Corrosion Behavior of Lead-Free Copper Alloy Castings and Their Crystallized Substances of Cu$_2$S and Bi

Yoshinobu Yasuda$^{1,2,*}$, Hiroyuki Abe$^1$, Ryozo Matsubayashi$^3$, Toru Maruyama$^4$ and Takumi Haruna$^4$

$^1$Northeastern Industrial Research Center of Shiga Prefecture, Hikone 522–0037, Japan
$^2$Science and Engineering, Kansai University, Suita 564–8680, Japan
$^3$Biwalite Co., Ltd., Hikone 522–0037, Japan
$^4$Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita 564–8680, Japan

In this study, we aimed to understand the corrosion behavior of Pb-free Cu alloys (Japan Industrial Standards (JIS) CAC411 and CAC901) and their crystallized substances (Cu$_2$S and Bi, respectively) particles in a 3.0 mass% NaCl aqueous solution, in comparison with those of a Cu alloy (JIS CAC406), its crystallized substance (Pb) particles, and a Cu alloy (JIS CAC403) with no crystallized substances. A Cu$_2$S specimen was produced via sintering Cu$_2$S powders, and a Bi specimen was produced by Bi electro-plating on a Cu substrate. The measured corrosion potentials of CAC411, CAC901, and CAC403 were close to that of Sn instead Cu. The corrosion current density peak near the corrosion potential of CAC403, which was the highest Sn concentration, was the largest in comparison with those of the other Cu alloys. Conversely, rapid increase in the current density, which was shown for all the Cu alloy at the potential above −0.20 V vs. Ag/AgCl, was similar to that of Cu. Therefore, it was concluded that these increase in current densities of Cu alloys was due to the dissolution of the Cu matrix. Cu$_2$S was converted into CuS during the anodic reaction. However, the corrosion potential of Cu$_2$S was higher than those of Cu and CAC411. Therefore, it was concluded that the Cu$_2$S particles in CAC411 act as cathodic sites and remain stable during the natural corrosion. The corrosion potential of Bi was higher than that of CAC901 and slightly lower than that of Cu. Further, at the potentials below −0.10 V vs. Ag/AgCl, Bi was thought to be covered with the passive film of Bi$_2$O$_3$ that was expected to protect Bi from corrosion. Therefore, it was concluded that the Bi particles in CAC901 hardly suffer severe corrosion. The corrosion potential of Pb was lower than those of the Cu and CAC411 alloys expect for CAC406. In addition, Pb exhibited a large anodic current density and dissolved actively around the corrosion potential of Cu. Therefore, it was concluded that the Pb particles dissolved preferentially during the corrosion of CAC406 owing to the galvanic corrosion. It was finally concluded that the Cu$_2$S and the Bi particles in CAC411 and CAC901, respectively, hardly suffer severe corrosion than the Pb particles in CAC406 in chloride-containing aqueous solutions like sea water. [doi:10.2320/matertrans.M2017196]

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1. Introduction

The Cu alloy casting containing Pb, which is classified as CAC406 in JIS (Japan Industrial Standards) and C83600 in ASTM (American Society for Testing and Materials standards), has been used as the main material of the parts for water supply equipment like disks and seats in valves. Pb is beneficial in Cu alloy castings because it reduces casting defects, improves the stop-water capability and enhances the free-cutting properties$^1$. However, the Pb particles crystallized in CAC406 preferentially dissolve in an early stage of immersion in water$^{2,3}$, and the dissolved Pb is harmful to environment and human health. Thus, the applicability of the Cu alloy containing Pb for water-supply equipment is severely limited$^4$.

Recently, Pb-free Cu alloys have been developed, such as CAC411 (C83470 in ASTM) and CAC901 in JIS, which contain sulfide (Cu$_2$S and ZnS) and Bi particles, respectively$^{5-10}$. However, few studies on the corrosion of these Pb-free Cu alloys have been conducted. In our previous study$^{3,11}$, the corrosion properties of CAC411, CAC901, and CAC406 were evaluated via measuring the anodic polarization curves of the alloys in a 3.0 mass% NaCl aqueous solution. A peak in the anodic current density was observed with CAC406 due to the dissolution of Pb. In addition, the anodic polarization curves of CAC411 and CAC901 were similar each other, and contain no peaks associated with the dissolution of the crystallized substances$^{3,11}$. However, the corrosion behavior of CAC411, CAC901, and their crystallized substances remained unclear in detail. Therefore, this study has been conducted to evaluate the corrosion properties of CAC411, CAC901, and their crystallized substances in comparison with those of CAC406 and its crystallized substance.

