (SO_4^{2-}), and benzotriazole (BTA). For Cl^- and SO_4^{2-}, sodium salts and BTA used were of special reagent grade (Kanto Chemical Co., Inc. Tokyo, Japan). The concentrations applied in the previously reported rapid filling test were used, with H_2O_2 and BTA adjusted to 10 mg/L and Cl^- and SO_4^{2-} adjusted to 100 mg/L [9].

2.3. Pitting Corrosion Resistance Tests

The test specimens were cut to a length of 50 mm and used as received, referring to the copper elution test method [14]. The specimens were pretreated with or without acetone degreasing. The ends of the specimens were sealed with silicone rubber, and test solution was poured into the copper tube from the top and left at room temperature for 1 h. After the test, the test solution was drained off, the tubes were rinsed thoroughly with pure water, and left in the room, and the inner surface was examined after cutting in half. A digital microscope (DMV5000; Leica Microsystems, Wetzlar, Germany) was used to measure the number of localized micromounds on the inner surface of the copper tubes.

2.4. Immersion Tests

The test specimens were immersed in 1 L of test solution for 30 days, after which the appearance of the specimen was examined. 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. In addition, the amount of copper eluted was measured 7 days after the start of the test by inductively coupled plasma optical emission spectroscopy (ICP-OES) (ULTIMA2; Horiba JovinYbon, Ltd., Kyoto, Japan) at a wavelength of 324.75 nm. After the immersion test, the inner surface of the test specimen was examined with a digital microscope (DMV5000; Leica Microsystems).

3. Results and Discussion

3.1. Consideration of Pretreatment in the Pitting Corrosion Resistance Tests

Figure 1 shows the appearance of as received copper tubes after the test. Under conditions without degreasing with acetone as shown in **Figure 1(a)**, no micromounds were observed on the inner surface of as received copper tubes after the test. Under conditions with acetone degreasing by ultrasonic cleaning as shown in **Figure 1(b)**, micromounds were observed on the entire inner surface of as received copper tubes after the test. This was presumably due to residual oil

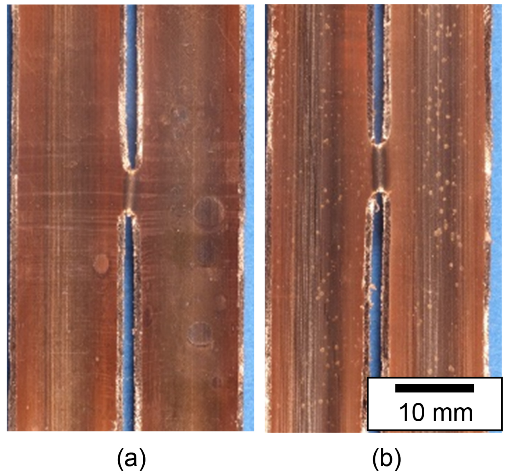

Figure 1. Images of the inner surfaces of copper tubes after immersion tests: (a) not degreased with acetone; (b) degreased with acetone.

on the inner surface of the as received copper tubes, as the cotton pads turned yellowish when wiped with a degreasing cotton pad soaked in acetone. The above observations suggested that acetone degreasing by ultrasonic cleaning is a necessary pretreatment for better evaluation of pitting corrosion resistance using commercially available copper tubes.

3.2. Evaluation of Corrosion Resistance of Copper Tubes with High Residual Carbon Amount

Figure 2 shows the appearance of as received and expanded copper tubes after the test. Micromounds with an overall blackish and circular orange color were seen. Figure 3 shows the relations between number of micromounds or amount of copper eluted after 7 days of immersion and the expansion ratio. The number of micromounds in the as received copper tubes was about 100/cm^2. The number of micromounds was lower in the expanded copper tubes at 75 kPa and higher in the expanded copper tubes at 150 kPa than the as received copper tubes. The numbers of micromounds before and after the expansion process were 0.1% - 2% of the expanded copper tubes < as received copper tubes < 5% - 6.5% of the expanded copper tubes, showing a difference in the occurrence situation. The average amount of copper ion elution after 7 days of immersion was about 0.07 mg/L for the as received copper tubes, about 0.18 mg/L for the expanded 1.7% copper tubes, and about 0.33 mg/L for the expanded 5.4% copper tubes, indicating that the amount of copper ion elution increased with increasing expansion ratio. This was considered to be due to the increase in anode area caused by the breakdown of the carbon film on the inner surface by the expansion process. Figure 4 shows cross-sections after 1 month of immersion in an environment similar to that of an actual plant to examine the form of corrosion. Localized progression of corrosion was observed in the as received copper tubes, but no significant corrosion was observed in the expanded copper tubes. These

