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Comparative Study on Pitting Corrosion of Copper Tubes in Pitting and Pitting-Free Area

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Field tests for the copper tube in the area where pitting corrosion has often occurred were carried out in order to investigate the initiation and the propagation of pits. For a comparative study, we installed the same field equipment in two areas (pitting and pitting-free areas) to measure the corrosion potential of copper tubes and the electric conductivity of tap water. The electric conductivity in the pitting area was higher than that in the pitting-free area during the whole period of examination. It was found that the pitting corrosion has occurred in both pitting and pitting-free areas, but the maximum pit in the pitting area after 12 months was about three times deeper than that in the pitting-free area after 12 months.

Keywords *: copper tube, pitting corrosion, tap water, field test, depth of pits*

1. Introduction

Copper tubes have come into wide use in pluming and building because of their excellent corrosion resistance, high thermal conductivity and ease of fabrication. Recently, however, many water leakage accidents from copper tubes have been reported in various districts of Japan. Most of these accidents are caused by the pitting corrosion of copper tubes. A pitting corrosion of copper has been classified into two types: one is a 'type I' pitting which has occurred in the hard water area (e.g. Europe),[1),3)] another is a 'type II' pitting which has occurred in the soft water area (e.g. Japan).[4),5)] The existences of the greenish-blue corrosion products covered pits are the common characteristics of both type I and type II pitting. However, the pitting occuring recently in Japan belongs to neither type I nor type II, because this pit is not covered with the mound consisting of corrosion products. This new type pitting is called 'moundless' pitting.[6)] Fig. 1 shows the typical moundless pitting occurred on the inner surface of the copper tube for a water supply system. The propagation rate of this pit is relatively high so that the water leakage trouble due to this pit sometimes occurred in two or three years after the fabrication. The cause of this pit is attributed to the tap water running inside the copper tube,[7),8)] but detailed mechanisms and countermeasures are still not completely clarified.

Field tests have been carried out in order to simulate the moundless pitting corrosion of copper tubes. For a comparative study, we installed the same field test equipment in two areas: one is the area where the moundless pitting has frequently occurred (called as 'pitting area'), another is the area where the pitting has not occurred (called as 'pitting-free area'). Long-term measurements of the corrosion potential of copper tubes and the electric

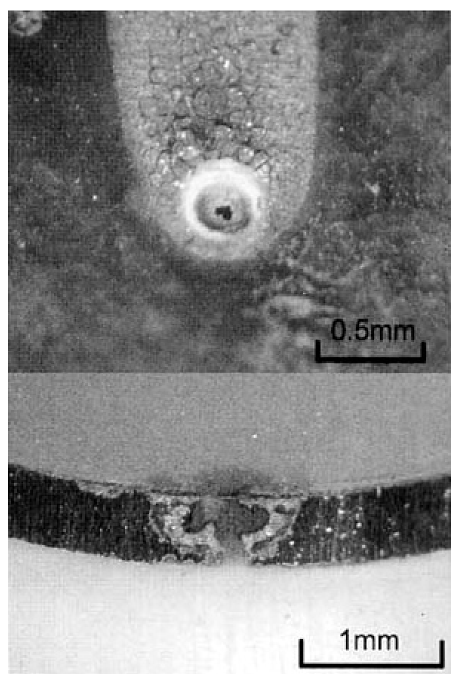

Fig. 1. The morphology of a typical moundless pit occurred on the surface of copper tube for a water supply system

conductivity of tap water were carried out using this field test equipment to investigate the electrochemical behavior of these copper tubes. We sampled a part of the copper tube from field test equipment and inspected the inner surface with optical microscope and SEM in six-month intervals.

2. Experimental

JIS 1220 phosphorus deoxidized copper tubes (22.22 mm external diameter and 0.81mm thickness) were used as specimens. The field test equipment used is illustrated in Fig. 2. This equipment consists of 6 copper tubes (each length is 2000mm) connected in series. The centers of the third and forth tubes are equipped with silver-silver chloride (Ag/AgCl) reference electrodes to measure a corrosion potential of the copper tubes. Each end of the third and forth tube is equipped with a temperature sensor and conductivity cell respectively to measure the temperature and the electric conductivity of tap water. A data logger automatically collected values of corrosion potential, temperature and electric conductivity. Tap water was drained from the copper tubes for an hour twice a day by controlling the electronic valve. This field test equipment was set up in the pitting and pitting-free area. These two areas differ in the quality of tap water because sources of water supply differ. Chemical analyses of the water in pitting and pitting-free area are given in Table 1. It should be noted that the water in pitting area shows high conductivity, hardness, sulfate and residuals. The parts of copper tubes were cut out of the field test equipment as sample specimens to inspect the inner surface. Anodic and cathodic polarization curves of these samples were measured in the 50ppm SO_4^{2-} solution.

