Localized “Ants’ Nest” Corrosion in Copper Tubes Caused by Ginkgo Fruit Juice

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1. Introduction

Ants’ nest corrosion (ANC) in thin-walled copper tubes in air-conditioning systems was first noticed about 20 years ago. The corroded copper tubes were mainly used in heat-transfer units such as air-conditioners, refrigerators, evaporators, solar-systems, radiators and condensers. The corrosion occurred on both the interior and exterior surfaces of the copper tubes and formed meandering microtunnels in the copper tubes resulting in perforation. It has been suggested that this type of corrosion is caused by decomposition products from chlorinated organic solvents used to degrease the tubes and from some types of lubricant oil used during the copper tubing stamping process.

The decomposition products include carboxylic acids and chlorides. More recently, volatile organic substances from vinegar-containing seasonings, cosmetics, synthetic building materials, woods, insecticides and paints have been suspected as causes of the corrosion. The localized corrosion was first simulated by the author in vitro in a humid atmosphere in the presence of carboxylic acids and aldehydes. The morphology of this corrosion in copper tubes differs according to the type of corrosive substance. Severity of corrosion and morphological change with different types of aldehydes have been studied.

A Ginkgo fruit has a strong smell, and juice from the fruit irritates the skin. It has been thought that this volatile organic substance in ginkgo fruits may cause corrosion of metals and alloys.

In this report, the severity and morphological features of ANC caused by ginkgo fruit juice are described.

1. Experimental

Fig. 1 shows photographs of (a) a ginkgo tree-lined street in Hokkaido University campus, (b) ginkgo fruits and (c) ginkgo nuts. Ginkgo fruit juice was obtained by squeezing ginkgo fruits. The juice was used in both undiluted and diluted forms as corrosive solutions. 1-month and 3-month exposure tests were conducted in a 1-liter air-tight glass vessel in the absence and presence of 5 different concentrations (1, 5, 10, 50 and 100 vol% of ginkgo fruit juice). The copper tubes used in the experiments were phosphorus deoxidized copper (JIS H 3300: Cu 99.9, P 0.015-0.040), and each copper tube was 100 mm in length, 9.6 mm in outer diameter and 0.36 mm in wall thickness. Each copper tube was placed in a test tube and kept in a gas phase so as not to come into direct contact with the corrosive solutions. After the exposure periods, the copper tube specimens were taken out from the glass vessel and dried in air. The exposed surfaces of the copper tubes were then examined. A section was cut from each of the exposed copper tubes and embedded in polyester resin for cross-sectional observation under an optical microscope and a scanning electron microscope. A JXA-8900 electron probe microanalyzer (EPMA) was used for area analysis.

2. Results and Discussion

The main components of the ginkgo fruit juice were...
acetic acid (CH₃COOH, 0.45 wt%), lactic acid (CH₃ CH(OH)COOH, 1.4 wt%) and glucomic acid (C₆H₁₂ O₇, 2.2 wt%).

Of these three acids, only acetic acid has a volatile and aggressive nature toward copper.

Fig. 2 shows the surface appearances of the copper tubes exposed to a humid atmosphere in the absence or presence of ginkgo fruit juice after 1-month and 3-month exposure. The metallic luster of the as-received copper tubes faded with exposure time, and surfaces of the tubes darkened. Bluish-green corrosion products formed on the top end of the copper tubes, and the amount of corrosion product increased with increasing concentration of ginkgo fruit juice. The remaining area of the copper tube surface maintained its metallic luster, and no corrosion was found in the un tarnished areas of the copper tubes after 3 months. This bluish-green corrosion product is thought to be cupric acetate⁵) or copper acetate hydrate, Cu(CH₃ COO)₂•2H₂O¹⁰).

Fig. 3 and Fig. 4 show cross-sectional microphotographs of corroded areas of the copper tubes, at the same magnifications, that had been exposed to atmosphere over ginkgo fruit juice for 1 month and 3 months, respectively. Slight corrosion was observed in the copper tubes that had been exposed to atmosphere without ginkgo fruit juice for 1 month and 3 months, while ANC was observed in the copper tubes that had been exposed to vapor of ginkgo fruit juice. A combination of hemispherical micropits was observed in the copper tubes exposed to ginkgo fruit juice for 1 month. Severity of the corrosion increased with increase in the concentration of ginkgo fruit juice, as shown in Fig. 3. The hemispherical micropits are typical localized corrosion in copper tubes exposed to an
Porous copper oxide with fine voids is seen in the affected area (in grey color). Directional pits were observed in the copper tubes exposed to ginkgo fruit juice at concentrations of 1, 5 and 10 vol%, as shown in Fig. 4. The maximum penetration depths for 1-month and 3-month exposure were 48 µm and 102 µm, respectively. Two typical cases of ANC were selected and analyzed using EPMA. Fig. 5 (a) shows Cu-rich areas of a directional pit shown in Fig. 4 (c). Fig. 5 (b) shows O-rich areas of the same pit. Fig. 6 (a) shows Cu-rich areas of a round-shaped pit shown in Fig. 5 (c). Fig. 6 (b) shows O-rich areas of the same pit. The affected areas in these figures indicate the existence of copper oxide and microvoids in the copper oxide.

A possible mechanism of this ANC is as follows. Acetic acid in ginkgo fruit juice acidifies the surface water on the copper and penetrates through defects in the air-formed copper oxide films. Copper then dissolves in the surface water to produce Cu₂O.

\[ 2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \]  

(1)

At the same time a cuprous complex forms between acetic acid and cuprous ions in the water layer.

\[ Cu + CH_3COOH \rightarrow Cu(CH_3COO) + H^+ + e^- \]  

(2)

The complex in water migrates from dissolution sites by local changes in complex concentration, temperature and humidity. The complex is oxidized to cupric complex.

\[ CuCH_3COO + CH_3COOH \rightarrow Cu(CH_3COO)_2 + H^+ + e^- \]  

(3)

The cupric complex in the microtunnel reacts with copper at active sites within the pit to give a cuprous complex.

\[ Cu(CH_3COO)_2 + Cu \rightarrow 2Cu(CH_3COO) \]  

(4)

Cu(CH_3COO) is oxidized again, as in equation (3). This catalytic reaction occurs continuously and results in perforation.

The cathodic reaction is mainly an oxygen-reduction reaction.

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  

(5)

References


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