2. Experimental Procedure

2.1 Preparation of Cu alloy castings, Cu$_2$S, and Bi specimens

Cu alloy specimens of several Cu-Sn-Zn based alloys such as CAC411, CAC901, CAC406, and CAC403 were prepared by casting. The chemical compositions and metallographic images of these Cu alloy specimens are shown in Table 1 and Fig. 1, respectively. CAC411, CAC901, and CAC406 contained tiny particles of sulfides (Cu$_2$S and ZnS), Bi, and Pb, respectively. Analyzing the images captured using an optical microscope (Olympus Co., DSX500), the area ratios of the sulfide particles in CAC411 and the Pb particles

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cu (mass%)</th>
<th>Sn</th>
<th>Pb (mass%)</th>
<th>Zn (mass%)</th>
<th>Bi (mass%)</th>
<th>Ni (mass%)</th>
<th>S (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC411</td>
<td>91.1</td>
<td>4.1</td>
<td>0.1</td>
<td>2.8</td>
<td>-</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>CAC901</td>
<td>87.1</td>
<td>5.5</td>
<td>0.1</td>
<td>6.0</td>
<td>0.4</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>CAC406</td>
<td>84.7</td>
<td>4.5</td>
<td>5.2</td>
<td>4.3</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>CAC403</td>
<td>89.0</td>
<td>9.7</td>
<td>0.1</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1 Chemical compositions of the Cu alloy specimens.

$^*$Graduate Student, Kansai University

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in CAC406 were measured as 4.2% and 4.6%, respectively. CAC403 contained the highest concentration of Sn among other Cu alloy specimens, which generally exhibits better corrosion resistance in sea water than CAC406. Corrosion properties of Cu, Sn, and Zn, which are the major components of all the tested Cu alloy specimens, were also evaluated. In addition, corrosion properties of the crystallized substances of Cu$_2$S, Bi, and Pb precipitated in the alloys were separately evaluated. ZnS was not picked up because it has such a low conductivity as insulator$^{2,13)}$. The Cu, the Sn, the Zn, and the Pb specimens were cut from pure metal sheets with purities greater than or equal to 99, 99.9, 99.5, and 99.9 mass%, respectively.

Cu$_2$S specimen was produced via sintering Cu$_2$S powders (Sigma Aldrich, 325 mesh) in a carbon mold with an inner diameter of 20 mm. The Cu$_2$S powders were placed in the carbon mold in the chamber of a plasma sintering machine (Sumiseki Materials Co., Ltd., SPS-1030), which was then filled with N$_2$ gas and pressurized to 30 MPa. The carbon mold was heated at a rate of 0.83°C s$^{-1}$ to 600°C, held at the sintering temperature for 600 s, and then cooled to room temperature in the chamber. The top and side surfaces of the sintered Cu$_2$S specimen were polished to completely remove the carbon papers used as the release agent.

Bi specimens were produced via electro-plating. Table 2 shows the chemical components of a Bi plating solution. The Bi plating solution was heated at 50°C under stir by a hot stirrer. A Cu sheet and a Pt sheet were used as the plating substrate and the counter electrode, respectively. A constant current density of either 0.02 or 0.04 A cm$^{-2}$ was applied to the substrate submerged in the Bi plating solution until the total electric charge density reached 640 C cm$^{-2}$ or higher.

The Cu alloy and the Cu$_2$S specimens were finished to a mirror surface by buffing with diamond abrasive grains (−1 µm) after polishing with SiC papers (−#1200) in wet. The Cu specimen was immersed in an aqueous solution of 5 vol% H$_2$SO$_4$ to remove the oxide film on the surface. The Sn, the Zn, the Bi, and the Pb specimens were subjected to wet polishing using SiC papers.

