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論　文

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Influence of P concentration on Ant's Nest Corrosion in Copper Tubes*

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Ant's nest corrosion has been observed in phosphorus deoxidized copper [C12200 : 0.015 to 0.040%P] tubes used for heat transfer in air-conditioning units. The corrosion starts on the outer surface of the copper tubes. Recently it has been reported that oxygen-free copper [C10200] tubes showed superior resistance against the ant's nest corrosion comparing to C12200 copper tubes. In order to confirm the recent observation, influence of the content of phosphorus (in the range of 0.04 - 1%) in the copper tubes on ant's nest corrosion was investigated. It was found that resistance against the ant's nest corrosion increased with increase of the phosphorus content in copper. When the phosphorus content was increased to 0.2% or more, the form of the ant's nest corrosion varied from randomly dispersed directional pits, the typical feature of the ant's nest corrosion, to round shaped pits; the growth rate of these pits was decreasing. This trend was maintained for inner-grooved copper tubes. The copper with high phosphorus content can be considered as a promising material for the copper tubes resistant to the ant's nest corrosion, which starts on the outer surface of the copper tubes due to environmental factors.

Keywords: *ants' nest corrosion, oxygen free copper, phosphorus deoxidized copper, corrosion rate, formic acid, corrosion resistance*

1. Introduction

Heat exchangers for air conditioners are an example of big market for copper tubes. The variety of corrosion in copper tubes used to supply refrigerant in air conditioners, is small comparing to copper tubes used to supply hot and cold water and cold air for air conditioning. The ant's nest corrosion is a big problem among the few types of corrosion occurring in air conditioners. From past experience, it is known that the ant's nest corrosion is caused by organic solvents used to remove the process oil. Since the process oil is used during the hairpin bending of general copper tubes, an organic solvent (1.1.1 trichloroethane) is used to remove the oil afterwards. Decomposition of the 1.1.1 trichloroethane produces acetic acid. The resulting acetic acid acts as a corrosive medium that causes the ant's nest corrosion from the inner surface of copper tubes. This problem was significantly reduced due to sufficient drying during the oil removal process and prohibition of the use of organic solvents by laws and regulations related to environmental protection.

However, in recent years, the rate of occurrence of the ant's nest corrosion from the outer surface of copper pipes is rapidly increasing due to environmental factors active during the usage of air conditioners. Although the mechanism of the ant's nest corrosion formation has been generally clarified, unfortunately, effective measures have not yet been adopted in practice. Phosphorus deoxidized copper (C12200 : 0.015 to 0.040%P) has been mainly adopted for copper tubes used in air conditioner heat exchangers. Recent research reports have demonstrated the influence of

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phosphorus content on the occurrence of the ant's nest corrosion [1), 2)], and excellent corrosion resistance of oxygen-free copper C10200 not containing phosphorus has been reported [3), 4)]. Since after investigation of the influence of phosphorus concentration in copper on the occurrence of ant's nest corrosion, we found out that the corrosion resistance can be significantly improved by adding a large amount of phosphorus, we want to report the new results.

2. Experimental method

Since we had concerns about possible influence of shape of copper samples on the ant's nest corrosion, we carried out the preliminary investigation of tubes, plates and rods. Blanks with 102 mm diameter and 13 mm wall thickness were manufactured from phosphorus deoxidized copper by hot extrusion and made into tubes, plates and bars. Tubes were made from blanks by drawing them to diameter 9 mm and wall thickness 0.29 mm after the hot extrusion. Plates were made by cutting hot extruded tubes and rolling them to wall thickness 0.6 mm. Round bars were cut from hot extruded copper tubes and drawn to diameter 4 mm. In the final step, all samples were recrystallized in a bright annealing furnace. All samples were subjected to the ant's nest corrosion test. Test results demonstrated that the ant's nest corrosion occurs in samples regardless of their shape and without visible difference in corrosion degree. Therefore, it was decided, that shape does not affect the corrosion.

