TECHNICALLY
speaking

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Characteristics of Anodically Electrolyzed Water — Dissolution Behavior of Copper or Copper Oxide Film

Anodically electrolyzed dilute aqueous solution of NaCl (NaCl-AEW), as well as Na_2SO_4 (Na_2SO_4-AEW), shows high redox potential and dissolved oxygen concentration, with additional generation of free chlorine for NaCl-AEW. The objective of this study is to evaluate the characteristics of both AEWs and to compare the dissolution rates of oxygen-free copper, which is immersed in AEW, HCl or H_2SO_4 solution at the same pH (=2.48). The result showed that the dissolution rate of oxygen-free copper immersed in NaCl-AEW was 4.2 times as high as that in HCl solution, and that in Na_2SO_4-AEW was 3.0 times as high as that in H_2SO_4 solution. The explanation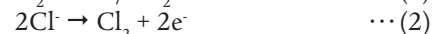 is that free chlorine in NaCl-AEW accelerates the dissolution rate and increases the surface roughness of copper, and dissolved oxygen in Na_2SO_4-AEW accelerates copper dissolution.

Additionally, when copper with thermal-oxide film was immersed in NaCl-AEW or Na_2SO_4-AEW, copper thermal-oxide film, as well as the underlying copper, was dissolved to form a natural-oxide film on its surface, which was similarly formed when copper with thermal-oxide film was immersed in HCl or H_2SO_4 solution. To conclude, AEW has the possibility to apply to etching or the pretreatment of copper as an alternative to HCl or H_2SO_4 solution.
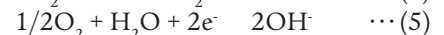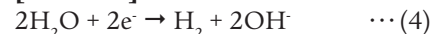
Electrolyzed water is a generic term for solutions obtained by electrolyzing diluted aqueous solutions of electrolyte salts [1]. When a diaphragm-type electrolytic apparatus is used for electrolysis, anolyte (anodically electrolyzed water) and catholyte (cathodically electrolyzed water) are generated in the anode compartment and the cathode compartment, respectively. Sodium chloride (NaCl) is commonly used as an electrolyte for generating electrolyzed water. At the anode, oxygen (O_2) and hydrogen ions (H^+) are formed by the oxidation of water, as well as chlorine (Cl_2) by oxidation of chloride ions (Cl^-). Dissolved chlorine (Cl_2 (aq)) consequently reacts with water (H_2O) to yield hypochlorous acid (HOCl) and hydrochloric acid (HCl). As a result, anolyte exhibits an increased redox potential and acidity and is also called acidic electrolyzed water. Meanwhile, at the cathode, hydrogen (H_2) and hydroxyl ions (HO^-) are formed by the reduction of water and dissolved oxygen. As a result, catholyte exhibits an increase in dissolved hydrogen concentration, a decrease in dissolved oxygen concentration, a remarkably lowered redox potential and alkalinity, and can be referred to as alkaline electrolyzed water. Chemical reactions occurring at this time are shown as equations (1)–(5). When sodium sulfate (Na_2SO_4) is used as an electrolyte, Cl_2 is not generated at the anode, resulting in an elevated concentration of dissolved oxygen in the anode water.

[Anode]

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \qquad \cdots (1)$$
$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \cdots (2)$$
$$Cl_2 \text{ (aq)} + H_2O \leftrightharpoons HCl + HOCl \quad \cdots (3)$$

[Cathode]

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \cdots (4)$$
$$1/2O_2 + H_2O + 2e^- \quad 2OH^- \qquad \cdots (5)$$