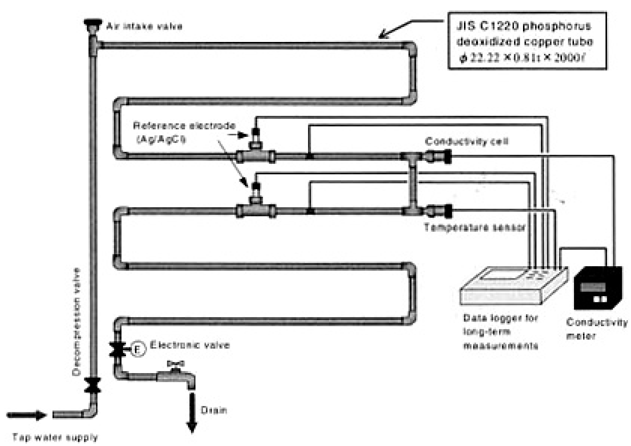

Fig. 2. Schematic diagram of the field test equipment.

3. Results and disscussion

3.1 Changes of corrosion potential and electric conductivity

Fig. 3(a) shows potential-time curves for copper tubes in the pitting and pitting-free area's water. The potential in the pitting area's water is higher than that in the pitting-free area's water for the first 200 days and gradually decrease from 200 to 320 days, followed by a gradual increase from 320 to 400 days. The potential in the pitting-free area's water is lower than that in the pitting area's water for the first 200 days and then shows a gradual increase. The potentials in pitting and pitting free area's water are almost equal in about 400 days.

Fig. 3(b) shows electric conductivity-time curves of tap water in the pitting and pitting-free area. The conductivity of pitting area's water is higher than that of pitting-free area's water for the duration of 400 days. The average of conductivity of the pitting area's water is about 15mS/m, which is twice as much as that of pitting-free area's water (7.7mS/m). The conductivity of the pitting area's water fluctuates seasonally between 7 and 18mS/m, while the conductivity of the pitting-free area's water is relatively constant throughout the year.

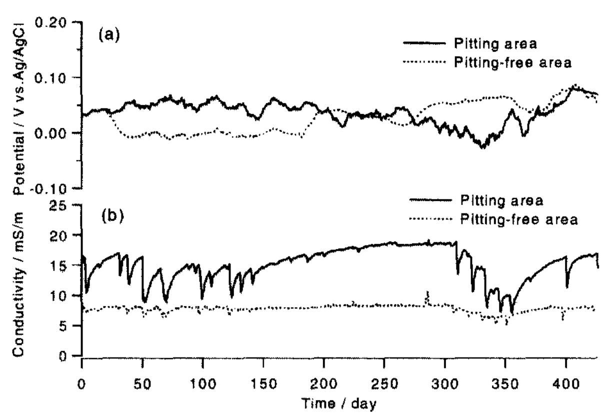

Fig. 3. Corrosion potential-time curves of copper tubes and electric conductivity-time curves of tap water in pitting and pitting-free area: (a) Corrosion potential, (b) Electric conductivity.

3.2 Inspection of the inner surface of copper tubes

Fig. 4 shows the inner surfaces of copper tubes after 6 and 12 months. Almost the whole inner surface of the copper tube in the pitting-free area after 6months is covered with a gray scale. Some pale green corrosion products that can be easily removed are observed on the lower surface of the copper tube in the pitting area after 6 months. The color of the upper surface in the pitting area after 6 months has changed into dark brown. The diffe

Table 1. Chemical composition of tap water in pitting and pitting-free area

	Pitting Area	Pitting-free Area
pH	7.0	7.2
Conductivity(mS/m)	14.8	8.3
M-alkalinity($CaCO_3$ppm)	9.6	17.2
Total hardness($CaCO_3$ppm)	45.0	21.7
Ca hardnesS($CaCO_3$ppm)	38.2	16.8
HCO_3^-(ppm)	11.7	20.9
SO_4^{2-}(ppm)	42.3	8.1
SiO_2(ppm)	31.1	32.7
Cl^-(ppm)	8.0	7.6
Total Fe(ppm)	<0.1	<0.1
Residuals(ppm)	115.0	76.3

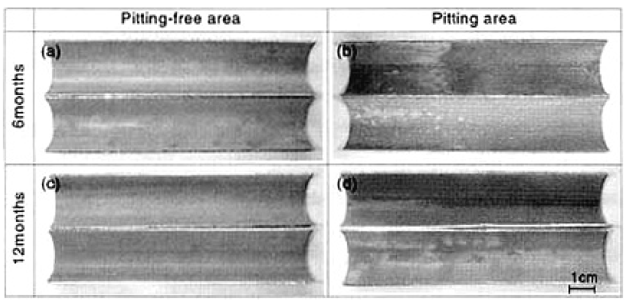

Fig. 4. Views of inner surface of copper tubes ; (a)pitting-free area after 6 months, (b)pitting area after 6 months, (c)pitting-free area after 12 months, (d)pitting area after 12 months

rence in appearance of inner surface of copper tube in the pitting-free area between 6 and 12months is hardly discernible. Many greenish-blue adhesive corrosion products are observed on the lower surface of the copper tube in the pitting area after 12 months. The upper surface in the pitting area after 12 months remains dark brown.