To investigate the influence of phosphorus concentration, ingots with different phosphorus concentration from 0.04% to 7% were prepared in a high frequency induction heating furnace and then cold rolled into plates. Since alloys containing 3% or more P developed cracks during rolling, corrosion resistance was evaluated for materials containing from 0.04% to 1%P, which could be rolled. Also, oxygen free copper and phosphorus deoxidized copper samples were similarly prepared as reference materials. All samples were softened in a bright annealing furnace in the final step of preparation.

Test methods [1), 2)] proposed by Miya, which reproduce the actual corrosion very well, were selected as test conditions to reproduce the ant's nest corrosion. 100 ml of aqueous solution of formic acid were placed in a 2 L polyethylene container and the test sample was exposed to the gas portion to evaluate the corrosion resistance. The concentration of the aqueous solution of the formic acid was set to 0.01 and 0.1%. **Fig. 1** shows conceptual diagram of the test method. The test period was set to 20, 50 and 80 days. Samples were subjected to daily heat cycles by keeping them in a thermostat at 40℃ for 22 hours and then leaving them at room temperature 20-25℃ for 2 hours. However, samples were kept at 40℃ during week holidays without cycling.

After the corrosion test surface oxide of the samples were removed using 5% diluted sulfuric acid. The diluted sulfuric acid was removed by water washing, and then samples were dried by air blow. The corrosion holes caused by the ant's nest corrosion have extremely small features, and are difficult to check visually on the surface. Therefore, the position of the corrosion holes was determined by dye penetration test. The dye penetration test normally uses penetrating liquid (dye penetrant), cleaning liquid and developing solution. Since the cleaning liquid may remove the penetrant from fine corrosion holes, the cleaning liquid was not used in this experiment. The excess penetrant was removed with paper wipes. When the developing solution is sprayed onto a copper tube after the penetrant has been removed, the penetrant remaining inside corrosion holes seeps out to the surface, and red spots appear. Large and clear red spots indicate areas with deep corrosion holes. The cross-section of these areas

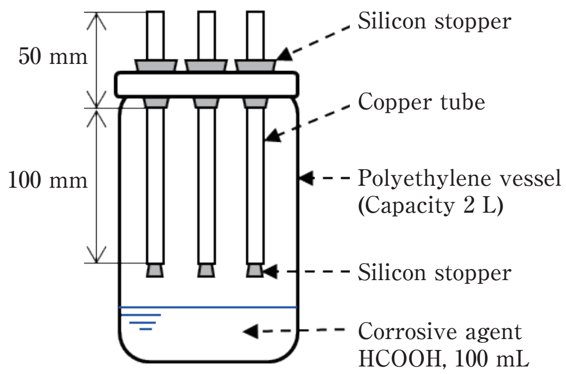

Fig. 1 Schematic diagram of the corrosion test cell.

was examined to investigate shape and depth of the corrosion.

3. Experiment results

3.1 Ant's nest corrosion in copper phosphorus brazing alloy

Fig. 2 shows a cross-sectional photograph of copper phosphorus brazing alloy (Cu - 7%P alloy) exposed to 0.01% and 0.1% formic acid atmosphere for 80 days. Results for tubes made from phosphorus deoxidized copper and oxygen free copper tested in the same container as reference materials are also shown. While the ant's nest corrosion was clearly noticeable in the reference materials, in the copper phosphorus brazing alloy with 7% phosphorus content only minor corrosion of about 10 μm was observed, and ant's nest-like progression of this corrosion was not observed. It was confirmed that the presence of a large amount of phosphorus in the copper improves the resistance to the ant's nest corrosion.