The features of electrolyzed water are its ability to generate thermodynamically unstable substances in aqueous solutions by electrolysis and to ensure work safety during the generation of acidic and alkaline solutions by means of electrochemical procedures without using hazardous acids and bases. Because anodically electrolyzed water (AEW) has a pH value of around
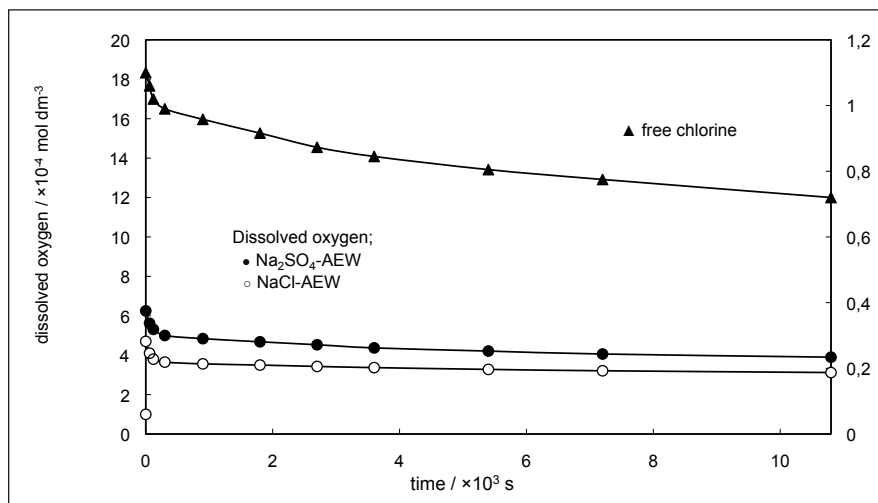

Fig. 1 Time course of dissolved oxygen and free chlorine concentrations after the end of electrolysis.

2.5 and a high redox potential, it is contemplated that the dissolution reaction of metals proceeds faster in AEW than in HCl or sulfuric acid (H_2SO_4) solution at the same pH.

Oxygen-free copper, which is used as material for precision electronic components, forms oxide film on the surface by heat treatment and natural oxidation. When oxygen-free copper is plated, HCl or H_2SO_4 solution is used for removal of oxide film, scale and rust on the surface [2]. It is also used in other processes such as etching. However, because HCl and H_2SO_4 solution are hazardous substances, the use of AEW alternative to these solutions has a great advantage over work safety and environment.

In this study, first the properties of AEW containing sodium chloride (NaCl-AEW) or sodium sulfate (Na_2SO_4-AEW) as an electrolyte were measured. Next the dissolution rates and surface morphology change of oxygen-free copper immersed in AEWs were compared with those in HCl or H_2SO_4 solution at the same pH, and the factors affecting the dissolution rate was discussed. Furthermore, the surface observation and analysis of copper with thermal-oxide film immersed in those solutions were performed when both its thermal-oxide film and underlaying copper were simultaneously dissolved, as well as determination of the dissolution loss of thermal-oxide film. Based on these results, the potential of AEW as alternative to HCl or H_2SO_4 solution in etching and the pretreatment of oxygen-free copper was discussed.

2. EXPERIMENTAL

2.1 Materials and Instrumentation
Oxygen-free copper plates (50 x 50 x 0.20 mm, Cu: 99.9 wt%; Hakudo Co. Ltd., Tokyo, Japan) were used as test specimens. NaCl and anhydrous Na_2SO_4 (both analytical reagent grade; Wako Pure Chemical Industries Ltd., Osaka, Japan) were used as electro-
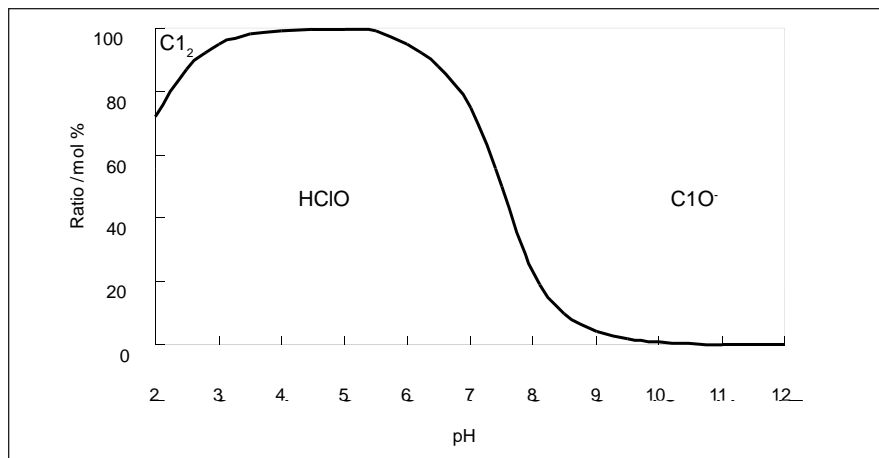