### Table 2 Components of the Bi plating solution.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(NO$_3$)$_3$·5H$_2$O</td>
<td>50 g L$^{-1}$</td>
</tr>
<tr>
<td>CaH$_2$Na$_2$O·2H$_2$O</td>
<td>100 g L$^{-1}$</td>
</tr>
<tr>
<td>NaNO$_3$·2H$_2$O</td>
<td>50 g L$^{-1}$</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>Adjustment to pH 0.2 or under</td>
</tr>
<tr>
<td>Polyethylene glycol</td>
<td>0.01 g L$^{-1}$</td>
</tr>
</tbody>
</table>

#### 2.2 Corrosion tests

The polarization curves of the specimens were measured using a potentiostat-galvanostat (Hokuto Denko Co., HZ-7000). A saturated silver/silver chloride electrode (Ag/AgCl: 0.199 V vs. SHE at 25°C) and a Pt electrode were used as reference and counter electrodes, respectively. Test solution was a 3.0 mass% NaCl aqueous solution that was deaerated via bubbling with N$_2$ gas (purity 99.99%) for more than 3.6 ks. The specimen subjected to the surface treatment was covered with sealant except for an exposed area of 1.0 cm$^2$ and placed in the deaerated test solution of 250 mL, a temperature of which was maintained at 30°C. A cathodic potential of −0.70 V vs. Ag/AgCl was applied for 600 s to the CAC411, the CAC901, the CAC406, and the CAC403 specimens to remove the oxide films before the corrosion tests. After measurement of corrosion potential for 600 s, a polarization curve was measured for each specimen at a potential sweep rate of 0.83 mV s$^{-1}$. Each anodic polarization curve was measured in the range from the corrosion potential of the specimen to 1.00 V vs. Ag/AgCl, and each cathodic polarization curve was measured in the range from the corrosion potential of the specimen to the potential 200 mV lower than the corrosion potential.

Corrosion properties of the Cu$_2$S, the Bi, and the Pb specimens were evaluated via potentiostatic polarization tests at the characteristic potentials that derived from the polarization curves. The potentiostatic polarization test was conducted for 3.6 ks. The reference electrode, the counter electrode, the test solution, and the test temperature were the same as those used in the measurement of the polarization curves. The corrosion products formed by the potentiostatic polarization tests were identified by an X-ray diffraction system (Rigaku Co., RINT2200). The X-ray diffraction patterns were measured using Cu Kα source by the θ/2θ method.

The Cu$_2$S specimen was additionally subjected to potentiostatic polarization tests at several given potentials in 30 mL of the test solution for 3.6 ks without deaeration. The specimen was prepared by burying it in an epoxy resin except for the exposed surface area of 0.25 cm$^2$. The surface of each specimen was finished into a mirror surface via buffing with the abrasive diamond grains. After the potentiostatic polarization test, the test solution was diluted with distilled water to a volume of 50 mL and quantitatively analyzed by an inductively coupled plasma (ICP) emission spectroscope (Shimadzu Co., ICPS-8100) to determine the amounts of Cu and S that dissolved from Cu$_2$S.

The Bi specimen was subjected to a cyclic voltammetry (CV) measurement. The test solutions were 0.60 mass% H$_3$BO$_3$ aqueous solutions containing NaCl at concentrations.
up to 0.73 mass%. Before the test, the test solutions were adjusted to a pH of 7.8 with an NaOH aqueous solution, deaerated by bubbling with the N₂ gas and heated to 30°C. The Bi specimen was subjected to cathodic polarization at −1.50 V vs. Ag/AgCl for 300 s, followed by the CV measurement in the range from −1.50 to 0.80 V vs. Ag/AgCl at a potential sweep rate of 5.0 mV s⁻¹.

The surfaces of the tested specimens were observed using a scanning electron microscope (SEM; JEOL Ltd., JSM-6380LV) and further analyzed using an energy dispersive X-ray spectroscope (EDS; EDAX Inc., Genesis2000).

