Electrochemical Analysis of the Pitting Potential of Tin-plated Copper in Artificial Fresh Water Containing Chloride, Sulfate, and Bicarbonate Ions

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ABSTRACT

Tin-plated copper tubes have been widely used in cold and hot water service systems. However, leakage accidents caused by pitting corrosion can occur in such tubes; therefore, it is necessary to evaluate the effects of major environmental factors on the occurrence of local corrosion to ultimately suppress this corrosion. In the present study, the anodic polarization curves of a tin-coated copper electrode were measured in simulated freshwater containing Cl–, SO42–, and HCO3−. The anodic current increased suddenly and sharply due to the breakdown of the passive layer and the initiation and growth of pitting generation at the pitting potential. The pitting potential shifted to a more negative direction with increasing Cl− and SO42− concentrations. In contrast, the pitting potential shifted to more noble potentials upon increasing the HCO3− concentration, indicating that HCO3− has an inhibitory effect on pitting attack by Cl− and SO42−. The quantitative relationship between each anion concentration and the pitting potential was determined by multiple regression analysis. A plot of the pitting potential predicted from the created regression equation and the measured values of the pitting potential showed a positive linear relationship.

Keywords : Polarization Curve, Freshwater Corrosiveness, Tin-plated Copper, Multiple Regression Analysis

1. Introduction

Since tin-plated copper exhibits an excellent corrosion resistance, thermal conductivity, and workability, tubes based on this material are often used as building materials in water and hot water supply pipes and heat exchangers. However, it has been reported that water leakage accidents occur because of corrosion to the pipes, depending on the usage environment. The majority of this corrosion has been attributed to pitting corrosion, which is known to be a local corrosion that can occur in such tubes; therefore, it is necessary to evaluate the effects of major environmental factors on the occurrence of local corrosion to ultimately suppress this corrosion. In general, the environmental contribution of a material to local corrosion can be evaluated from the critical potential required for local corrosion. Several studies on tin pitting corrosion have been analyzed by potentiodynamic polarization measurement that the pitting potential is defined by examination of the corresponding Pourbaix diagrams. Further studies on tin pitting corrosion have also been reported, and the effects of freshwater containing Cl−, SO42−, and HCO3− on tin pitting corrosion have been investigated. More specifically, Wahab et al. revealed by potentiodynamic polarization measurement that the pitting potential of a tin electrode shifted in a less noble direction as the Cl− concentration increased. However, there are no reports in which the comprehensive effects of Cl−, SO42−, and HCO3− on the pitting corrosion of tin-plated copper have been analyzed by potentiodynamic polarization measurements.
Thus, we herein report our analysis of the pitting corrosion of tin-plated copper based on potentiodynamic polarization measurements in a solution containing Cl\(^{-}\), SO\(_4^{2-}\), and HCO\(_3^{-}\), which are the main corrosion factors in a freshwater environment. Subsequently, the relational expressions between the measured pitting corrosion potentials and the Cl\(^{-}\), SO\(_4^{2-}\), and HCO\(_3^{-}\) concentrations are determined by multiple regression analysis. Finally, the effect of each component on the occurrence of pitting corrosion is quantitatively evaluated using a multiple regression analysis formula.

2. Experiment

2.1 Test solution

The solution concentrations of aggressive anions that enhance the corrosiveness of water (i.e., Cl\(^{-}\) and SO\(_4^{2-}\)) are key in determining the degree of tin-plated copper pitting corrosion, as is the concentration of HCO\(_3^{-}\), which greatly affects scale formation. To imitate the freshwater environment, various concentrations of sodium chloride (purity 99.5\%, Wako Pure Chemical, Japan), sodium sulfate (purity 99.0\%, Wako Pure Chemical, Japan), sodium bicarbonate (99.0\% purity, Wako Pure Chemical, Japan), and ultrapure water were used for mock tests (the concentrations of the solutions examined were 10, 30, 100, and 300 ppm). The temperature of each test solution was maintained at 25°C.

