Dissolved-Oxygen-Induced Intensive Pitting Corrosion
of Amorphous ZrCu Alloys in Thin NaCl Solutions

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Intensive pitting corrosion of amorphous (a-) Zr50Cu45 and a-Zr50Cu50 were observed by immersion in 0.2–200 mM NaCl solution open to air at room temperature. The decreased corrosion rate in Ar-purged NaCl solution and no corrosion in ultrapure water open to air suggested that dissolved O2 and Cl− played an important role on the corrosion of the ZrCu-base amorphous alloys. The open-circuit potential showed a negative shift with increasing the NaCl concentration from 0.2 to 200 mM like that of pure Cu. These observations suggest that the corrosion of the ZrCu-base amorphous alloys in the NaCl solutions was triggered by Cu dissolution which was induced by the reduction of dissolved O2. The dissolution of Cu and Zr self-catalytically progressed by the local concentration of Cl− and hence the corrosion pits and holes were intensively formed even at the thinner NaCl concentrations.

1. Introduction

Amorphous alloys often show superior corrosion resistance compared with the corresponding crystalline counterparts and it can be attributed to the microscopically uniform structure owing to atomically random configurations. As like as the crystalline alloys, however, the corrosion resistance of amorphous alloys depends on the alloy compositions, sort of electrolytes and the surface states etc. In the pioneer work on the corrosion behavior of metal-metal amorphous systems, it was reported that the corrosion resistance of amorphous (a-) Zr50Cu50 was much better than that of the crystalline state in 0.5 M H2SO4, 1 M HNO3, 1 M NaOH, 1 M HCl and 9.5 mM (3 mass%) NaCl solutions.1) But the corrosion resistance of a-Zr50Cu50 in 1 M HCl and 9.5 mM NaCl solutions was relatively poorer than those in the other solutions. The formation of corrosion pits immediately after 40 s from the immersion in 0.6 M NaCl solution (pH 7) was found from the in situ surface observation of Zr50Cu40Al10 bulk metallic glass.2) From the electrochemical tests, the good corrosion resistance in 1 mM NaCl solution (pH 8) was reported for a-Cu86Zr14Al Y 3 and attributed to the formation of protective oxide surface films.3) In contrast, the same alloy showed no passivation in 10 mM NaCl solution (pH 8) and was susceptible to pitting corrosion. For a-Zr100−xCux (X = 40, 50 and 60) alloys in HCl solutions, it was reported that adsorption of Cl− at weak points of the surfaces induced the selective dissolution of less noble Zr, while Cu remained around the attacked regions and rearranged under open-circuit condition or low anodic polarization.4) At higher anodic potentials, the formation of CuCl films with a highly porous structure was observed. A galvanic coupling effect between the Cu-enriched pit regions and Zr-enriched regions at the alloy surface additionally triggered the pit propagation in depth and the pits spread over the alloy.5) The formation of rosette-like patterns composed of nanostructured Cu dendrites was reported for Zr50Cu35 metallic glass immersed in 0.1 M HCl + 0.1 M CuCl2 solution.6) The formation of Cu-rich nanocrystals with the size of 5–10 nm was observed on the walls inside the corrosion pits of a-Zr55 Ti3 Cu20 Al10 Ni5 immersed in hydrofluoric acid.7) From the corrosion tests of a-Zr52 Ti6 Al10 Cu18 Ni14 in 250 mM H2SO4 + 25 mM NaCl or 25 mM HCl solutions, it was reported that the bulk metallic glass prepared by copper mold casting showed superior corrosion resistance compared with the melt-spin ribbons. It was suggested that surface topological defects like air pockets played an important role on the corrosion.7) Not immersion in solution but keeping in air, the formation of ZrO2 layers at the surface was reported for a-Zr50Cu50.8)

As mentioned above, the corrosion resistance of ZrCu-base amorphous alloys is not so high in the solutions containing the halogen ions more than ~10 mM. Recently, we found that a-Zr100−xCux (X = 45 or 50) showed intensive pitting corrosion only by immersion in 0.2 mM NaCl solution open to air. Further, the corrosion rate showed a slight increase in spite of the large increase in NaCl concentration from 0.2 to 200 mM. In the present study, the process of the intensive pitting corrosion for a-Zr100−xCux (X = 45 or 50) in the NaCl solutions is discussed from the structural and morphological investigations of the corroded specimens and the corrosion products. It is suggested that the Cu dissolution by dissolved O2 starts at the surface areas where the passivation layers are defectively formed and the corrosion is self-catalytically progressed by the local concentration of Cl−.

