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Study of Corrosion on Film Properties of High Strength Cu-Sn-Zr Alloys in Tap Water

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Abstract

Corrosion has been reported to occur in the copper tubes of heat exchangers in multiple-circulation hot water supply systems. We have been investigating the applicability of high-strength Cu-0.65 mass% Sn-0.014 mass% Zr-0.020 mass% P alloy to counteract this corrosion. Immersion tests, electrochemical measurements, and field tests were performed. Excellent corrosion resistance of the alloy was established under conditions with flowing water due to the formation of composite films containing tin. The alloy is expected to be better than copper as a corrosion-resistant material for heat exchanger tubes.

Keywords

Cu-Sn-Zr Alloy, Corrosion Resistance, Heat Exchanger, Hot Water Supply System, Flow Condition

1. Introduction

Many publicly funded hospitals and facilities that provide long-term care for the elderly have adopted multi-circulation type hot water supply systems that use multiple water heaters instead of boilers to reduce energy consumption and decrease the space required for the equipment. Although the number of cases was small compared to conventional hot water supply systems, depending on the usage environment, the heat exchanger copper tubes in water heaters have been reported to be prone to corrosion. We studied these corrosion issues [1] [2]. This corrosion was shown to be due to the interactions among three factors, *i.e.*, low pH of the groundwater used, flow rate, and microbubbles produced by pressure fluctuations [1]-[13]. We have focused on the effects of low pH of the groundwater as an environmental factor. We performed pH neutralization to reduce free carbon dioxide by sprinkling water in the water tank. This method prevented some corrosion, but the effect was insufficient [2]. Therefore, we focused on Cu-Sn type alloys. With regard to the corrosion resistance of Cu-Sn type alloys, previous studies indicated that corrosion does not occur at an Sn concentration of 1.00 mass% [13] and corrosion occurs at 0.24 mass% [14]. Based on these reports, it was considered that there was a Sn concentration that could be expected to result in corrosion resistance between 0.24 mass% and 1 mass%. Therefore, taking productivity into consideration, we examined the application of high-strength Cu-Sn-Zr alloys for commercial products with intermediate Sn concentrations [15] [16]. In this study, the corrosion resistance of high-strength Cu-Sn-Zr alloy was investigated by immersion test, polarization curve measurement, and actual facility test.

2. Experimental

2.1. Specimen Materials

The alloy tube specimens used in the experiment were composed of high-strength Cu-0.65 mass% Sn-0.014 mass% Zr-0.02 mass% P alloy with an external diameter of 15.88 mm, wall thickness of 0.71 mm, and length of 125 mm (hereafter referred to as the "alloy"). In addition, JIS H3300 C1220 copper tubing with an external diameter of 15.88 mm, wall thickness of 0.71 mm, and length of 125 mm was used as a reference (hereafter referred to as "copper"). The specimen surface was degreased with acetone and treated with 3.0 mass% sulfuric acid prior to the tests. In immersion tests, the specimen surface was sealed leaving the inner surface for polarization curve measurement was sealed leaving an area of 1 cm^2.

2.2. Test Solution

Table 1 shows the results of water quality analysis for the test solution. The test

Table 1. Water quality of raw water for test.

Contents	Laboratory Test	Actual facilities Test
pH	6.6	6.4
Electric Conductivity	5.9	10.8
Acid Consumption [mg $CaCO_3$/L]	21	27
Total Hardness [mg $CaCO_3$/L]	15.8	37
Calcium Hardness [mg $CaCO_3$/L]	7.6	26
Cl^- [mg/L]	<5	<5
SiO_2 [mg/L]	12.4	20
Fe [mg/L]	<0.1	<0.1
Cu [mg/L]	0.05	<0.01
SO_4^{2-} [mg/L]	<10	<10
NH_4^+ [mg/L]	<0.1	<0.1
Free Carbon Dioxide [mg/L]	—	20

solution for laboratory tests (immersion test and polarization curve measurement) consisted of tap water from a laboratory at Gifu University (raw water is well water), and the pH was adjusted with potassium dihydrogen phosphate and disodium hydrogen phosphate to pH 6, 6.5, or 7. The chloride ion concentration of the test solution was adjusted to 100 mg/L in tap water using sodium chloride. The test solution for the actual facility test was well water from Gifu-shi, Gifu prefecture, and the pH was neutralized by sprinkling water into the water tank [3].