3. Results and Discussion

3.1 Characteristics of the Cu₂S and the Bi specimens

Figure 2 shows the X-ray diffraction patterns of the sintered Cu₂S and the Bi plating film. The specimens were identified as Cu₂S (chalcopyrite) and Bi, respectively. Maruyama et al. previously identified the sulfides in CAC411 as Cu₂S and ZnS⁸. Therefore, the Cu₂S specimen was confirmed to be the same compound as one of the sulfides in CAC411. Figure 3 shows the images of the surfaces of the Cu₂S and the Bi specimens, and a cross-section of the Bi specimen after surface polishing. It was verified that the Cu₂S specimen was almost densely sintered without large defects, and that the Bi deposited in a particulate form. On examining the cross-section of the polished Bi specimen, the film was found to have a thickness of about 150 µm, and no defects penetrating from the Bi surface to the Cu substrate. Therefore, it was judged that corrosion tests could be conducted on the Bi specimen without the influence of the Cu substrate.

3.2 Measurement of the polarization curves

3.2.1 Cu alloys

Figure 4 shows the polarization curves of the four Cu alloy specimens in the 3.0 mass% NaCl aqueous solution. The corrosion potentials of CAC411, CAC901, and CAC403 were nearly −0.45 V vs. Ag/AgCl. The shapes of the anodic polarization curves of these Cu alloy specimens were roughly the same in the ranges from their respective corrosion potentials to 0.40 V vs. Ag/AgCl. Because the shapes of the curves were independent of the presence of the crystallized substances, it is concluded that the anodic polarization curves of the Cu alloys in this potential range were mainly derived from the anodic reaction of the matrix. The anodic polarization curves contained small anodic current density peaks (P₁) of 5 to 17 μA·cm⁻² at −0.42 V vs. Ag/AgCl. Moreover, the P₁ peak of CAC403, having the highest Sn concentration, was the largest among those of the three Cu alloys. When the applied potential was above that at which P₁ occurred, the anodic current density slightly decreased. In the potential range from −0.20 to 0.06 V vs. Ag/AgCl, the current densities rapidly increased as the potential rose, and additional peaks (P₂) were observed. When the applied potential was more than that at which P₂ was observed, the anodic current density slightly decreased. When a potential more than 0.40 V vs. Ag/AgCl was applied, the current density of CAC411 increased as the potential rose, but those of CAC901 and CAC403 did not change significantly.

Conversely, the corrosion potential of CAC406 was −0.54 V vs. Ag/AgCl, which was lower than those of the CAC411, CAC901, and CAC403. The shape of the anodic polarization curve for CAC406 was different from those of the other Cu alloy specimens in the potential range of −0.10 V vs. Ag/AgCl and below. Further, a peak in the anodic current density (P₃) occurred around the corrosion po-
potential. When the applied potential was greater than that at which $P_3$ observed, the current density slightly decreased, but remained higher than those measured with the other Cu alloy specimens at potentials to $-0.10 \text{ V vs. Ag/AgCl}$ and below.

### 3.2.2 Cu, Sn, and Zn

The polarization curves of the Cu, the Sn, and the Zn specimens, which are the main components of the Cu alloy specimens, are shown in Fig. 5. In the polarization curve of Cu, the current density rapidly increased as the potential rose in the range from the corrosion potential ($-0.28 \text{ V vs. Ag/AgCl}$) to $0.12 \text{ V vs. Ag/AgCl}$, and then decreased slightly when the potential rose further. Therefore, it was concluded that the increase in the current densities of the Cu alloy specimens in the range from $-0.20$ to $0.06 \text{ V vs. Ag/AgCl}$ resulted from the active dissolution of Cu matrix. When the potential rose further, the current density of Cu increased again, while the current densities of the Cu alloys did not.