2. Experimental

Ingots of Zr100−xCux (X = 45 or 50) were prepared by arc-melting of 99.6% pure Zr and 99.99% pure Cu in 99.9999% pure Ar atmosphere of 60 kPa. Prior to alloying the metals, a piece of Ti was melted as an oxygen getter. The alloy ingot prepared was cut into small pieces by using a wheel saw. These pieces were used for the starting material of the amorphous specimen. A thin tape of a-Zr46Cu54 (X = 45
or 50) with the width about 1.2 mm and the thickness about 30 \( \mu \)m was prepared by melt spinning in a chamber filled with 99.9999% pure Ar of 70 kPa. The tape was cut into ribbon-shaped specimens with the length of about 50 mm. The both flat surfaces of the ribbon specimens were polished by using an emery paper (1000 grid) in running water to avoid heat-up by polishing. After polishing, the ribbons were cleaned with ethanol in an ultrasonic bath. For some of the specimens, the one end of about 20% in length remained unpolished (partially-polished) in order to check the effect of the surface polishing.

For the immersion test, 0.2, 2, 20 and 200 mM NaCl solutions were prepared with >99.9% pure NaCl (Kanto Chemical Co., Japan) and ultrapure water (resistivity >18 M\( \Omega \)cm). The amorphous ribbon was immersed in the NaCl solution open to air at room temperature, where the specimen with the typical weight of about 12 mg was immersed in the NaCl solution of about 20 cm\(^3\). For the surface-polished specimens, the mean interval between the polish and the immersion was about 7.2 ks. In order to survey the effect of dissolved O\(_2\), 0.2 and 200 mM NaCl solutions purged by 99.99% Ar for 24 h in prior to the immersion test were also prepared and the Ar-purge was continued during the whole immersion test. The dissolved O\(_2\) concentrations were measured for 0.2 and 200 mM NaCl solutions open to air and those after Ar-purge for 24 h. The results are listed in Table 1. The open-circuit potential and potentiodynamic polarization curve for the specimen in the NaCl solution were measured by an electrochemical analyzer (ALS 660A-G) with a silver-silver chloride reference electrode. In the present study, all potentials were converted to the saturated calomel electrode (SCE) scale. The potentiodynamic polarization curve was recorded in a potentiostat mode with a scan speed of 1 mV/s. During the open-circuit potential and polarization curve measurements, the solution in the analyzer cell was purged by N\(_2\) gas.

The corroded ribbon was removed from the NaCl solution and rinsed well with ultrapure water for the weight measurement and the morphology observations. The surface morphology of the corroded specimens was observed by a scanning electron microscope (SEM, JEOL JSM-5600) and an optical microscope (OM). The crystallographic structure of the corroded specimens was investigated by the X-ray diffraction (XRD) technique (PANalytical X’pert diffractometer) with Cu-K\(_\alpha\) radiation (40 keV and 30 mA). The solutions after the immersion test were centrifuged and the corroded products were corrected. Then, the corroded products were dried on a glass plate, and the structure was investigated by the XRD measurement.

### Table 1 Dissolved O\(_2\) concentrations measured for 0.2 and 200 mM NaCl solutions open to air and those after Ar-purge for 24 h. The results for ultra pure water were also shown.

<table>
<thead>
<tr>
<th>NaCl concentration/mM</th>
<th>dissolved O(_2) concentration/mg/l</th>
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<tbody>
<tr>
<td></td>
<td>open to air</td>
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<tr>
<td>0.2</td>
<td>8.4</td>
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<tr>
<td>200</td>
<td>8.4</td>
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<tr>
<td>ultrapure water</td>
<td>8.4</td>
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3. Results and Discussion