2.3. Immersion Test

Test pieces were immersed in 300 mL of test solution in a 500-mL beaker and left for 72 hours in the open air at room temperature (RT). The tests were conducted under two conditions: stirring and stagnant (stirring speed 300 rpm). Immersion potential was measured during the tests with reference to Ag/AgCl, and the potentials in the following discussion are given with reference to this reference electrode unless otherwise stated. Immersion potential was measured three times for each material using an electrometer (HE-104A; Hokuto Denko Co., Meguro-ku, Tokyo, Japan).

2.4. Anodic and Cathodic Polarization Measurement

The polarization curve was measured in 500 mL of test solution in a cell with a capacity of 1 L at RT. Test solution and conditions were the same as described in the immersion test. The anodic polarization curves were obtained by deoxidizing the test solution with nitrogen gas, and the cathodic polarization curves were measured in the open air. The working electrode was the test material with reference to an Ag/AgCl electrode and Pt as the counter electrode. Polarization curve measurement was performed three times for each material using a potentiostat (HZ-5000; Hokuto Denko Co.) using the potentiodynamic method with a sweep speed of 10 mV/min.

2.5. Actual Facility Test

Figure 1 shows a schematic diagram of the heat exchanger used in the test. A

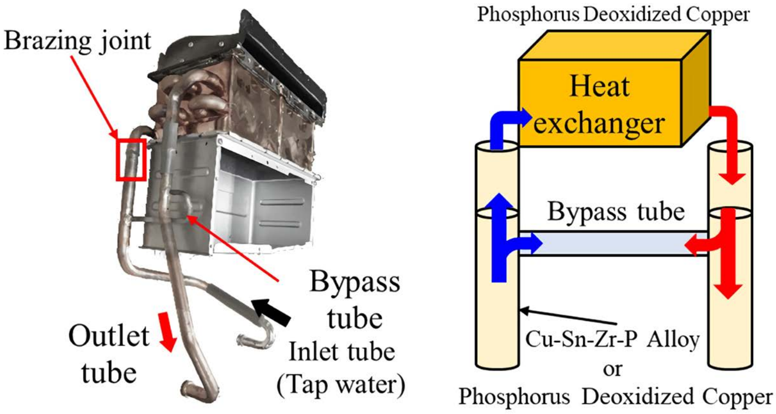

Figure 1. Schematic diagrams of heat exchanger for actual facilities test.

heat exchanger using alloy tubing for the inlet pipe was made. In addition, a heat exchanger using copper tubing as the inlet pipes was made as a reference. The test was conducted with the same multiple-circulation hot water supply system as described previously [3]. The water temperature was about 343 K and the flow rate was 56 L/min. The inner surface of each test material was examined with a digital microscope (DMV5000; Leica, Buffalo Grove, IL) and scanning electron microscopy (SEM) (S-4800; Hitachi High-Technologies Co., Minato-ku, Tokyo, Japan), and energy dispersive X-ray spectrometry (EDX) analysis (EX-250; HORIBA, Ltd., Kyoto-shi, Kyoto, Japan) was performed on the SEM observation site.

3. Results and Discussion

3.1. Immersion Test

Figure 2 shows the measurement results of the immersion potentials of the alloy in stirring and stagnant solutions at several pH values. Similar behavior was observed at immersion potential with stirring at all pH values. The immersion potential rose to about 0 V vs. Ag/AgCl after 6 hours at pH 6, after 10 hours at pH 6.5, and after 11 hours at pH 7. It subsequently dropped slightly and stabilized at about 0 V vs. Ag/AgCl at pH 6, about −0.01 V vs. Ag/AgCl at pH 6.5, and about −0.02 V vs. Ag/AgCl at pH 7 after 60 hours. On the other hand, the immersion