2.2 Electrochemical measurements

The measurements were performed according to the three-electrode method using a potentiostat (Hokuto Denko Hz-7000). The laboratory equipment diagram is shown in Fig. 1. As the working electrode, a copper rod (CU-112594 \(5.6 \mu m\), a custom-made product) were used. The copper rod electrode was prepared by soldering a copper wire onto a copper rod measuring \(\sim 1\) cm in length, and embedding it in epoxy resin. The electrode area of the copper rod electrode was set to 0.2 cm\(^2\), and it was polished using Emery Paper No. 2000. Subsequently, the electrode was degreased with methanol and washed with pure water. The tin-plated copper plate electrode (area \(=0.2\) cm\(^2\)) was covered with masking tape (851A manufactured by 3M) containing a \(5\) mm hole that had been cut out using a punch. The electrode was washed with methanol and pure water without polishing to ensure a constant plating thickness. A platinum wire was used as the counter electrode, and a saturated potassium chloride/silver/silver chloride electrode (SSE) was used as the reference electrode. Sodium sulfate was used as the salt for the salt bridge. Prior to carrying out the measurements, the sample was immersed in the test solution for 3 min, and the potential after that time was taken as the natural potential. Immediately after measurement of the natural potential, the potential was scanned from the natural potential to 0.5 V vs. SSE at a scan rate of 100 mV min\(^{-1}\). After measuring the anodic polarization curve, the electrode surface was observed by optical microscopy. All measurements were performed in triplicate.

3. Results and Discussion

3.1 Anode polarization curve results

Initially, to understand the difference in polarization behaviors between copper and tin-plated copper, the anodic polarization curves of these two materials were measured (see Fig. 2). Subsequently, to imitate the freshwater environment, a mixed solution containing a chloride ion concentration of 5.8 ppm, a sulfate ion concentration of 10 ppm, and a bicarbonate ion concentration of 31.0 ppm was used as the test solution.

The natural potential of the tin-plated copper electrode showed a less noble potential than that of the copper electrode. In the polarization curve of copper, the current value increased sharply because of active dissolution from the natural potential to \(-0.2\) V, and beyond \(0.2\) V, the current value became constant regardless of the potential; this was attributed to resistant polarization caused by a low solution concentration. In contrast, the anodic current of the tin-plated copper was very small at the natural potential (close to 0 V) owing to passivation, but the current increased sharply over 0 V. This was due to the fact that re-passivation did not occur above 0 V, and an increase in the number of pits was observed, in addition to promotion of pit growth. These results were confirmed by observation of the surface by optical microscopy (Fig. 3), where several holes were observed as small brighter areas.

![Figure 1](image1.png)  
**Figure 1.** Schematic representation of the experimental set-up. WE, CE, and RE represent the working electrode, counter electrode, and reference electrode, respectively.

![Figure 2](image2.png)  
**Figure 2.** Anodic polarization curves of the copper and tin-plated copper electrodes in synthetic freshwater containing chloride ions (5.8 ppm), sulfate ions (10.6 ppm), and bicarbonate ions (31.0 ppm). Scan rate = 100 mV min\(^{-1}\).
In the case of the tin-plated copper, the potential range in which the passive current flows was wide, and the potential for film destruction was clear. Therefore, the pitting potential \( E_{\text{pit}} \) of the tin-plated copper is considered to be an important value that can be used as an index to indicate the possibility of pitting corrosion in a certain environment. It is noted that a similar pitting potential appeared even when a tin electrode was used (data not shown). The potential at a current density of 10 µA cm\(^{-2}\), which can be regarded as the growth of pitting corrosion, is defined as the \( E_{\text{pit}} \).

Figure 4a shows the anodic polarization curve measured in the NaCl solution (10–300 ppm Cl\(^-\)), while Fig. 4b shows the anodic polarization curve measured in the Na\(_2\)SO\(_4\) solution (10–300 ppm SO\(_4^{2-}\)). From the polarization curves shown in Fig. 4, it can be seen that the pitting potential shifts to a lower potential as the concentrations of chloride and sulfate ions are increased. This was attributed to the fact that these ions are corrosive to tin-plated copper, and so an increase in their concentrations results in enhanced pitting corrosion.

Figure 5 shows a plot of the logarithm of \( E_{\text{pit}} \) against the chloride ion concentration and the sulfate ion concentration. A linear relationship was found in both cases, which is the same tendency reported for stainless steel and aluminum.\(^{21,22}\)

Figure 6 shows the anodic polarization curves measured in the bicarbonate ion solution (10–300 ppm HCO\(_3^-\)). As shown, a rapid increase in the current value caused by pitting corrosion was not observed. Furthermore, observation of the surface after polarization by optical microscopy confirmed that pitting corrosion did not occur, thereby indicating that the bicarbonate ion does not corrode tin-plated copper.