#### 3.1 Surface morphologies of corroded a-Zr\(_{55}\)Cu\(_{45}\) and a-Zr\(_{50}\)Cu\(_{50}\)

The OM images for a-Zr\(_{55}\)Cu\(_{45}\) corroded in 20 mM NaCl solution open to air for 8 days are shown in Figs. 1(a) and (b). As shown in Fig. 1(a), the smooth surface with metallic silvery color turned to the dug and rough one with dark-brown color by corrosion. Corrosion holes were formed and the specimen became so brittle that the ribbon was broken into several pieces. In the magnified OP image (Fig. 1(b)), copper-colored dendric precipitates were observed at the corroded surfaces. The corrosion of a-Zr\(_{55}\)Cu\(_{45}\) in 200 mM NaCl solution for 8 days was slightly more intensive than that in 20 mM NaCl solution and the ribbon was broken into smaller pieces. The corrosion of a-Zr\(_{55}\)Cu\(_{45}\) in 20 mM NaCl solution for 8 days was milder than that in 20 mM NaCl solution, i.e. the number density of the corrosion hole was less than that in 20 mM NaCl solution and the copper-colored dendric precipitates were observed only near the intensively corroded holes. The corrosion of a-Zr\(_{55}\)Cu\(_{45}\) in 0.2 mM NaCl solution for 8 days was mildest and the number density of the corrosion hole was least. Further, some part of the surface became dark gray and brown but the dendric precipitates were hardly observed. It is noted that for the partially-polished specimens immersed in 0.2 and 2 mM NaCl solutions, the corroded part in the unpolished region was less than that in the polished region. Not shown here but the similar morphology changes mentioned above were observed for a-Zr\(_{50}\)Cu\(_{50}\) after corrosion in 0.2–200 mM NaCl solutions.
solutions open to air for 8 days. The corrosion holes and the copper-colored dendritic precipitates were intensively formed for the a-Zr_{55}Cu_{45} specimens corroded in 20 and 200 mM NaCl solutions. The corrosion holes and the copper-colored dendritic precipitates in 2 mM NaCl solution were less than those in 20 mM NaCl solution. The surfaces of a-Zr_{55}Cu_{50} corroded in 0.2 mM NaCl solution turned to dark gray and brown from metallic silver but almost no Cu dendrites were found at the surfaces.

In addition to a-Zr_{55}Cu_{45} and a-Zr_{50}Cu_{50}, the corrosion behaviors of 99.99% pure Cu and 99.5% pure Zr in the NaCl solutions were also investigated for comparison. Not shown here but Cu showed a slight corrosion in 200 mM NaCl solution for 8 days open to air, i.e. the Cu surfaces became dark and the color of the solution near Cu turned to light blue. From the Pourbaix diagram reported for pure Cu in 100 mM NaCl solution, pure Cu dissolves at pH 5.4 and the potential of 0.658 V vs. SCE (the reduction potential for dissolved O\(_2\) at pH 5.4 in the present NaCl solutions open to air). It is noted that the Tafel relationship between the potential and the current density was observed in the anodic branch of polarization curve for pure Cu in 0.2–200 mM NaCl solutions (see Fig. 8(b)). These suggest that pure Cu was corroded by the reduction of dissolved O\(_2\) in NaCl solution at pH 5.4. On the other hand, no corrosion was observed for pure Zr immersed in 200 mM NaCl solution open to air. It is known that Zr is electrochemically less noble than Cu although pure Zr shows the higher corrosion resistance because of the surface passivation.

Figures 2(a) and (b) show the SEM images of polished and unpolished a-Zr_{55}Cu_{45} specimens corroded in 200 mM NaCl solution open to air, respectively. As shown in Figs. 2(a) and (b), the morphology of the corroded surfaces were almost the same between polished and unpolished specimens. In Figs. 2(a) and (b), as well as corrosion pits, porous structures covered with a thin film are seen. It suggests that the corrosion of the specimen inside progressed through the pits formed at the surface. The porous structure covered with a lacy film was reported for the corrosions of ZrCu-base amorphous alloys and for stainless steels. It was reported that a multilayered structure with ZrO\(_2\) and metallic Cu was formed at the surfaces of a-Zr_{50}Cu_{50} kept in air. These indicate that thin surface passivation films of Zr oxides were formed in the present specimens keeping in air after the surface polish. As shown in Fig. 2(c), the dendritic precipitates were observed in the SEM images of the specimens corroded in 2, 20 and 200 mM NaCl solutions. The atomic ratios between Zr and Cu were estimated using energy dispersive X-ray analysis technique. The results for the precipitates marked by circles A and B in Fig. 2(c) were about 2:98 and 7:93, respectively. Combined with the OM image in Fig. 1(c), it is suggested that the Cu dendrites precipitated at the surfaces during the corrosion. As already mentioned, the formation of the Cu precipitates was reported for a-Zr_{100-x}Cu\(_x\) (X = 40, 50, 60) immersed in 0.1 M HCl solution, Zr_{55}Cu_{45} metallic glass ribbons immersed in 0.1 M HCl + 0.1 M CuCl\(_2\) solution and a-Zr_{59}Ti_{13}Cu_{20}Al_{10}Ni\(_8\) immersed in hydrofluoric acid.