3.2 Influence of P concentration on the ant's nest corrosion

Fig. 3 shows on a cross-sectional photograph the progression of corrosion in formic acid atmosphere when the phosphorus concentration is changed from 0 to 1%. When exposed to 0.01% formic acid

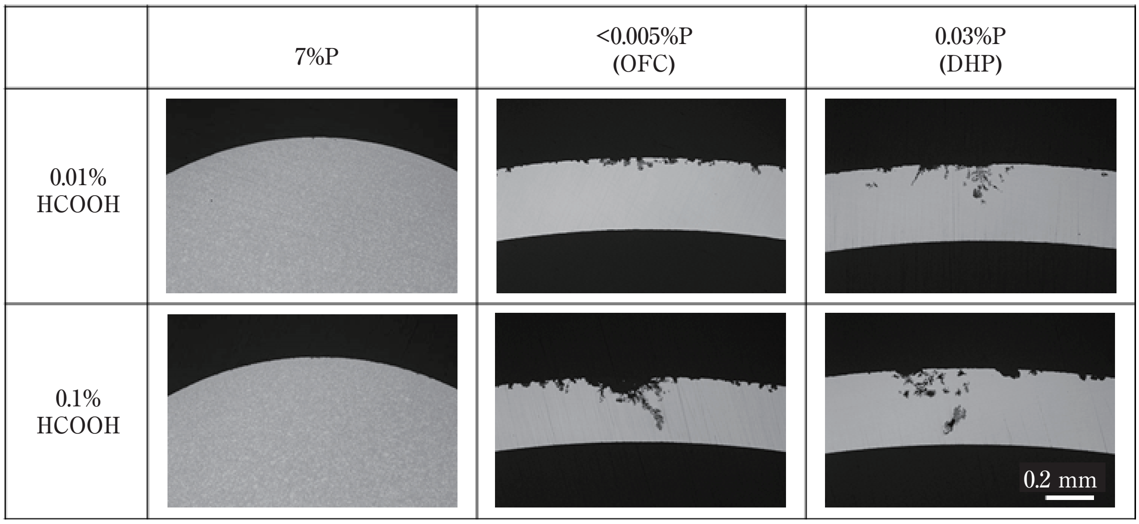

Fig. 2 Cross-sectional images of Cu-7mass%P, Oxygen free copper and Phosphorus deoxidized copper tubes after 80 days exposure to 0.01 or 0.1% formic acid vapor.

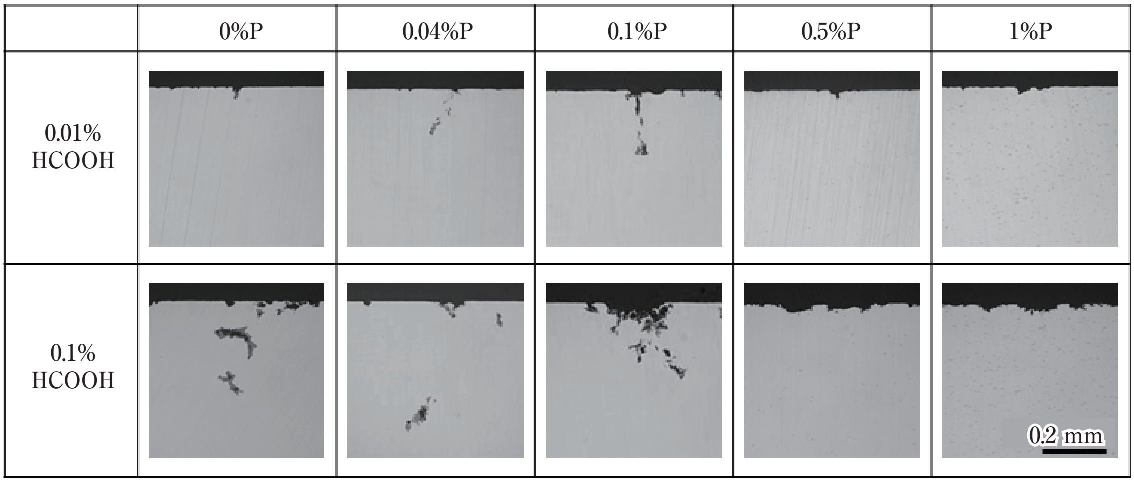

Fig. 3 Maximum corrosion depth of the copper alloy tubes after 20 days exposure to 0.1% formic acid vapor as a function of phosphorus content.

atmosphere, the ant's nest corrosion of 200 μm and 210 μm depth occurred in 0.04%P (phosphorus deoxidized copper) and 0.1%P samples, respectively. Only slight corrosion of 50 μm or less depth was observed in the sample with 0%P (oxygen free copper) and >0.1%P content, and, more interestingly, this corrosion did not progress to form ant's nets-like structures.