Fig. 5 shows optical micrographs of the inner surface of the copper tubes after removing scales and corrosion products with ultrasonic agitate in dilute sulfuric acid. Many very small pits are observed on the surface of the specimen in the pitting-free area after 6months (Fig. 5(a)). The specimen in the pitting area after 6 months has a rough and uneven surface and few observable pits (Fig. 5(b)). Pits on the surface of the specimen in the pitting-free area propagate themselves after 12months (Fig. 5(c)). There are many visible pits on the surface of the specimen in the pitting area after 12 months (Fig. 5(d)). Fig. 6 shows SEM micrographs of the surface of copper tubes after 12months. Many pits are observed on the surface both in the pitting-free area and in the pitting area. However, the pitting-free area and the pitting area differ in the size of pits. The pits diameter of the pitting-free area is about 10μ m at most, while the pits diameter of the pitting area

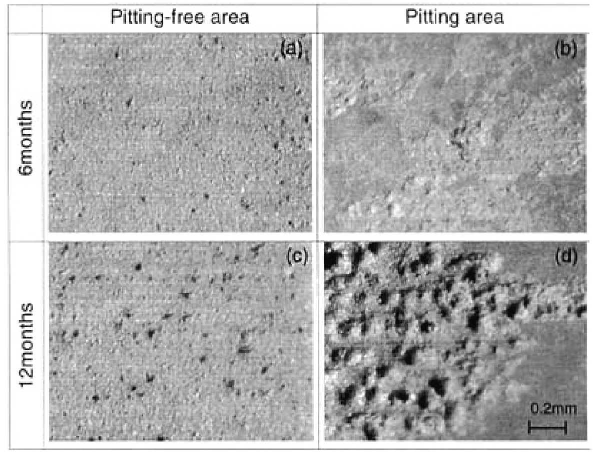

Fig. 5. Optical microscope images of inner surface of copper tubes after removing corrosion products with ultrasonic agitate in dilute H_2SO_4 : (a) pitting-free area after 6 months, (b) pitting area after 6 months, (c) pitting-free area after 12 months, (d) pitting area after 12 months.

is about 100μ m. Fig. 7 shows cross sectional views of copper tubes after 12 months. Pits are discernible in the picture of the pitting-free area. Pits which has about 80μ m in depth are observed in the picture of the pitting area.

We measured the depth of many pits (at least 50 per sample) by using the depth of focus of the optical microscope and calculated the average of the depth of pits. Fig. 8 shows the time evolution of the depth of pits in the pitting and pitting-free area. The error bars in Fig. 8 correspond to the scatter in measured values. The averages of the depth of pits in the pitting and pitting-free area after 6 months are 14.3μ m and 12.9μ m respectively. There is little difference in the pit depth between the pitting and pitting-free area after 6 months. The averages of the depth of pits in the pitting and pitting-free area after 12 months are 86.8μ m and 18.6μ m respectively. There is a great difference in the pit depth between the pitting and pitting-free area after 12 moths. In the case of a pitting corrosion, the maximum depth of pits is more important than the average of pits because only one deepest pit causes the water leakage accident. The maximum

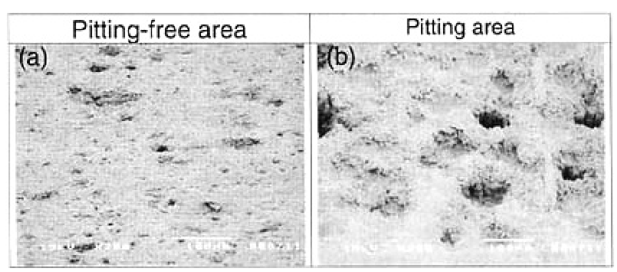

Fig. 6. SEM micrographs of pits on the surface of copper tubes after 12 months ; (a) pitting-free area, (b) pitting area

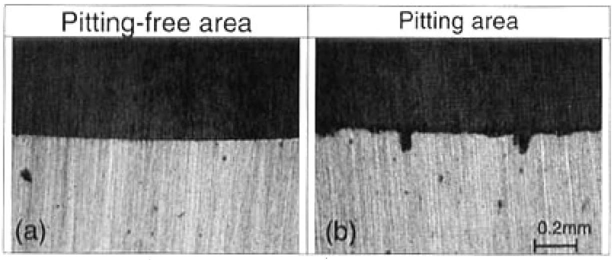

Fig. 7. Cross sectional views of copper tubes after 12 months ; (a) pitting-free area, (b) pitting area.