### 3.2 Weight losses of a-Zr_{55}Cu_{45} and a-Zr_{50}Cu_{50} corroded in NaCl solutions

The time variations of relative decrease in the specimen weight of a-Zr_{55}Cu_{45} immersed in 0.2 and 200 mM NaCl solutions are plotted in Figs. 3(a) and (b), respectively. In the case of the immersion in the solutions open to air, O\(_2\) and CO\(_2\) in air are dissolved in the solutions. As listed in Table 1, the dissolved O\(_2\) concentrations of 0.2 and 200 mM NaCl solutions and ultrapure water open to air were close.
to the saturated dissolved \(O_2\) concentration of 8.5 mg/l reported for water in the air at 295 K. The dissolved \(O_2\) concentrations of 0.2 and 200 mM NaCl solutions and ultrapure water were decreased to 0.7, 1.2 and 1.9 mg/l by Ar-purge for 24 h, respectively. As shown in Figs. 3(a) and (b), the weight losses by corrosion was much decreased by Ar-purge of the solutions. The \(pH\) value measured for the NaCl solutions open to air were about 5.4 and that for ultrapure water was 5.5. These values indicated the dissolution of \(CO_2\). The value of \(pH\) 5.66 measured for Ar-purged 200 mM NaCl solution also indicated the dissolution of \(CO_2\). It should be noted that the metallic surfaces of a-Zr\(_{55}\)Cu\(_{45}\) were maintained in the ultrapure water open to air over 8 days. These observations suggest that the dissolved \(O_2\) as well as \(Cl^-\) is responsible for the corrosion of a-Zr\(_{55}\)Cu\(_{45}\) in the NaCl solutions open to air. The porous structures covered with the thin film as shown in Figs. 2(a) and (b) indicate that the corrosion initiated at the defective areas of the surface passivation. It was reported that the passivation of Zr in the ZrCu-base amorphous alloys was hindered by chloride ions and the atomically distributed Cu atoms.\(^4,13\) After the initiation of the corrosion pits at the surface, the corrosion progresses into the inside of specimen. The lower corrosion rate of unpolished a-Zr\(_{55}\)Cu\(_{45}\) compared with that of polished one (Fig. 3(b)) can be attributed to the less number density of the defective areas at the passivation layers.

Not shown here but the decreases in the specimen weight for 2 and 20 mM NaCl solutions were similar to those in 0.2 or 200 mM shown in Figs. 3(a) or (b). For the weight measurement, the specimen was removed from the solution, rinsed with ultrapure water and then dried in air for one hour. From the SEM and OP observations, some of the corrosion products were found at the surfaces. Further, small amounts of the solution might remain in the corrosion pits. The slight increase in the weight observed for partially-polished specimen in 0.2 mM NaCl solution open to air for 2 days in Fig. 3(a) can be attributed to these residual corrosion products and the solutions. The observed data in Figs. 3(a) and (b) indicate the lower bound in the weight loss by corrosion.