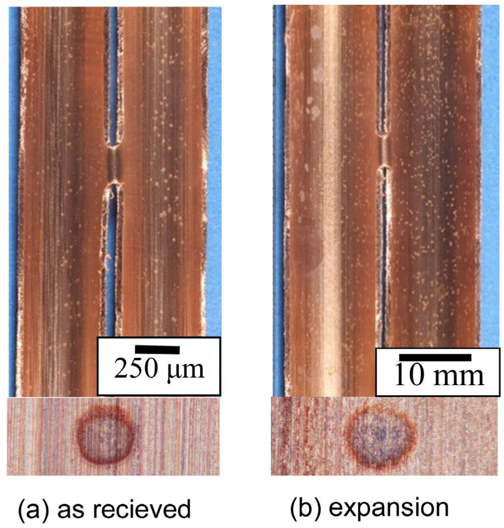

Figure 2. Images of the inner surfaces and the micromounds after immersion tests: (a) as received copper tubes; (b) expanded copper tubes.

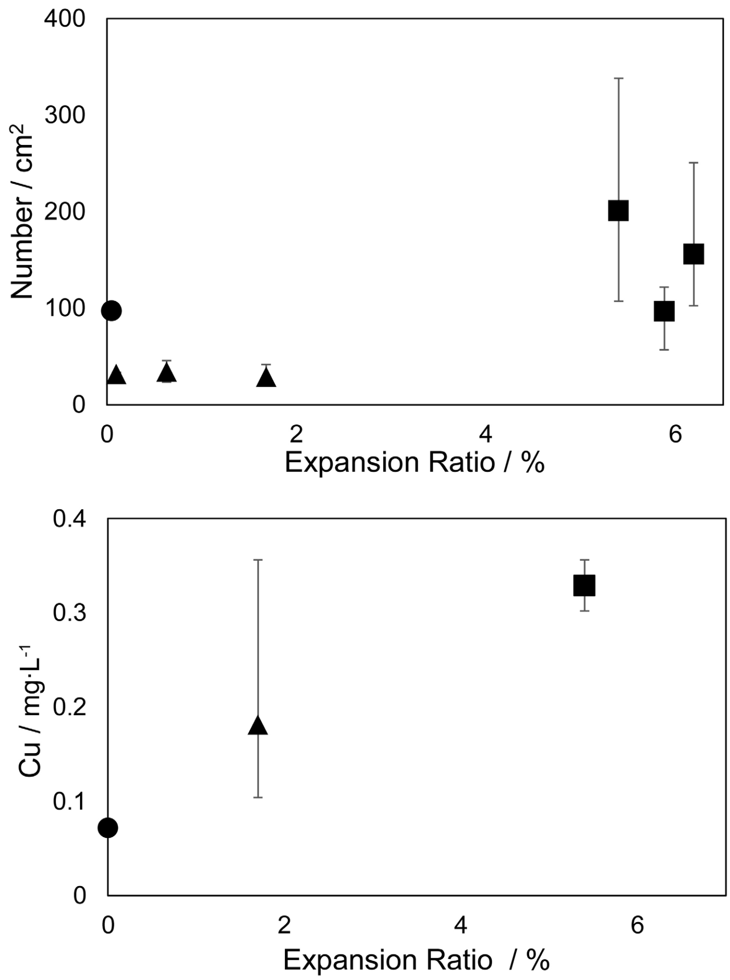

Figure 3. Relations between number of micromounds or copper ion concentration eluted from copper tubes and expansion ratio.