On the other hand, when exposed to 0.1% formic acid atmosphere, significant ant's nest corrosion has occurred in 0.04%P (phosphorus deoxidized copper) and 0.1%P samples as well as 0%P samples (oxygen free copper). The corrosion depth was 400 μm, 250 μm, and 300 μm, respectively. Corrosion of about 100 μm maximum depth was observed in samples with P content exceeding 0.1%, but corrosion did not progress to form ant's nest-like structure, as in the case of the test in the 0.01% formic acid atmosphere. As the amount of phosphorus increases, the corrosion depth becomes shallow, and its progress slows.

Fig. 4 shows the relationship between phosphorus content and corrosion depth of test samples exposed to 0.1% formic acid. The deepest corrosion was observed in 0.04%P samples (phosphorus deoxidized copper), followed by 0%P samples (oxygen free copper). In samples with phosphorus content of 0.1% or more, the corrosion tended to be shallower, than in 0%P samples (oxygen free copper). Considering that the minimum bottom wall thickness of inner grooved copper pipes currently used in air conditioners is 0.25 mm, increasing P content in the Cu - P alloy can be a promising countermeasure against the ant's nest corrosion.

3.3 Resistance to the ant's nest corrosion in inner grooved pipes

To verify the corrosion resistance of inner grooved copper pipes used as heat transfer tubes in air conditioners, test inner grooved pipes with outer diameter of 6.35 mm, wall thickness of 0.24 mm and phosphorus content from 0 to 0.30% were manufactured.

Fig. 5 shows the relationship between the corrosion test period and the maximum corrosion depth when inner grooved pipes with different P content are exposed to 0.01% formic acid atmosphere for period from 20 to 80 days. The deepest corrosion of at least 0.24 mm depth penetrating the walls during 20 days' period was observed in the 0.027%P sample (phosphorus deoxidized copper). On the other hand, the corrosion depth 120 μm was observed in the 0%P sample (oxygen free copper), 110 μm in the 0.22%P sample, 80 μm in the 0.24%P sample, and 70 μm in the 0.3%P sample. In all cases, only a slight corrosion was observed, without significant difference in the degree.

Fig. 6 shows the relationship between the corrosion test period and the maximum corrosion depth when

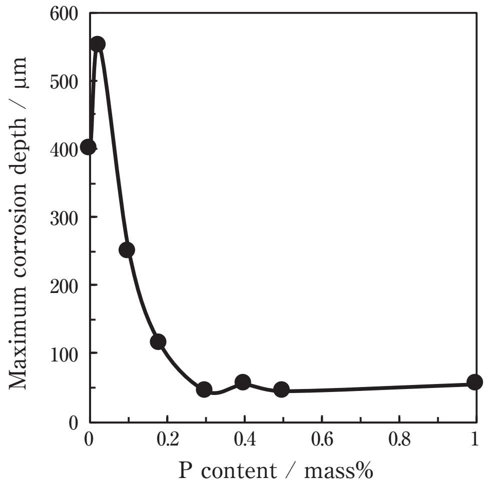

Fig. 4 Cross-sectional images of the deepest corrosion pit occurred on the copper alloy tubes after 20 days exposure to 0.01 or 0.1% formic acid vapor.

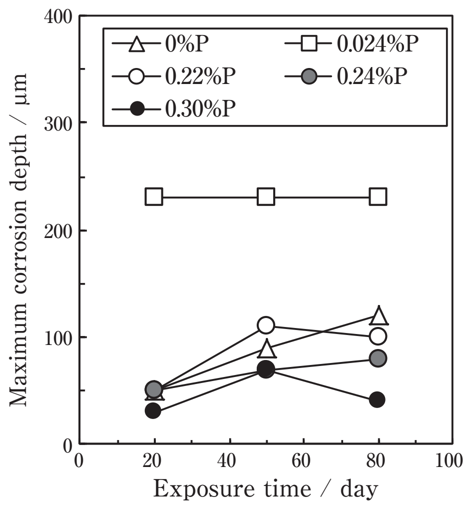

Fig. 5 Maximum corrosion depth of various copper tubes as a function of exposure time to 0.01% formic acid vapor.