The results in Figs. 3(a) and (b) show that the intensive corrosion of a-Zr\(_{55}\)Cu\(_{45}\) proceeds even in NaCl solution open to air as thin as 0.2 mM. In Fig. 3(a), the weight loss by corrosion observed for the partially-polished specimen was almost the same to that for the fully-polished specimen after taking into account the fractional area of the unpolished part (about 20% in maximum). The weight losses by corrosion in 200 mM NaCl solution were slightly larger than those in 0.2 mM NaCl solution. As mentioned above, the SEM and OP observations suggested that the change in the surface morphology by corrosion in 200 mM NaCl solution was more intensive than that in 0.2 mM NaCl solution. The mean corrosion rate was estimated from the result in Fig. 3(a) as the lower bound. The estimated value was about 0.17 mm/ year for fully-polished a-Zr\(_{55}\)Cu\(_{45}\) immersed in 0.2 mM NaCl solution. The corrosion rate of \(1.6 \times 10^{-3}\) mm/year was reported for a-Zr\(_{50}\)Cu\(_{50}\) immersed in 9.5 mM NaCl solution open to air for 350 h.\(^1\) The corrosion rates of 0.12 and 0.20 mm/year were reported for surface-polished a-Cu\(_{50}\)Zr\(_{45}\)Al\(_5\) and a-Cu\(_{40}\)Zr\(_{50}\)Al\(_5\) in 9.5 mM NaCl solution open to air, respectively.\(^14\) In Fig. 3(b), the weight losses for the fully- and partially-polished a-Zr\(_{55}\)Cu\(_{45}\) specimens in 200 mM NaCl solution are plotted. In the figure, the result for the unpolished specimen in 200 mM NaCl solution is also shown. The time variation in weight loss for the partially-polished specimen was the same to that for the fully-polished specimen. The weight loss of the unpolished specimen was smaller than that for the fully-polished specimen. It is suggested that in 200 mM NaCl solution, the corroded parts expanded to the unpolished region of the partially-polished specimen.

The time variations of relative decrease in the specimen weight of a-Zr\(_{50}\)Cu\(_{50}\) immersed in the NaCl solutions are plotted in Fig. 4. Similar to the case of a-Zr\(_{55}\)Cu\(_{45}\) (Figs. 3(a) and (b)), the weight loss of a-Zr\(_{50}\)Cu\(_{50}\) showed a much decrease by Ar-purge of the solution. Further, the metallic surfaces of a-Zr\(_{50}\)Cu\(_{50}\) were maintained in the ultrapure water open to air over 8 days. These observations again indicate that dissolved \(O_2\) and \(Cl^-\) are responsible for the corrosion of a-Zr\(_{100-x}\)Cu\(_x\) in the NaCl solutions. The time variation of weight loss of a-Zr\(_{50}\)Cu\(_{50}\) in the NaCl solutions open to air looked like that of a-Zr\(_{55}\)Cu\(_{45}\). However, the amount of the weight loss showed a slight increase with the increase in the
NaCl concentration and the amount of the weight loss in 0.2 mM NaCl solution open to air was smaller than that of a-Zr53Cu47. From the Zr-Cu phase diagram, the single-phase state of ZrCu intermetallic compound is thermally equilibrium above 984 K whereas the two-phase state of Zr7Cu and Cu10Zr7 intermetallic compounds below 971 K at the Cu content of 50 at%. The two-phase state of ZrCu and Cu10Zr7 intermetallic compounds is thermally equilibrium above 984 K whereas that of Zr7Cu and Cu10Zr7 intermetallic compounds below 971 K at the Cu content of 55 at%. These features indicate that just above the liquidus line, the liquid at the Cu content of 50 at% is more atomically homogeneous than that at 55 at%. It is surmised that a-Zr50Cu50 possesses more homogeneous atomic distribution of Cu and Zr than a-Zr53Cu47 and relatively ununiform a-Zr55Cu45 is more corrosion-sensitive than a-Zr50Cu50 especially at the thinner NaCl concentrations.

3.3 XRD spectra of corroded specimens and corrosion products

Figure 5 shows the XRD patterns for the a-Zr55Cu45 specimens after the immersion in the NaCl solutions for 8 days and that in the as-spun state. For the as-spun state, only broad components reflecting the amorphous state were observed at around 38° and 66°. In the spectra of the corroded specimens, sharp peaks from fcc Cu were appeared. As already mentioned, the Cu precipitates were seen in the SEM (Fig. 2(c)) and OM images (Fig. 1(b)) of the corroded specimens. The formation of a small amount of CuO was detected from the XRD spectra of the corroded a-Zr55Cu45 specimens. The formation of CuO as well as fcc Cu was observed at around 38° and 54°, which are identified as CuO and Cu, respectively, in the XRD database. The similar XRD patterns with broad peaks at around 32° and 54° were reported for Zr(OH)4 and ZrO(OH)2 fineparticles prepared by ammonia-induced precipitation of zirconyl chloride. On the other hand, the sharp peaks in Fig. 6 were well explained by the reflections from paratitcamite (Cu2(OH)3Cl) according to the XRD database. These observations suggest that the Zr anions migrated into the NaCl solutions finally formed zirconium hydroxides whereas the Cu anions the paratitcamite.