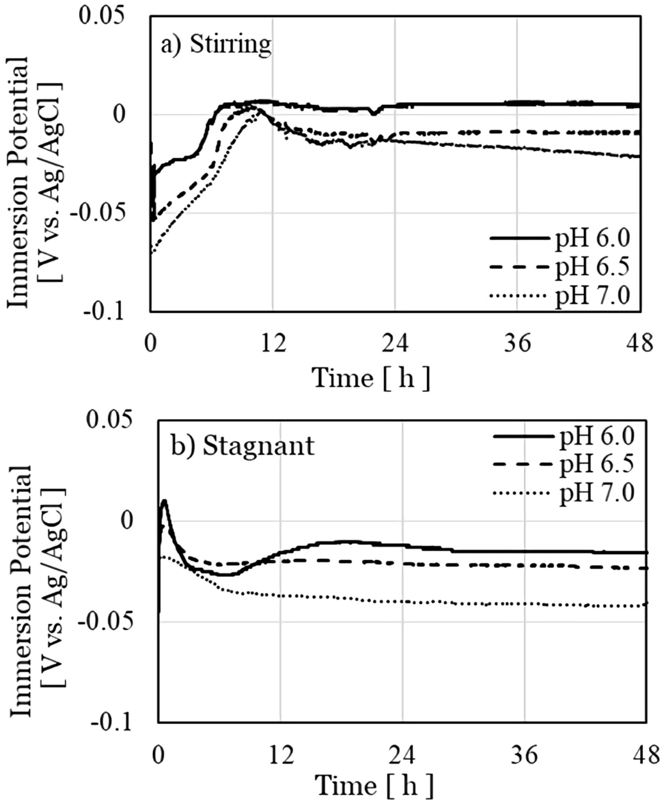

Figure 2. Changes in immersion potentials of the alloy under (a) stirring and (b) stagnant solutions at several pH values.

potential without stirring rose rapidly to 0.01 V vs. Ag/AgCl in the initial 25 hours of immersion and subsequently dropped. The potential at pH 6 then rose slightly to about −0.01 V vs. Ag/AgCl and stabilized around this level at pH 6.5 and 7 stabilized about −0.02 V vs. Ag/AgCl and −0.04 V vs. Ag/AgCl. In both stirring and stagnant solutions, the lower the pH, the higher the potential. The potential was higher in solution with stirring than under stagnant conditions at all pH values examined. **Figure 3** shows observations and EDX results of the inner surfaces of the alloy tubes in the stirring and stagnant solutions at pH 7. The surface under stirring conditions had an ocher color, while the surface under stagnant conditions had a pale scale attached. On SEM, a rough grainy surface was observed with stirring, while a smooth surface was observed under stagnant conditions. EDX analysis revealed copper, oxygen, and tin on the surface under stirring conditions, but copper, oxygen, and phosphorous were detected on the surface under stagnant conditions. The alloy tubing was considered to produce a dense film containing tin under a flowing environment. The difference in immersion potential between stirring and stagnant conditions was assumed to be due to the differences in film formation.

3.2. Polarization Curve Measurement

Figure 4 shows anodic and cathodic polarization curves of the alloy and copper at pH 6.5. The current density rose rapidly for both the anodic and cathodic polarization curves, and potential change with rising current density was very small. Therefore, the intersection of the anodic and cathodic polarization curves was evaluated as the corrosion current density. The corrosion current density of the alloy was about 1.1 × 10^{-6} A/cm^2 under stirring conditions, about 4.6 × 10^{-6}