The corrosion potential of Sn was $-0.49 \text{ V vs. Ag/AgCl}$, and was approximately equal to those of CAC411, CAC901, and CAC403 as shown in Fig. 4. In the anodic polarization curve of Sn, the anodic current density rapidly increased as the potential rose in the range from the corrosion potential to $0.20 \text{ V vs. Ag/AgCl}$, decreased slightly as the potential rose to $0.30 \text{ V vs. Ag/AgCl}$, decreased rapidly, and then moderately as the potential rose further. It was hypothesized that the anodic current density peaks observed in CAC411, CAC901, and CAC403 at $-0.42 \text{ V vs. Ag/AgCl}$ ($P_1$ in Fig. 4) resulted from the anodic dissolution of Sn contained in the Cu matrix. In a previous study, Sn and Cu were detected in the corrosion products that formed on the surface of CAC411 after potentiostatic polarization at $0.20$ and $1.00 \text{ V vs. Ag/AgCl}$, and it was concluded that formation of insoluble Sn(OH)Cl on the surface of the specimen caused the decreasing current density as potential rose above $0.20 \text{ V vs. Ag/AgCl}$. In addition, in the studies by Robbiola et al. and Channouf et al. using a Cu-10 mass% Sn alloy, it was revealed that the layer of corrosion products including Cu and Sn acted as a barrier against corrosion. Therefore, the present results suggest that Sn improves the corrosion resistance of Cu alloys in the NaCl aqueous solution.

The corrosion potential of Zn was $-1.10 \text{ V vs. Ag/AgCl}$. The anodic current density of Zn increased as the potential rose across the entire range of anodic polarization, which indicates that Zn actively dissolves in the test solution. Therefore, it was concluded that Zn has a minimal effect on the improvement to the corrosion resistance of the Cu alloys in the NaCl aqueous solution.

### 3.2.3 Cu2S, Bi, and Pb

Figure 6 shows the polarization curves of the Cu2S, the Bi, and the Pb specimens, which represent the crystallized substances contained in CAC411, CAC901, and CAC406, respectively. In the figure, (a)–(f) denote the potentials at which the potentiostatic polarization tests were conducted: $1.00 \text{ V vs. Ag/AgCl}$ for Cu2S; $0.00, 0.10$, and $0.40 \text{ V vs. Ag/AgCl}$ for Bi; and $-0.20$ and $0.40 \text{ V vs. Ag/AgCl}$ for Pb, respectively.

The corrosion potential of Cu2S was $0.06 \text{ V vs. Ag/AgCl}$, which was higher than those of CAC411, Cu, and Sn. In the anodic polarization curve of Cu2S, the current density increased monotonically as the potential rose.

The corrosion potential of Bi was $-0.35 \text{ V vs. Ag/AgCl}$, which was higher than that of CAC901, and slightly lower than that of Cu. In the anodic polarization curve of Bi, the current density rapidly increased as the potential rose from $-0.10 \text{ V vs. Ag/AgCl}$, exhibited a peak at $-0.04 \text{ V vs. Ag/AgCl}$, decreased as the potential rose in the range from $-0.04$ to $0.10 \text{ V vs. Ag/AgCl}$, and sharply increased as the potential rose further.

The corrosion potential of Pb was $-0.56 \text{ V vs. Ag/AgCl}$, which was almost equal to that of CAC406. The anodic current density of Pb rapidly increased as the potential rose from the corrosion potential to $-0.33 \text{ V vs. Ag/AgCl}$, indicating that Pb actively dissolved. Pb seemed to be in a passive state in the potential range above $-0.35 \text{ V vs. Ag/AgCl}$. The shape of the anodic polarization curve was close to that of CAC406 in the range from the corrosion potential to $-0.15 \text{ V vs. Ag/AgCl}$ as shown in Fig. 4. Previous studies also pointed out that the anodic current density of CAC406 in the range from the corrosion potential to the peak potential resulted from the selective dissolution of Pb.

Figure 7 shows the surfaces of the Cu2S, the Bi, and the Pb specimens after measuring the anodic polarization.
curves. Most of the Cu$_2$S surface was flat with no corrosion products, but had some cracks. Conversely, corrosion products were observed on the entire surfaces of the Bi and the Pb specimens.