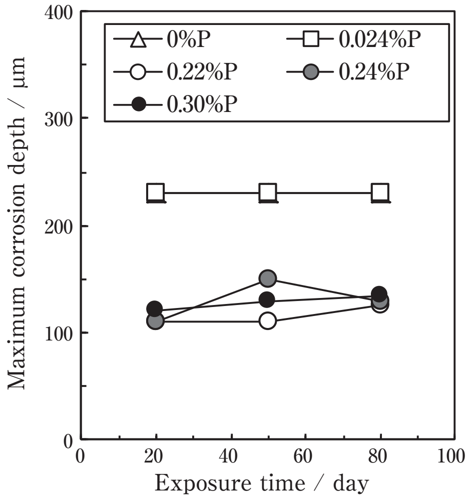

Fig. 6 Maximum corrosion depth of various copper tubes as a function of exposure time to 0.1% formic acid vapor.

inner grooved pipes with different P content are exposed to 0.1% formic acid atmosphere for period from 20 to 80 days. In the 0%P (oxygen free copper) and 0.027%P (phosphorus deoxidized copper) samples, corrosion of 0.24 mm or more depth penetrating the copper pipe walls has been observed. On the other hand, in samples with large phosphorus content of 0.22~0.30%P regardless of the test period the corrosion of 100 to 150 μm depth with slow progress has been observed.

Fig. 7 shows the cross-sectional photograph of the corroded portion of the sample exposed to 0.01% and 0.1% formic acid atmosphere for 80 days.

In 0%P (oxygen free copper) and 0.027%P (phosphorus deoxidized copper) samples, the so-called typical ant's nest corrosion has occurred inside the walls in a complex pattern. However, in samples made from alloys with large phosphorus content of 0.22 to 0.30%, no ant's nest corrosion was observed, but all corrosion has occurred in the form of pitting.

4. Considerations

4.1 Production of phosphoric acid in the outer layer of copper tubes

In alloys with large phosphorus content the corrosion changes its form, becoming a pitting corrosion. This is presumed to be due to the fact that phosphoric acid is formed in the surface layer of the material with high concentration, and pH level inside corrosion pits is lowered. The formation of the phosphoric acid in copper tubes has been noted in heat pipes in the past [5]. In heat pipes made from the phosphorus deoxidized copper, the phosphoric acid is detected in pure water used inside pipes as working liquid. It is believed that this happens due to elution of phosphorus from the material and formation of the phosphorus acid. Then, 3.4 g portions of chip powder from samples with different phosphorus concentrations (0.1 to 0.5%) were prepared, and immersed in 30 ml of 100 ppm formic acid at room temperature for 30 days.

Fig. 8 shows the measurement results of the phosphoric acid concentration in the solution after test. If the phosphorus content in the copper is below 0.2%, the concentration of the phosphoric acid is