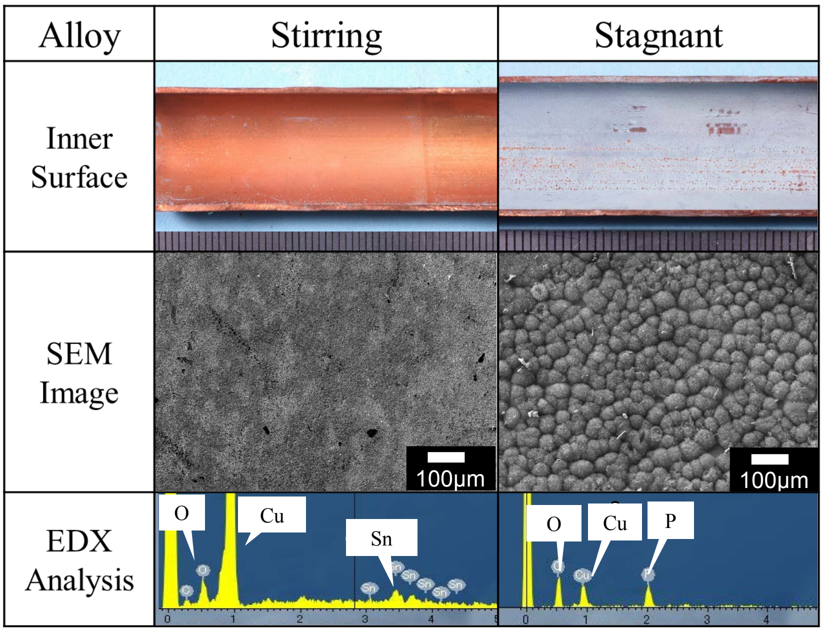

Figure 3. Observations and EDX results of the inner surfaces of the alloy tubes under stirring and stagnant conditions at pH 7.0.

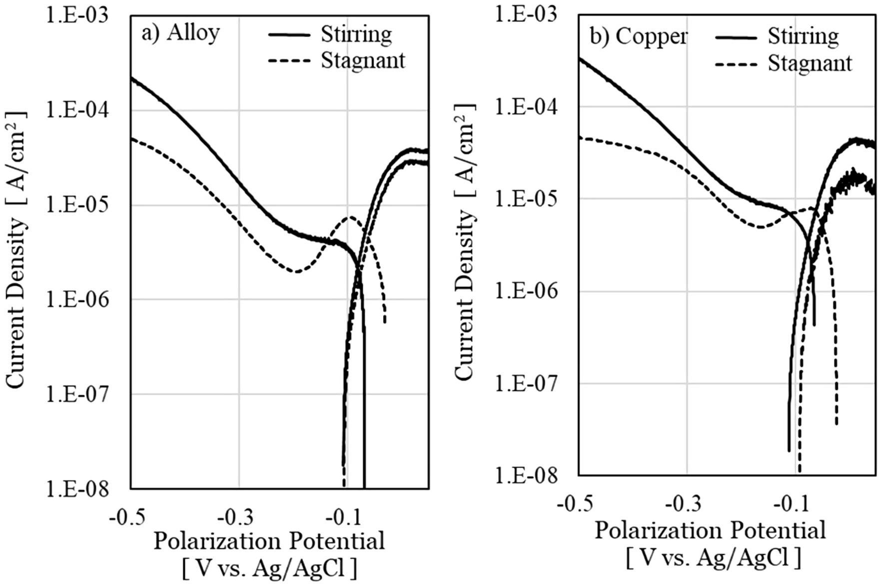

Figure 4. Anodic and cathodic polarization curves at pH 6.5 of (a) the alloy and (b) copper.

A/cm^2 under stagnant conditions. On the other hand, the corrosion current density of the copper was about 5.7 × 10^{-6} A/cm^2 under stirring conditions and about 5.6 × 10^{-6} A/cm^2 under stagnant conditions. There was no significant difference in corrosion current density between stirring and stagnant conditions. Figure 5 shows the effects of pH on the corrosion current density of each test solution. The corrosion current density was lower under stirring conditions than stagnant conditions at all pH values examined. In addition, agitation had a greater effect on the polarization behavior of alloys than pH.