Subsequently, the polarization behavior of tin-plated copper was investigated in a mixed solution of chloride ions, sulfate ions, and bicarbonate ions. Figure 7 shows the polarization curves when the chloride ion concentration was fixed at 10 ppm, the sulfate ion concentration was fixed at 10 ppm, and the bicarbonate ion concentration was 10, 30, or 100 ppm. From the obtained curves, it was apparent that the pitting potential shifted in the noble direction as the bicarbonate ion concentration was increased. Furthermore, it was found that pitting corrosion did not occur when the bicarbonate ion concentration was 100 ppm. In general, in the presence of significant concentrations of chloride and sulfate aggression anions, the passivation film is locally disrupted and reaction products are produced. Hydrolysis of the corroded material then occurs, causing a local decrease in pH and promoting further pit growth. However, when bicarbonate ions are present in the solution, the pH buffering capacity of the bicarbonate ions appears to suppress pitting corrosion by preventing the above-mentioned local decrease in pH.

3.2 Multiple regression analysis

Multiple regression analysis was used for a quantitative evaluation into the degree to which each ion species affects the tin-plated copper. Multiple regression analysis is a method of predicting the value of the dependent variable from information related to the independent variable through correlation between the observed variables, and each coefficient can be estimated by the least squares method.
Initially, the pitting potential of the tin-plated copper was measured in various solutions simulating the freshwater environment, and the results are listed in Table 1. Multiple regression analysis was then performed on the presented results using Eq. (1), and each parameter of the regression equation was estimated:

\[
E_{\text{pit}} = a \log \left[ \frac{\text{Cl}^-}{C_0} \right] + b \log \left[ \frac{\text{SO}_4^{2-}}{C_0} \right] + c \log \left[ \frac{\text{HCO}_3^-}{C_0} \right] + d \]  \hspace{1cm} (1)

where \( a \), \( b \), and \( c \) are the regression coefficients, and \( d \) is a regression constant.

The formula for substituting each parameter estimated by the regression analysis is shown below:

\[
E_{\text{pit}} = -77.1 \log \left[ \text{Cl}^- \right] - 34.9 \log \left[ \text{SO}_4^{2-} \right] + 57.6 \log \left[ \text{HCO}_3^- \right] + 92.9 \]  \hspace{1cm} (2)

The logarithm of the chloride ion concentration and the logarithm of the sulfate ion concentration are negative because the pitting potential shifts to a lower potential, indicating their tendency to promote corrosion. In contrast, the positive logarithmic coefficient of the bicarbonate ion concentration indicates that the pitting potential shifts to a more noble potential as the bicarbonate ion concentration is increased, thereby suppressing corrosion. In addition, a plot of the pitting potential predicted from the created regression equation and the measured values of \( E_{\text{pit}} \) is shown in Fig. 8, which confirms a positive linear relationship.

| Test solution | Cl\(^-\) [ppm] | SO\(_4^{2-}\) [ppm] | HCO\(_3^-\) [ppm] | \( E_{\text{pit}} \) [mV vs. SSE] |
|---------------|----------------|----------------|----------------|----------------|
| No.1          | 10             | 10             | 10             | 17.1           |
| No.2          | 10             | 10             | 30             | 68.5           |
| No.3          | 10             | 100            | 10             | -5.28          |
| No.4          | 30             | 10             | 10             | 0.416          |
| No.5          | 30             | 10             | 30             | 35.5           |
| No.6          | 30             | 30             | 10             | -1.97          |
| No.7          | 30             | 30             | 30             | 5.28           |
| No.8          | 30             | 100            | 100            | 53.9           |
| No.9          | 100            | 10             | 100            | -49.4          |
| No.10         | 100            | 100            | 100            | -49.4          |
| No.11         | 100            | 300            | 300            | 14.2           |
| No.12         | 300            | 300            | 300            | -47.3          |
| No.13         | 300            | 10             | 300            | 28.9           |
| No.14         | 300            | 300            | 10             | -113           |
| No.15         | 300            | 30             | 100            | -61.8          |
| No.16         | 600            | 600            | 10             | -150           |
| No.17         | 600            | 600            | 300            | -95.1          |
4. Conclusion

We herein report the relationship between the pitting corrosion of a tin-coated copper electrode and the composition of freshwater containing Cl\(^{-}\), SO\(_4^{2-}\), and HCO\(_3^{-}\) ions. A quantitative relationship between the Cl\(^{-}\), SO\(_4^{2-}\), and HCO\(_3^{-}\) concentrations and the pitting potential (\(E_{\text{pit}}\)) was determined by multiple regression analysis, since these ions are important corrosion factors in freshwater environments. As a result, it was possible to quantitatively evaluate the pitting potential of tin-plated copper in simulated freshwater. Using the created regression equation, the pitting potential of tin-plated copper can be predicted from the water quality (i.e., the Cl\(^{-}\), SO\(_4^{2-}\), and HCO\(_3^{-}\) concentrations).

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