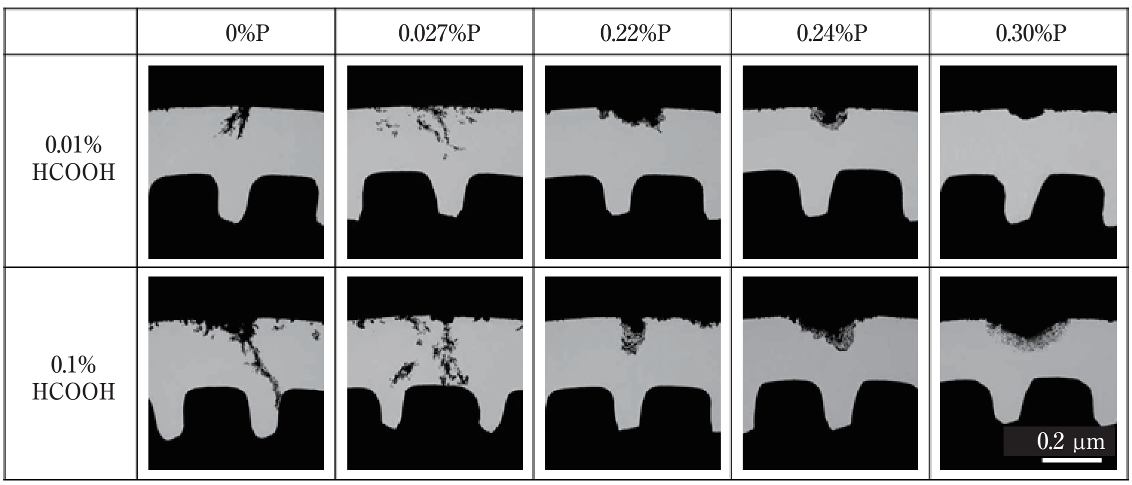

Fig. 7 Cross-sectional images of the deepest corrosion pit occurred on various copper tubes after 80 days exposure to 0.01 or 0.1% formic acid vapor.

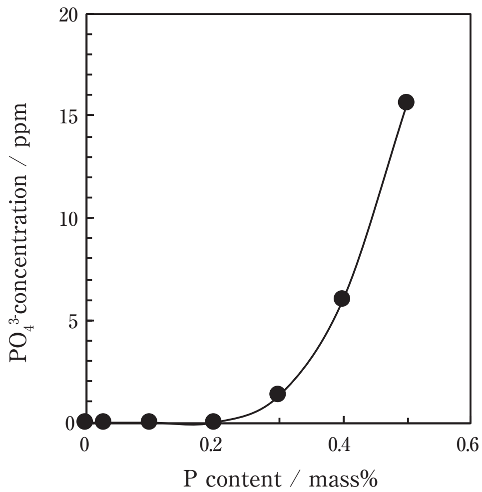

Fig. 8 PO_4^{3-} concentration dissolved from the copper alloy chips as a function of phosphorus content.

below detection limit. However, when the phosphorus content is increased to 0.3% the concentration of the acid becomes 1 ppm, and for the phosphorus content 0.5% the concentration becomes 16 ppm. As the phosphorus content in the material grows, the concentration of the detected phosphorus acid also increases. Thus, the elution of phosphorus and formation of the phosphoric acid, when the content of P in the material is large, was confirmed.

4.2 Influence of the phosphoric acid on the ant's nest corrosion

It was presumed that in alloys with large P content, phosphorus contained in the copper is dissolved, forming the phosphoric acid, and thus affecting the corrosion behavior. In this work, we investigated the influence of the phosphoric acid on the ant's nest corrosion by immersion test. Approximately 70 mm of the 150 mm long copper tube (three samples with 0%, 0.027% and 0.24%P content) was immersed in the 1 L glass sealed bottle filled with 500 ml of the aqueous formic acid solution. The test was carried out at room temperature for 64 days. The formic acid was prepared in three concentrations: 0.001% (pH 3.8), 0.01% (pH 3.2) and 0.1% (pH 2.6). In addition, the tests were conducted for tests solutions prepared from formic acid with 0.001% and 0.01% concentration by adjusting its concentration to the same pH 2.6 as for the 0.1% formic acid using added phosphoric acid. A sealed bottle was prepared for each copper tube. The glass bottles were closed until the end of the experiment. After the test, the copper tubes were taken out and checked for corrosion using dye penetration test. Cross-section observation was carried out for areas where signs of corrosion were observed.

Fig. 9 shows the cross-sectional photographs taken after the test. For samples immersed in the formic acid with 0.001% concentration, the ant's nest corrosion was observed only in samples with 0.027%P content (phosphorus deoxidized copper). For samples immersed in the formic acid with 0.01% concentration, the ant's nest corrosion was observed only in samples with 0%P content (oxygen free copper). At this time, a reddish-brown oxide film was formed on the surface of both samples, but on other samples this oxide film was not observed, looking like corrosion of the whole surface. On the other hand, in the test liquid in which pH was adjusted to 2.6 by adding phosphoric acid, the oxide film was not observed in any material regardless of the formic acid concentration in the liquid, displaying signs of corrosion of the whole surface, without ant's nest corrosion occurrence. Furthermore, no sample among those immersed in formic acid with 0.1% concentration displayed signs of the ant's nest corrosion. However, while the reddish-brown oxide film was formed in samples with 0%P and 0.027%P content, in samples with large phosphorus content the formation of the oxide film was not observed; these samples exhibited the signs of the whole surface corrosion.