3.3 Potentiostatic tests to the specimens representing the crystallized substances

3.3.1 Cu$_2$S

Figure 8 shows the X-ray diffraction pattern of the Cu$_2$S specimen that was subjected to the potentiostatic polarization test at 1.00 V vs. Ag/AgCl for 3.6 ks. The pattern informed that CuS was detected in addition to Cu$_2$S. Kato et al. previously measured the anodic polarization curves of Cu$_2$S and CuS in CuSO$_4$ and H$_2$SO$_4$ aqueous solutions, respectively. In the resulting curves, peaks were detected in the anodic current density of Cu$_2$S at 1.5 and 2.7 V vs. SCE and in the anodic current density of CuS in the range from 2.5 to 3.0 V vs. SCE. The authors suggested that Cu$_2$S and CuS react according to eqs. (1) and (2), respectively:$$\text{Cu}_2\text{S} \rightarrow \text{CuS} + \text{Cu}^{2+} + 2\text{e}^- \quad (1)$$

$$\text{CuS} \rightarrow \text{Cu}^{2+} + \text{S} + 2\text{e}^- \quad (2)$$

Figure 9 shows the relation between the applied potential and the amounts of Cu and S in the test solution after the potentiostatic polarization tests for 3.6 ks. The current efficiency of dissolution of Cu$^{2+}$ that was calculated on the basis of reactions in eq. (1) is superimposed on the figure. The amounts of Cu and S dissolved in the test solution were small when a potential of 0.20 V vs. Ag/AgCl was applied. Conversely, the amount of Cu rapidly increased as the potential rose to 0.50 V vs. Ag/AgCl, although the amount of S remained small for all test potentials. At potentials of 0.50 V vs. Ag/AgCl and higher, the current efficiency was nearly 100%. Given the Gibbs energies of formation for Cu$_2$S, CuS, and Cu$^{2+}$ of −86.2, −53.6, and 65.5 kJ·mol$^{-1}$, respectively, the standard electrode potential for eq. (1) was calculated to be 0.31 V vs. Ag/AgCl. Assuming that the concentration of Cu$^{2+}$ in the test solution was $10^{-6}$ mol·L$^{-1}$, the equilibrium potential for eq. (1) was 0.13 V vs. Ag/AgCl, which was close to the observed corrosion potential of Cu$_2$S. Therefore, it was concluded that the anodic reaction of Cu$_2$S significantly occurred according to eq. (1), although the reaction in eq. (2) hardly occurred.

When the Cu$_2$S specimen was subjected to 1.00 V vs. Ag/AgCl for 3.6 ks, the Cu$_2$S on the surface was converted into CuS, and cracks formed on the surface. Given that densities of Cu$_2$S and CuS are 5.6 and 4.6 g·cm$^{-3}$, respectively, their molar volumes are 28 and 21 cm$^3$·mol$^{-1}$, respectively. Thus the volume reduction due to the reaction was estimated to be approximately 25%. Therefore, it is likely that the cracks in the Cu$_2$S develop owing to volumetric shrinkage.

3.3.2 Bi

Figure 10 shows the changes in the current densities of the Bi specimen during the potentiostatic polarization tests at the potentials shown in Fig. 6. When potentials of 0.00 and 0.10 V vs. Ag/AgCl were applied, the current densities were measured to be 3 and 8 mA·cm$^{-2}$, respectively. However the current densities rapidly decreased in the range from 0 to 0.18 ks, and decreased slowly to 0.08 and 0.11 mA·cm$^{-2}$, respectively until 3.6 ks. Conversely, when a potential of 0.40 V vs. Ag/AgCl was applied, the current density was maintained at 2.3 mA·cm$^{-2}$ until 3.6 ks. Upon
observing the surfaces of the Bi specimens after the potentiostatic polarization tests via naked eyes, clear films with interference color formed at the potentials of 0.00 and 0.10 V vs. Ag/AgCl, and white corrosion products accumulated at the potential of 0.40 V vs. Ag/AgCl.

Figure 11 shows the X-ray diffraction patterns of the Bi specimens after the potentiostatic polarization tests. BiOCl and Bi$_2$O$_3$ were detected as small diffraction peaks on the specimens at the potentials of 0.00 and 0.10 V vs. Ag/AgCl, and more significant diffraction peaks were detected on the specimens at the potential of 0.40 V vs. Ag/AgCl. Both BiOCl and Bi$_2$O$_3$ are poorly soluble substances.

Because a significant diffraction peaks of Cu, which was the substrate for the Bi specimen, was detected on the specimen to which the potential of 0.40 V vs. Ag/AgCl was applied, it was concluded that the dissolution reaction of Bi rapidly proceeded at this potential.