3.4 Open circuit potential and polarization curve

Figures 7(a)–(c) show the time variations of open circuit potential (OCP) for pure Zr (99.5%, φ 0.381 mm), pure Cu (99.9%, φ 0.60 mm) and the a-Zr55Cu45 ribbon specimen in 0.2–200 mM NaCl solutions, respectively. Figures 8(a)–(c)
show the polarization curves for the Zr wire, the Cu wire and the a-Zr_{55}Cu_{45} specimen in 0.2–200 mM NaCl solutions, respectively. The measurements of OCP and the polarization curves were performed in the following sequence. After the initial value of OCP (OCP_{init}) was measured at 300, 600 or 900 s from the immersion, the cathodic branch of the polarization curve was recorded from OCP_{init}. Then, OCP was checked again and the anodic branch of the polarization curve was recorded from OCP_{init}. For a-Zr_{55}Cu_{45} in 0.2 mM NaCl solution, OCP was further checked after the polarization measurement of the anodic branch. During the measurements, the solution in the analyzer cell was purged by N_{2} gas.

For pure Zr, OCP_{init} was the same between 2, 20 and 200 mM NaCl solutions. The values of OCP in 2, 20 and 200 mM NaCl solutions showed a similar positive shift from those of OCP_{init} with the immersion time. The positive shift of OCP was attributed to the formation of passivation layers at the surfaces.\(^{18-21}\) The low current densities in the anodic branches in Fig. 8(a) also indicated the formation of the passivation layers at the surface of pure Zr. OCP_{init} in 0.2 mM NaCl solution was more negative than those in 2, 20 and 200 mM NaCl solutions and the increase in OCP by time was slightly larger. It may indicate that the passivation layers of pure Zr are more gradually formed at the thinner NaCl concentrations.

For pure Cu, the value of OCP_{init} showed a negative shift with the increase in the NaCl concentration. The negative shift of OCP in pure Cu with the NaCl concentration was attributed to the low solubility product of CuCl, i.e. the counter decrease in Cu\(^{+}\) concentration was induced by the increase in Cl\(^{-}\) concentration.\(^{22}\) The following reaction was reported for Cu in Cl\(^{-}\) media: \(^{23}\)

\[
\text{Cu} + \text{Cl}^{-} \rightleftharpoons \text{CuCl} + e^{-},
\]

where the equilibrium potential \(E_{eq}\) in acidic Cl\(^{-}\) media was given as,

\[
E_{eq} = -0.105 - 0.059 \log[\text{Cl}^{-}] (\text{V vs. SCE}).
\]

The shift in \(E_{eq}\) by the Cl\(^{-}\) concentration change from 0.2 to 200 mM is \(-0.177\) V from eq. (2) and the close value of \(-0.20\) V was observed in Fig. 7(b). It was reported that CuCl with the low solubility reacts with excess Cl\(^{-}\) to form the soluble complexes such as CuCl_{2}\(^{-}\) and CuCl_{3}\(^{2-}\).\(^ {24}\) In contrast to the case of Zr, almost no time variations in OCP suggest that the passivation layers of pure Cu were not formed in the NaCl solutions.

For a-Zr_{55}Cu_{45}, OCP_{init} showed a negative shift with increasing the NaCl concentration as like as that for pure Cu (Fig. 7(b)). The NaCl concentration dependence in OCP_{init} suggests that the dissolution of Cu governed the corrosion of a-Zr_{55}Cu_{45} in the NaCl solutions. In Fig. 7(c), OCP in 0.2 mM NaCl solution showed a positive time shift and that in 200 mM NaCl solution turned to a slight negative one. It indicated that the formation of the passivation layers gradually progressed at the surface of a-Zr_{55}Cu_{45} in the thinner NaCl solutions but became inhibited at the thicker NaCl solutions.