In the immersion test, no oxide film was observed in any of the alloys with large phosphorus content. From the experiments conducted so far, it is believed, that the mechanism inhibiting the corrosion in alloys with large phosphorus content can be explained as follows.

It is a well-known fact that in case of the ant's nest corrosion in the phosphorus deoxidized copper, the formation of cuprous oxide (Cu_2O) is observed on the surface of samples around corroded areas. On the other hand, in the tests described above, the cuprous oxide was absent on surfaces of all samples when the phosphoric acid was present. From this fact, it is considered, that the following copper corrosion reaction occurs on the surface of the phosphorus deoxidized copper and the countermeasure material.

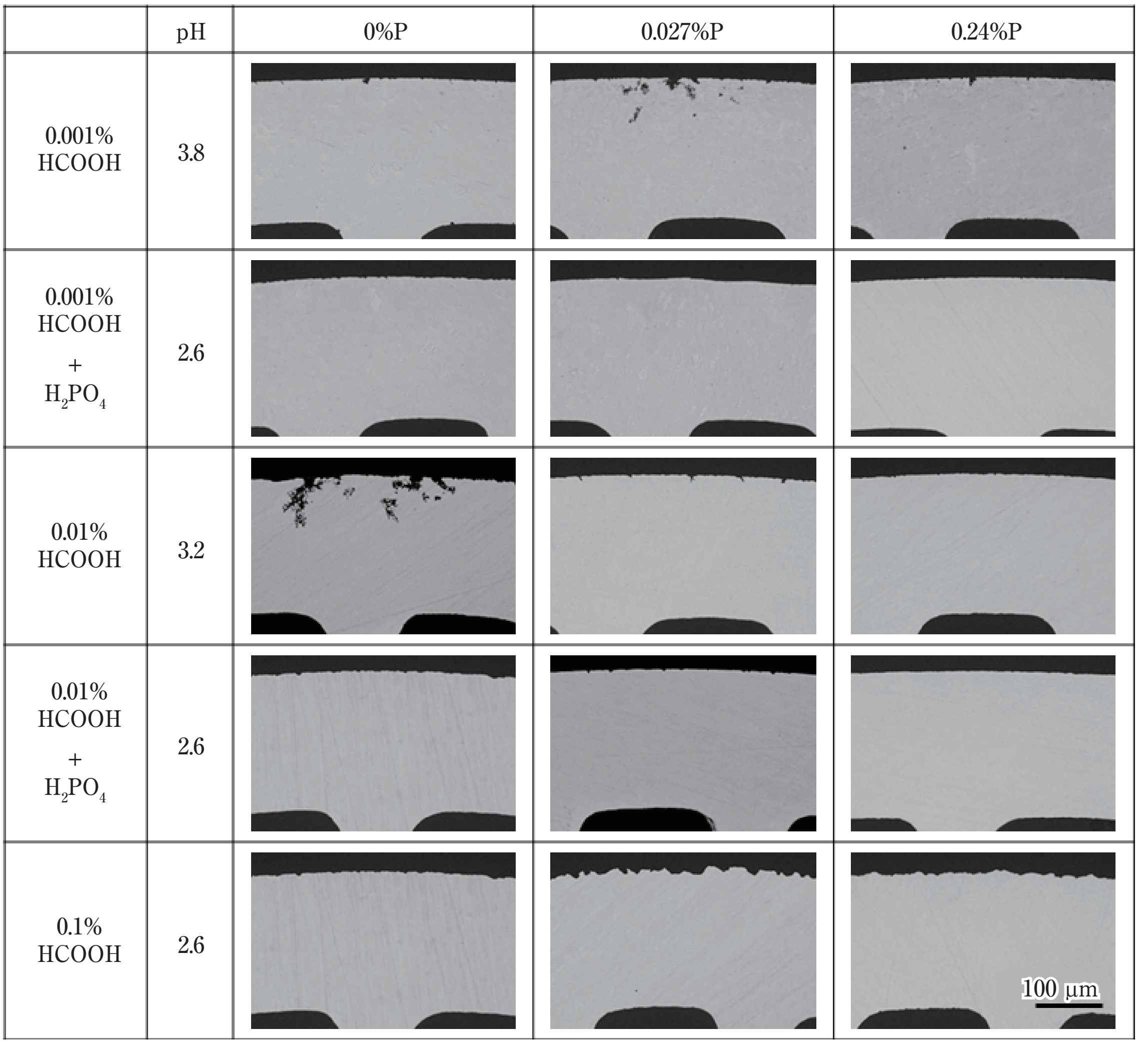

Fig. 9 Cross-sectional images of the deepest corrosion pit occurred on various copper tubes after 80 days exposure to 0.01 or 0.1% formic acid vapor.

(Anodic reaction)

$2Cu \rightarrow 2Cu^{+} + 2e^{-}$

(for neutral: $2Cu^{+} + H_2O \rightarrow Cu_2O + 2H^{+}$)

P (in the copper) + $4H_2O \rightarrow H_2PO_4^{-} + 6H^{+} + 5e^{-}$

(Cathodic reaction)

$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$

(for neutral: $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$)

Phosphorus is eluted from copper during the anodic reaction of copper dissolution, producing the phosphoric acid. It is presumed that suppression of pH increase (neutralization) of the surface accompanying the cathodic reaction caused by generation of phosphoric acid preservation of the pH of the copper surface layer at low level prevents formation and deposition of the cuprous oxide. The behavior of the alloy observed this time can be explained by the stronger pH lowering effect caused by 10 times larger phosphorus content than in the phosphorus deoxidized copper. As a result, in the 0.027%P sample (phosphorus deoxidized copper) immersed in the 0.001% formic acid Cu_2O is formed causing discoloration. On the other hand, in the 0.2%P sample the discoloration did not occur even under the same immersion conditions, exhibiting signs of the whole surface corrosion.