3.3. Actual Facilities Test

Figure 6 shows the results of observation of the inner surfaces and cross-sections of the alloy and copper tubing. The inner surface of the alloy had changed to grayish green after 6 months of use. Moreover, examination of cross-sections showed that the surface layer was smooth and there was no progression of corrosion. On the other hand, the inner surface of the copper had changed to light purple after 6 months of use. In addition, the surface roughness, which was considered a sign of erosion corrosion on the surface layer, was observed from the cross-section observations. Figure 7 shows the results of EDX analysis on the inner surface and cross-section of the alloy tube. On EDX analysis, tin was strongly detected in the inner surface layer of the alloy pipe after 6 months of use. A composite film composed mainly of tin was formed on the inner surface layer. This result showed in good agreement with the immersion test results under stirring conditions.

3.4. Effects of Additive Elements on the Polarization Behavior of the Alloy

The results of immersion tests, polarization curve measurements, and actual

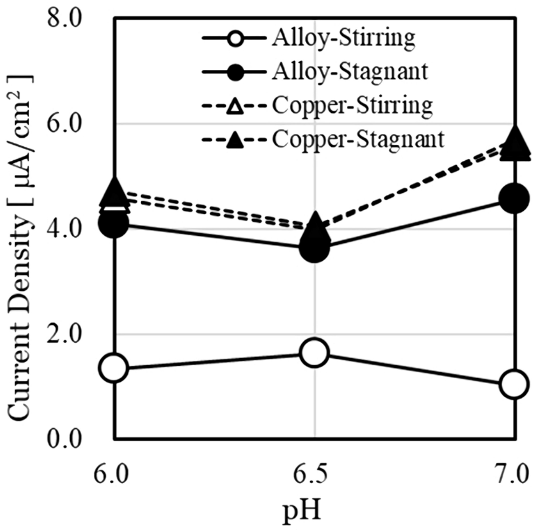

Figure 5. Effects of pH on the corrosion current density of tubes.

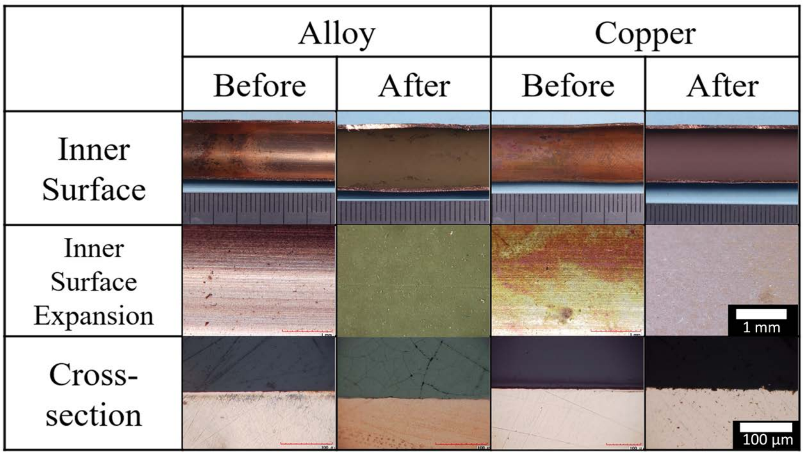

Figure 6. Observations of the inner surfaces and cross-sections of the alloy and copper tubes.