In the polarization curves of pure Zr (Fig. 8(a)), a local minimum was seen in each branch. The potential difference...
between these two minima ($V_{\text{an-cath}}$) decreased with increasing the NaCl concentration. The observation of the two minima suggested that the surface state of pure Zr in the cathodic branch was different from that in the anodic branch. However, the details have not been known at the present. In Fig. 8(a), the saturation of current densities as low as an order of $10^{-6}$ A/cm$^2$ in the anodic branches suggest the surface passivation of pure Zr. For pure Cu, the current densities showed an exponential increase in the anodic polarization from OCP to about 0 V vs. SCE, i.e. the Tafel relationship between the potential and the current density was observed. The polarization curves for a-Zr$_{55}$Cu$_{45}$ can be characterized by the combination with those of pure Zr and pure Cu. In 0.2 mM NaCl solution, the current density in the anodic branch below $-0.06$ V vs. SCE was remained as low as an order of $10^{-6}$ A/cm$^2$, i.e. the passivation was observed. Above $-0.06$ V vs. SCE, the current density showed a rapid increase. It suggests that the pitting corrosion of a-Zr$_{55}$Cu$_{45}$ started at $-0.06$ V vs. SCE in 0.2 mM NaCl solution. At around OCP, a local minimum was seen in each branch of the polarization curve like the case of pure Zr. In 2 mM NaCl solution, a clear plateau region of the current density in the anodic branch was not observed and $V_{\text{an-cath}}$ was decreased compared with those in 0.2 mM. In 20 and 200 mM NaCl solutions, no plateau region in the anodic branch was observed and $V_{\text{an-cath}}$ became nearly zero, i.e. the curves looked like that of pure Cu. The results of OCP in Fig. 7 and the polarization curves in Fig. 8 suggest that the corrosion of a-Zr$_{55}$Cu$_{45}$ was governed by the dissolution of Cu. Further, the surface passivation becomes inhibited at the thicker NaCl concentrations.

3.5 Pitting corrosion process of a-ZrCu in NaCl solution open to air

In the present study, a-Zr$_{55}$Cu$_{45}$ and a-Zr$_{50}$Cu$_{50}$ showed the intensive pitting corrosion in the NaCl solutions open to air but no corrosion in ultrapure water open to air. Further, the corrosion rate showed the decrease by Ar-purge of the NaCl solutions. These results indicate that the coexistence of Cl$^{-}$ and dissolved O$_2$ is essential to the corrosion of the ZrCu-base amorphous alloys in the NaCl solutions open to air. On the other hand, the formation of dendritic Cu precipitates (Figs. 1(b) and 2(c)) and the negative shift in OCP with the NaCl concentration (Fig. 7(c)) were found in the present corrosion test. These observations suggest that as well as Zr, Cu dissolves in the NaCl solutions from the ZrCu-base amorphous alloys. The following process is proposed for the intensive pitting corrosion of the ZrCu-base amorphous alloys immersed in the NaCl solutions open to air. At the initiation of the corrosion, the dissolution of Cu by dissolved O$_2$ is induced at the surface areas where the Zr passivation layers are defectively formed. As already mentioned, the thin surface passivation films were formed in the present specimens keeping in air after the surface polish. The formation of multilayered structure of ZrO$_2$ and metallic Cu was reported at the surfaces of a-Zr$_{50}$Cu$_{50}$ kept in air.\(^{25}\) It was also reported that the formation of cupric chlorides was promoted at the Cu-enriched layers formed beneath the surface passivation layers and the passivation layers were locally damaged by the cupric chlorides.\(^{25}\) Once the Cu dissolution starts from the defective areas, non-passivated Zr comes to contact with the solution and the dissolution of Zr is induced by the dissolved O$_2$. At the same time, some of the Cu anions near the surface act as the oxidant for less noble Zr in the amorphous alloy and metallic Cu precipitates at the surface (selective etching of Zr\(^{25}\)). At the surface areas where the dissolution of Cu and Zr is occurred, Cl$^{-}$ is locally concentrated by the Cu and Zr anions. The increase in the Cl$^{-}$ concentration causes the decrease in OCP of the amorphous alloys (Fig. 7(c)). The decrease in the local pH near the corroded areas can be expected because of the consumption of hydroxyl ions by the Zr and Cu anions. The decreases in OCP and pH accelerate the dissolution of Cu and Zr, i.e. the corrosion is locally progressed (autocatalytic corrosion)\(^{21}\) and hence the intensive pitting corrosionse take a place even at thinner NaCl concentrations. The Cu anions which do not precipitate as the dendrites finally form the paratracamite with Cl and OH$^{-}$ and Zr anions the fine particles of ZrO$_2$, Zr(OH)$_3$ and/or ZrO(OH)$_2$ (see Fig. 6).