In the formic acid atmosphere exposure test described in the section 3.3, the corrosion in alloys with large phosphorus content looked like pitting, rather than the ant's nest. This can be explained by the fact that the effect of phosphorus manifests in the same way not only on the surface but also in pits. In other words, in the ant's nest corrosion, the cuprous oxide is present on the inner walls of the pits, and weak points of the cuprous oxide serve as starting points for subsequent corrosion progression, so the corrosion exhibits the branched form [2), 6), 7)]. It is assumed that a relatively large amount of phosphoric acid is produced in pits in alloys with large phosphorus content, generating many weak points of the cuprous oxide. Therefore, the direction of the corrosion progress in the pits is varied, the shape of corrosion becomes pitting-like due to lateral spread, and the spread of corrosion in the direction inside walls becomes slower than the ant's nest corrosion.

5. Conclusion

We investigated the influence of the phosphorus content in the material on the ant's nest corrosion occurring in phosphorus deoxidized copper tubes and obtained the following results.

(1) The corrosion test performed on copper plates with different phosphorus content confirmed the tendency of the corrosion depth to become more shallow when the phosphorus content is increased. Similar results were obtained for inner grooved pipes, without visible difference.

(2) When the phosphorus content in the copper reaches 0.2% or more, the form of corrosion in the formic acid environment changes from the ant's nest to pitting, and the rate of corrosion becomes slower than that of the ant's nest corrosion.

The ant's nest corrosion occurring on the outer surface of copper pipes due to environmental factors active when an air conditioner is used, has become a problem not only in Japan but in the whole world. It is expected, that the effect discovered in this work, will be an effective solution for the ant's nest corrosion problem that occurs in the currently used phosphorus deoxidized copper.

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