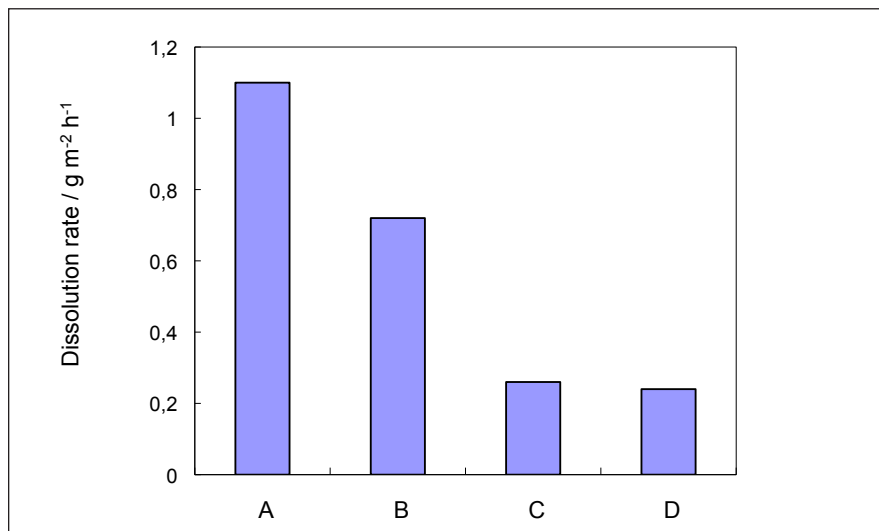Fig.2 dependence of molar concentration ratios Cl_2, HOCl, and OCl- on pH.

Fig. 3 Dissolution rate of oxygen-free copper immersed in NaCl-AEW (A), Na_2SO_4-AEW (B), HCl of pH 2.48 (C), or H_2SO_4 of pH 2.48 (D).
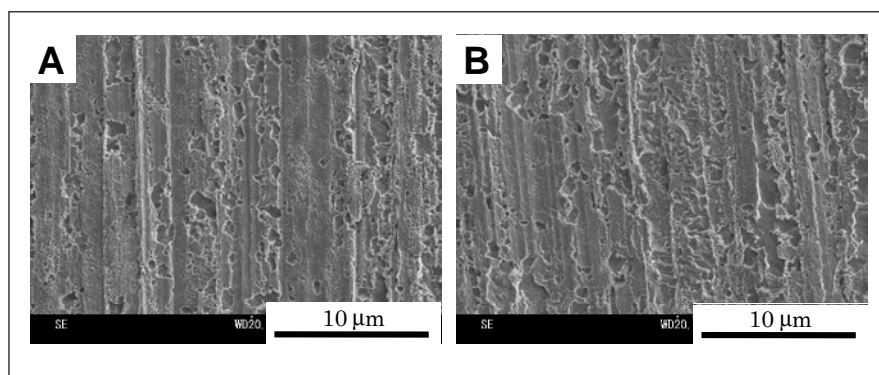

Fig. 4 SEM images of surface of oxygen-free copper which was immersed for 900 s in NaCl-AEW at a free chlorine concentration of 1.6×10^{-3} mol/dm³ (A) or 3.9×10^{-3} mol/dm³ (B).

lytes for preparing electrolyzed water. HCl, H_2SO_4, and sodium hydroxide (NaOH) solutions (analytical reagent grade; 0.1 mol/dm³; Wako Pure Chemical Industries, Ltd.) were used as acids and a base. Deionized water having an electrical conductivity of 10 MΩ·cm,

at pH7.4 was used. A diaphragm-type electrolytic apparatus (JED-007; Altec Co., Ltd., Tokyo, Japan) was used for preparing the electrolyzed water. A pH meter (Model F-22; Horiba Ltd., Kyoto, Japan), an ORP meter (TRX-90; Toko Kagaku Co. Ltd., Tokyo,