The mean corrosion rates of a-Zr$_{55}$Cu$_{45}$ and a-Zr$_{50}$Cu$_{50}$ showed the slight increase with the large increase in the NaCl concentration from 0.2 to 200 mM (Figs. 3 and 4). It was reported that the corrosion rate in the polarization test of crystalline Cu$_{50}$Zr showed the maximum at the NaCl concentration of 0.1 M.\(^{26}\) It was attributed to the formation of a passive Cu$_2$O layer at the Cl$^{-}$ concentrations higher than 0.3 M. Not for the ZrCu-base alloys but for the Fe-base alloys, the maximum corrosion rate was attained at around the NaCl concentration of 9.5 mM and it was explained by the decrease in the dissolved O$_2$ concentration with the increase in the NaCl concentration.\(^{27}\) It is surmised that the autocatalytic effect mentioned above becomes suppressed by the passive Cu$_2$O layer formation near the pits and/or the decrease in the dissolved O$_2$ concentration at the higher NaCl concentrations.

The passivation layers like ZrO$_2$ are formed at the surfaces of the ZrCu-base amorphous alloys kept in air.\(^{81}\) It is suggested that the native passivation layers of ZrCu-base amorphous alloys are not so continuous like those of pure Zr and the Cu dissolution is locally triggered at the defected areas of the passivation layers.

4. Conclusion

Intensive pitting corrosions were observed for a-Zr$_{55}$Cu$_{45}$ and a-Zr$_{50}$Cu$_{50}$ in 0.2–200 mM NaCl solutions open to air. The mean corrosion rates estimated from the decrease in weight immersed for 8 days showed a slight increase in spite of the wide variation in the NaCl concentration from 0.2 to 200 mM. From the potentiodynamic measurements, the open-circuit potential (OCP) of a-Zr$_{55}$Cu$_{45}$ showed a negative shift with increasing the NaCl concentration from 0.2 to 200 mM. The negative shift of OCP was like to that of pure Cu. These results indicate that the corrosion of a-Zr$_{55}$Cu$_{45}$ and a-Zr$_{50}$Cu$_{50}$ in the NaCl solutions open to air initiated by the dissolution of Cu. Further, the decrease in the corrosion rate by Ar-purge of the NaCl solution suggested that the dissolution of Cu was induced by the reduction of dissolved O$_2$ in the solution. No corrosion was observed for a-Zr$_{55}$Cu$_{45}$ and a-Zr$_{50}$Cu$_{50}$ in ultrapure water open to air. It indicated that
Cl\(^-\) also played an important role for the corrosion of a-Zr\(_{55}\)Cu\(_{45}\) and a-Zr\(_{50}\)Cu\(_{50}\). Since OCP shifted to the negative values with the increase in the Cl\(^-\) concentration and the chloride ions were attracted by the dissolved metal anions, the dissolution of Cu and Zr was accelerated and hence the intensive pitting corrosion took a place auto-catalytically. The XRD results for the corrosion products showed that the dissolved Zr formed ZrO\(_2\), Zr(OH)\(_4\) and/or ZrO(OH)\(_2\) and the dissolved Cu formed paratacamite (Cu\(_2\)(OH)\(_3\)Cl) as the corrosion products. Further, Cu dendrite precipitates were observed at the corroded surfaces, suggesting that the selective etching of Zr was simultaneously induced by the reduction of the Cu anions.

In conclusion, the corrosion of ZrCu-base amorphous alloys immersed in NaCl solutions open to air is induced by the dissolved O\(_2\). With the assist of Cl\(^-\), the corrosion is triggered by the Cu dissolution at the surface areas where the Zr passivation layers are defectively formed. After the initiation of the corrosion, the dissolution of Cu and Zr is auto-catalytically progressed and hence the intensive pitting corrosion is attained even at thinner NaCl concentrations.

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