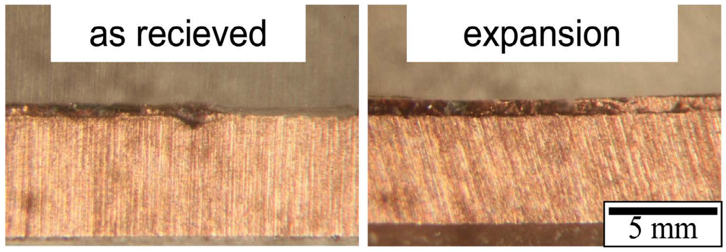

Figure 4. Cross-sections showing corrosion with time in test solution.

Figure 5. Condition of carbon film after the expansion process.

results suggest that the expanded copper tubes had a larger anode area due to the increase in expansion ratio, resulting in improvement of corrosion resistance.

3.3. Evaluation of Expansion Process

Previous reports presented schematic diagrams of the amount of residual carbon and the occurrence of corrosion based on the carbon film condition [9] [10]. In this study, it was inferred that the carbon film was destroyed by the expansion process using copper tubes with high residual carbon amount, as shown in **Figure 5**, and the anode area increased. As shown in Section 3.2, the form of corrosion changed from pitting corrosion to corrosion of the entire surface. It was considered essential to know the amount of residual carbon to implement corrosion countermeasures. However, acid washing was difficult and hazardous, and had a significant impact on cost. Therefore, by comparing the number of micromounds present at the start of corrosion with **Figure 4** in the previous report [9], it is possible to evaluate the corrosion resistance of copper tubes with unknown residual carbon amount by the rapid filling test, and that the corrosion resistance of copper tubes with high residual carbon amount could be improved by the expansion process.

4. Conclusion

This study showed that acetone degreasing is necessary as a pretreatment for better evaluation of pitting corrosion resistance using commercially available copper tubes. The increase in the expansion ratio increased the anode area, which was assumed to improve the corrosion resistance. It was inferred that even copper tubes with unknown residual carbon amounts can be evaluated for corrosion resistance by the rapid filling test. In the future, we will study the relationship between the diameter of copper tubes and the expansion ratio, as well as the relationship between the amount of residual carbon and the expansion ratio, in order to find the optimum expansion ratio. We also plan to evaluate the effects of other processing methods on corrosion resistance.

Acknowledgements

This research was supported by a 2019 research grant from the Japan Institute of Copper. We would also like to thank Mr. Akira Watanabe of Yazaki Energy Systems Corporation for his cooperation in expanding tubes used in this study.

Conflicts of Interest

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

References

[1] 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

[2] 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

[3] Cohen, A. and Myers, J.R. (1987) Mitigating Copper Pitting Through Water Treatment. *Journal AWWA*, **79**, 58-61. https://doi.org/10.1002/j.1551-8833.1987.tb02799.x

[4] Edwards, M. and Ferguson, J.F. (1993) Accelerated Testing of Copper Corrosion. *Journal AWWA*, **85**, 105-113. https://doi.org/10.1002/j.1551-8833.1993.tb06085.x

[5] 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

[6] 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

[7] 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

[8] 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.

[9] 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

[10] 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

[11] Shigetomo, Ueda. (1980) General and Pitting Corrosion. *Corrosion Engineering*, **29**, 426. https://doi.org/10.3323/jcorr1974.29.8_426

[12] Yashiro, H. and Tanno, K. (1996) Localized Corrosion of Stainless Steel. *Journal of*

the Surface Finishing Society of Japan, **47**, 2-6. https://doi.org/10.4139/sfj.47.2

[13] Kuratani, M., Iyasu, T., Tanaka, N., Yamada, Y. and Sakurada, O. (2021) XPS Analysis Carbon Film on Phosphorus Deoxidized Copper Tube. *Bunseki Kagaku*, **70**, 267-270. https://doi.org/10.2116/bunsekikagaku.70.267

[14] Tanaka, N., Watanabe, I., Ikeda, I., Obata, S., Goto, K., Yamada, Y. and Sakurada, O. (2018) Influence of Acid Treatment on Copper Ion Dissolution of High-Strength Cu-Sn-Zr Alloy Tubes in Tap Water. *Journal of Japan Institute of Copper*, **57**, 185-190.