From the results of the potentiostatic polarization tests to the Bi specimens, the anodic reaction formulas of Bi are hypothesized as shown in eqs. (3)–(5).

$$\text{Bi} + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{BiOCl} + 2\text{H}^+ + 3\text{e}^- \quad (3)^{21,22}$$

$$E^\circ = -0.029 \text{V vs. Ag/AgCl}$$

$$2\text{Bi} + 3\text{H}_2\text{O} \rightarrow \text{Bi}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad (5)^{23}$$

$$E^\circ = 0.172 \text{V vs. Ag/AgCl}$$

It was assumed that the pH was 7 ([H$^+$] = 1.0 × 10$^{-7}$ mol·L$^{-1}$), that [Bi$^{3+}$] was 1.0 × 10$^{-6}$ mol·L$^{-1}$, and that [Cl$^-$] was 0.51 mol·L$^{-1}$ because the 3.0 mass% NaCl aqueous solution was used in this study. In addition, the activities of BiOCl and Bi$_2$O$_3$ were assumed to be unity because they are poorly soluble substances. Under these assumptions, the equilibrium potentials of the reactions in eqs. (3)–(5) can be calculated as −0.299, 0.00, and −0.242 V vs. Ag/AgCl, respectively. The equilibrium potentials given in eqs. (3) and (5) were close to the corrosion potential of the Bi specimen as shown in Fig. 6. Therefore, it is suggested that the anodic reactions in eqs. (3) and (5) occur around the corrosion potential, and the reaction in eq. (4) occurs at slightly high potentials.

Grubač and Metikoš-Huković measured the CV curves of Bi in a basic borate aqueous solution, and found that the dependence of the equilibrium potential on pH as shown in eq. (6)$^{23,24}$. The results showed that the anodic current density of Bi remained constant even when the potential rose to about 2.00 V vs. Ag/AgCl, which suggests that Bi is in a passive state based on eq. (5).

$$E = 0.172 - 0.0591 \text{pH} \quad (\text{Unit of potential: V vs. Ag/AgCl})$$

Passivation was also confirmed by Vivier who assessed the CV curves recorded in a KOH aqueous solution$^{25}$. Figure 12 shows the CV curves of the Bi specimen in borate aqueous solutions at pH 7.8 containing various concentrations of NaCl. In the figure, $I_1$ to $I_3$ denote the potentials at which the current density is increasing, and $S_1$ and $S_2$ denote the potentials at which the current density is steady. In the solution without NaCl, the anodic current density was notably low and approximately constant even as the potential rose. Based on these results, it was confirmed that passivation occurred on Bi under the experimental conditions, as re-
ported previously in the literature\textsuperscript{23–25}. In the solution containing 0.37 mass\% NaCl, the current density sharply increased from the passive state at approximately $-0.10$ V vs. Ag/AgCl ($I_2$). When the potential rose further, the current density increased with oscillation ($S_2$) and then increased rapidly ($I_3$) again. In the solution containing 0.73 mass\% NaCl, the current density sharply increased in the range from 0 to 0.18 ks, and then slowly to 0.86 mA cm$^{-2}$ until 3.6 ks. These changes in the current densities were similar to those in Bi when the potentials of $0.20$ and $0.40$ V vs. Ag/AgCl were applied. However, the current density of Pb after 3.6 ks was about 8 times larger than that of Bi at 0.10 V vs. Ag/AgCl after 3.6 ks (0.11 mA cm$^{-2}$). Therefore, it was concluded that Pb corrodes more readily than Bi at potentials less than or equal to $0.10$ V vs. Ag/AgCl.

The X-ray diffraction patterns of the Pb specimens after the potentiostatic polarization tests are shown in Fig. 14. When the potential of $-0.20$ V vs. Ag/AgCl was applied, weak diffraction peaks were observed and considered to correspond to Pb(OH)Cl in the corrosion products. At 0.40 V vs. Ag/AgCl, strong diffraction peaks corresponding to Pb(OH)Cl and PbCl$_2$ were observed. PbCl$_2$ is a salt that is known to have a relatively high solubility of 1.2 mass\% at 30°C, while Pb(OH)Cl is less soluble\textsuperscript{20}. Therefore, it was assumed that only Pb(OH)Cl was deposited on the Pb specimen at $-0.20$ V vs. Ag/AgCl. Also, in a previous study of the corrosion of BC6 (present in CAC406) conducted by Takatani et al., Pb(OH)Cl was detected\textsuperscript{21}. On the other hand, the following process is hypothesized in the case of 0.40 V vs. Ag/AgCl, that is, a large amount of Pb$^{2+}$ is formed, a large amount of Cl$^{-}$ migrates, the two ions accumulate on the surface, and then the surface is covered with the soluble products of PbCl$_2$.