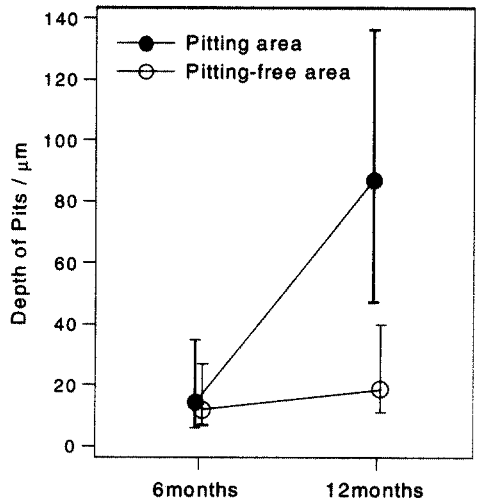

Fig. 8. Time evolution of depth of pits in pitting and pitting-free area.

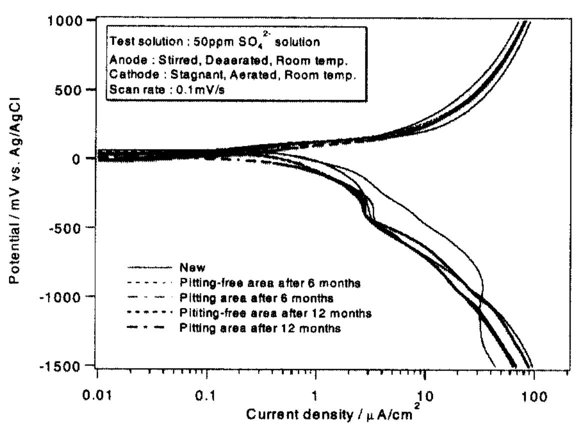

Fig. 9. Polarization curves for copper tubes in 50ppm SO_4^{2-} solution.

depth in the pitting area after 12 months is 136μ m, which is more than three times deeper than that in the pitting-free area after 12 months (40μ m).

3.3 Polarization curves for copper tubes after 6 and 12 months

The potentiodynamic polarization tests for copper tubes after 6 and 12 months were carried out in 50ppm SO_4^{2-} solution (pH=6.0, Conductivity=13.3mS/m). Fig. 9 shows polarization curves for copper tubes after 6 and 12months. The polarization curve for a new copper tube is also shown in Fig. 9. There is little difference in the anodic polarization curve among these copper tubes. A difference in the cathodic polarization curves between the new copper tube and copper tubes after 6 and 12 moths was observed. The cathodic polarization curve for a new copper tube has a plateau from -1000 to -1500mV(Ag/AgCl). The cathodic polarization curves for copper tubes after 6 and 12 months have a plateau at about -500mV(Ag/AgCl).

4. Conclusion

We have carried out the field test to examine the pitting corrosion of the copper tube in the pitting and pitting-free areas. The main results obtained are shown below.

1. The corrosion potentials of copper tubes in the pitting area was higher than that in the pitting-free area during the first 6 months, but these two corrosion potentials showed the same value 14 months later.
2. The conductivity of tap water in the pitting area was higher than that in the pitting-free area during the whole 14 months and fluctuated seasonally.
3. Many greenish-blue corrosion products has occurred on the inner surface of the lower part of the copper tube in the pitting area after 12 months, while the only gray scale has covered the inner surface of the copper tube in the pitting-free area after 12 months.
4. Pits were observed on the surface of the copper tubes both in the pitting and in the pitting-free area. However, the maximum depth of pit in the pitting area after 12 months was about three times deeper than that in the pitting-free area after 12 months.

References

1. H. S. Campbell, BNF Miscellaneous Publication, 574, (1972).
2. V. F. Lucey, BNF Research Report, A1838, (1972).
3. M. Pourbaix, J. V. Muylder, and P. V. Laer, *Corros. Sci.* **7**, 795 (1967).
4. E. Mattsson and A. M. Frederiksson, Br. *Corros. J*, **3**, 246 (1968).
5. T. Fujii, T. Kodama, and H. Baba, *Corros. Sci.* **24**, 901 (1984).
6. Y. Yamada and T. Atumi, Zairyo-to-Kankyo, **46**, 134 (1997)
7. M. Sakai and O. Seri, Proc. *11th Asian-Pacific Corrosion Control Conference*, VICCORA, Vietnam **2**, 482 (1999).
8. M. Sakai and O. Seri, Zairyo-to-Kankyo, **49**, 557 (2000).