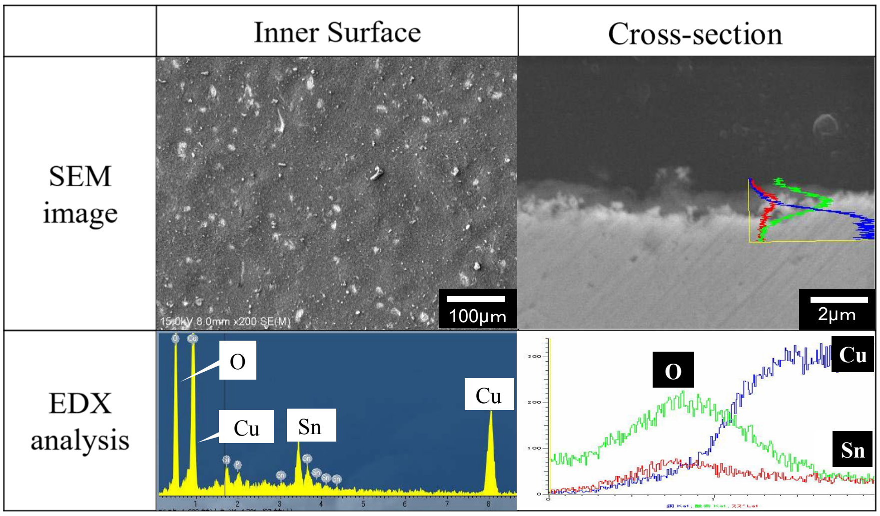

Figure 7. Results of EDX analysis of the inner surface and cross-section of the alloy tube.

machine tests indicated that the alloy produced a tin-containing film in a flowing environment and had good corrosion resistance. Therefore, to consider the corrosion resistance of the alloy, the anodic polarization curves of Cu-50 mass% Zr and 99.95 mass% Sn (hereafter referred to as "Cu-Zr" and "Sn") were measured in the same way as described for the alloy. **Figure 8** shows polarization curves of Cu-Zr and Sn at pH 6, 6.5, and 7. The tin results were as follows: natural electrode potential was about −0.75 V vs. Ag/AgCl. The current density rose rapidly with rising potential and maximum was observed at potential about −0.6 V vs. Ag/AgCl. After, the current density decreased and held constant round 1 μA/cm^2 in the potential range over −0.2 V vs. Ag/AgCl. On the other hand, Cu-Zr did not show passivation behavior as seen in Sn. The current density of Cu-Zr increased rapidly alone. The effects of pH on polarization curves of Cu-Zr and Sn were small. **Figure 9** shows the polarization curves of Cu-Zr, Sn, and the alloy in the solution at pH 6.5 under stirring and stagnant conditions. There was no difference in the anodic polarization behavior of Cu-Zr and Sn between stirring and stagnant conditions. The cathodic polarization behavior of the alloy was different between stirring and stagnant conditions. The natural electrode potential was lower under stirring conditions than stagnant conditions, and similar to the natural electrode potential of the anodic polarization curve for degassing because the cathode reaction was suppressed by the formation of the composite film containing tin. In addition, the diffusion limits current density of the cathodic polarization curve was stable with no undulations under stirring conditions.

3.5. Corrosion Resistance of Alloy Tube

Corrosion resistance of alloys was examined under stagnant conditions with no fluid flow, and copper ions were concentrated by the equilibrium of copper ions and base material on the surface of the material. It was difficult to form a composite

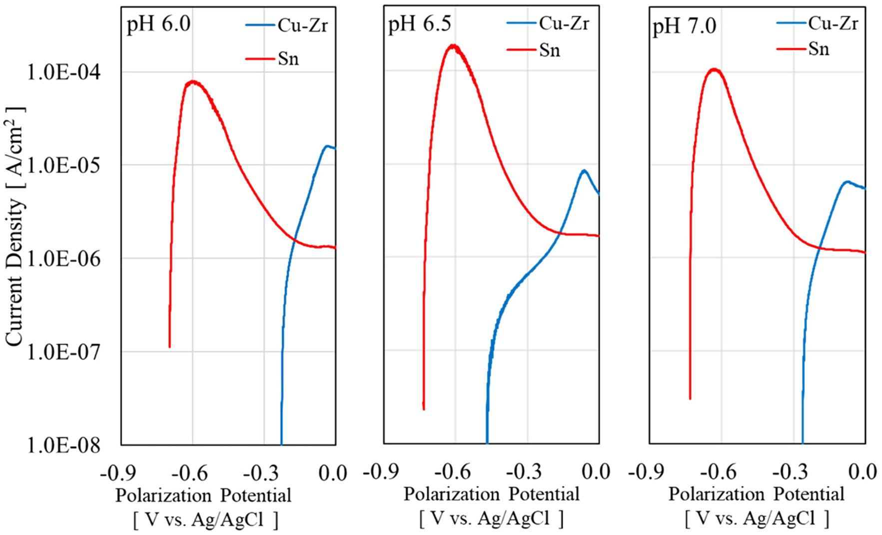

Figure 8. Anodic and cathodic polarization curves of Cu-Zr and Sn.