### 3.4 Corrosion behavior of the crystallized substances in the Cu alloys

Based on the above results, the natural corrosion of the crystallized substances in the Cu alloys was discussed below.

The following three facts were confirmed: the corrosion potential of CAC406 was close to that of Pb, the corrosion potential of Pb was lower than that of Cu, and the area ratio of the Pb particles to the surface of CAC406 was very small (~4.6\%). These findings suggest that the Pb particles corrode significantly and preferentially against the Cu matrix via galvanic corrosion. The Pb particles in CAC406 are covered by a film comprising PbCl$_2$ or Pb(OH)Cl, but the film does not sufficiently resist the dissolution of Pb. Thus, the rapid dissolution continues until the Pb particles completely dissolve, followed by that CAC406 corrodes at the same rate as the other Cu alloys.

The corrosion potential of Cu$_2$S was higher than those of CAC411 and Cu. Furthermore, the area ratio of the sulfides to the surface of the CAC411 was very small (~4.2\%). Thus,
the Cu₂S particles are considered to become cathodic sites and not to disappear readily in the vicinity of the corrosion potential of CAC411. Moreover, the Cu₂S particles are thought to have minimal influence on the corrosion of CAC411, unlike the Pb particles in CAC406.

The Bi particles in CAC901 are considered to remain unaffected under the natural immersion conditions in the solution, because the corrosion potential of Bi was higher than that of CAC901. When the corrosion potential of CAC901 rises above that of Bi, the Bi particles may be covered with a protective film of Bi₂O₃ and thereafter protected from the corrosion. However, it is noted that the corrosion resistance of Bi decreases under the conditions that CAC901 is immersed in solution containing Cl⁻ and its corrosion potential exceeds −0.10 V vs. Ag/AgCl.

4. Summary

This study investigated the corrosion behavior of Pb-free Cu alloys CAC411 and CAC901, and their crystallized substances Cu₂S and Bi, respectively, in a 3.0 mass% NaCl aqueous solution. The corrosion behavior was compared with those of CAC406 and its crystallized substances Pb. The important findings are summarized as follows.

The Cu alloys, with the exception of CAC406, experience preferential dissolution of Sn in Cu matrix under natural corrosion. In addition, the corrosion products including Sn contribute to the corrosion resistance of Cu alloys.

The corrosion potential of Cu₂S is higher than those of CAC411 and Cu. Cu₂S is converted to CuS and Cu²⁺ via an anodic reaction at potentials above 0.50 V vs. Ag/AgCl. Cu₂S resists notable dissolution in the potential range from −0.28 to 0.12 V vs. Ag/AgCl at which Cu dissolves activity.

The corrosion potential of Bi is higher than that of CAC901. Thus, the Bi particles in CAC901 are hardly attacked under natural immersion conditions. When the corrosion potential of CAC901 exceeds that of Bi up to −0.10 V vs. Ag/AgCl, Bi is covered and protected by a Bi₂O₃ passive film. When the potential of Bi exceeds −0.10 V vs. Ag/AgCl in solutions with Cl⁻, the corrosion resistance of Bi is reduced, because this film was converted into BiOCl.

Among the Cu alloys tested, CAC406 undergoes the highest peak in anodic current density near the corrosion potential. Further, the peak potential induces a larger current density in Pb than in Sn. Therefore, the dissolution reaction of Pb particles occurs preferentially, and continues until all of the Pb particles exposed to the test solution are dissolved.

When CAC411, CAC901, and CAC406 are naturally immersed in the 3.0 mass% NaCl aqueous solution, the Cu₂S particles in CAC411 and the Bi particles in CAC901 do not corrode significantly, while the Pb particles in CAC406 corrode readily.

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