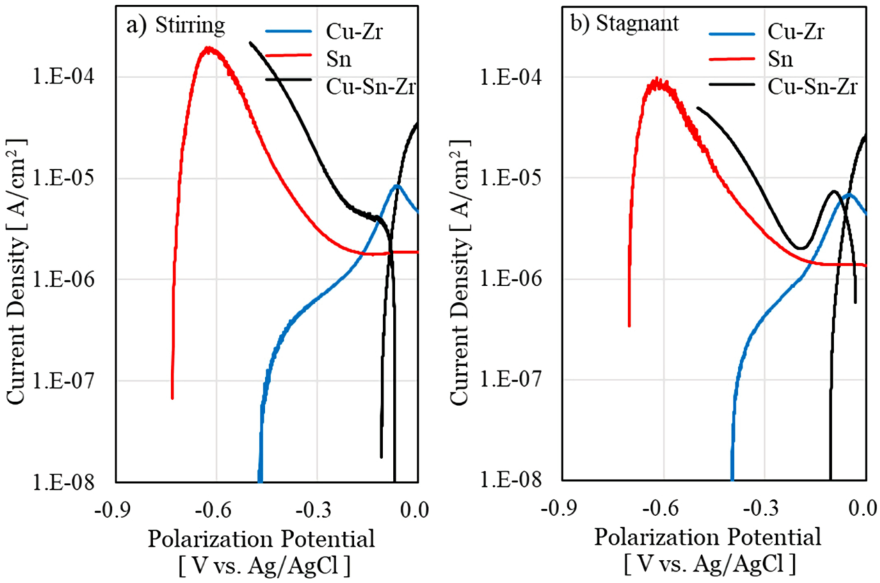

Figure 9. Polarization curves of Cu-Zr, Sn and the alloy in solution at pH 6.5 under (a) stirring and (b) stagnant conditions.

film containing tin and to show corrosion resistance. It was thought that tin showed no effect because the corrosion current density of the alloy under stagnant conditions was higher than that in the passivation area of tin. On the other hand, under stirring conditions, the concentration of copper ions was suppressed by the flow of liquid, and oxygen was supplied. Therefore, although the copper base material continued to dissolve, a composite film formed by the passivation of tin, and it showed good corrosion resistance due to the effect of tin. The above was also inferred from the observation that the corrosion current density of the alloy under stirring conditions was comparable to the current density in the passivation area of tin. Based on these results, the alloy was considered to form a composite film containing tin in a flowing environment, and this composite film was a corrosion-resistant film capable of suppressing the cathode reaction. Furthermore, previous studies indicated that the tin concentration at which corrosion resistance could be obtained was 1 mass% or more, but this study showed that corrosion resistance could be obtained even at 0.65 mass%. We will continue to study this critical value. In addition, it was considered from the results that the alloy exhibited corrosion resistance even at pH 6.5 or less, at which copper did not easily form a stable film. It has excellent corrosion resistance to low pH water quality, such as well water, and is expected to be widely used as a corrosion-resistant material for building equipment piping against the use of well water, which is growing in demand in Japan.

4. Conclusions

The results of this study can be summarized as follows.

1) Cu-Sn-Zr Alloy showed better corrosion resistance than copper in flowing environments in tap water.

2) The element contributing to the corrosion resistance of Cu-Sn-Zr alloy was found to be tin, and excellent corrosion resistance was obtained by forming a composite film containing this tin on the surface.

3) The minimum Sn concentration at which corrosion resistance was obtained in a Cu-Sn alloy was said to be 1.00 mass%, but it was found that 0.65 mass% still exhibits corrosion resistance.

4) The results of the laboratory test and the actual facilities test showed good agreement. In addition, the alloy was expected to be applicable to heat exchanger piping. It is expected that it can be widely used as a corrosion-resistant material for piping of building equipment against the use of well water, which is increasing in demand in Japan.

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Conflicts of Interest

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

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