Japan), and a dissolved oxygen meter (MO128; Mettler Toledo International Inc., Columbus, OH) were used for measuring the pH, redox potential, and dissolved oxygen concentration of AEW, respectively. A residual chlorine analyzer (PC compact MT; AquaLytic Co. Ltd., Dortmund, Germany) was used for measuring free chlorine concentrations. Free chlorine is the total amount of Cl_2 (aq), HOCl and hypochlorous ions (ClO^-). The principle of residual chlorine measurement is a colorimetric method by potassium iodine. An inductively-coupled plasma (ICP) emission spectrometer (iCAP 6000; Thermo Fisher Scientific, Waltham, MA) was used for the quantification of copper. A scanning electron microscope (SEM, S-4300SE; Hitachi Ltd., Tokyo, Japan) was used for surface observations. A surface roughness meter (Surfcom 480A; Tokyo Seimitsu Co. Ltd., Tokyo, Japan) was used for the measurement of surface roughness of the samples. An Auger electron spectroscopy analyzer (Model 680; Physical Electronics Inc., Chanhassen, MN) was used for conducting a surface analysis of the specimen. A focused ion beam (FIB) machining and observation instrument (FB-210; Hitachi Ltd.) and a scanning ion microscope (SIM) were used for the processing and observation of the cross section, respectively.

2.2. Preparation of AEW

An aqueous solution of 1.0 x 10^{-2} mol/dm^3 NaCl or Na_2SO_4 was used to prepare AEW. The electrolytic apparatus comprised an anode tank (0.7 dm^3) and a cathode tank (0.7 dm^3), which were separated by a diaphragm. Platinum-coated titanium plates of 74 mm x 113 mm were used as the electrodes. The electrolyzing conditions were at 0.6 A and 12 V for 15 min.

2.3 Determination of the dissolution rate of copper

Specimens were degreased with acetone and ethanol. Moreover the specimen
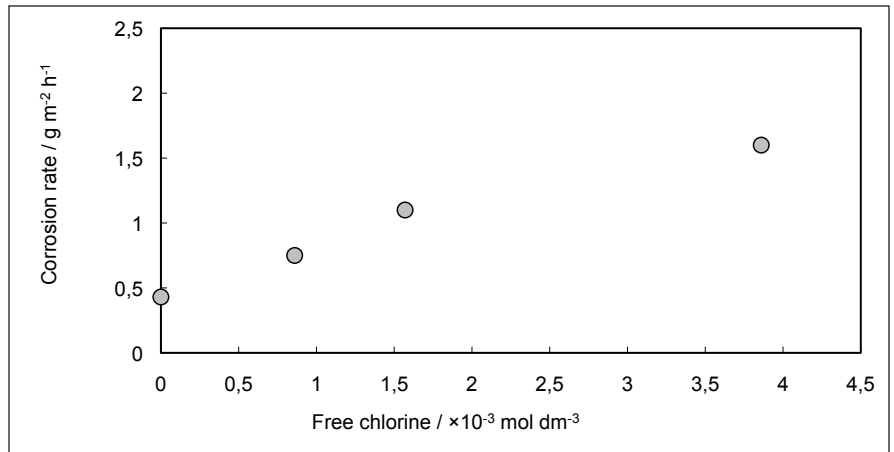

Fig. 5 Effects of free chlorine concentration on the dissolution rate of oxygen-free copper.
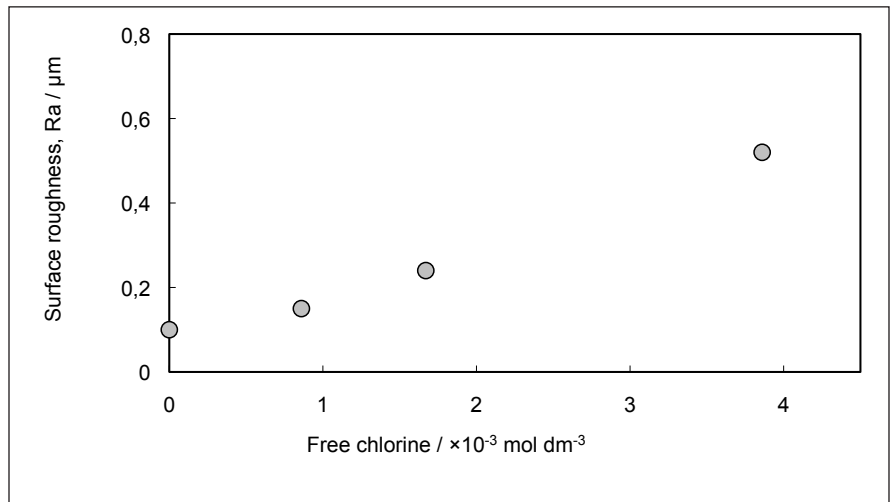

Fig. 6 Effects of free chlorine concentration on the surface roughness of oxygen-free copper.
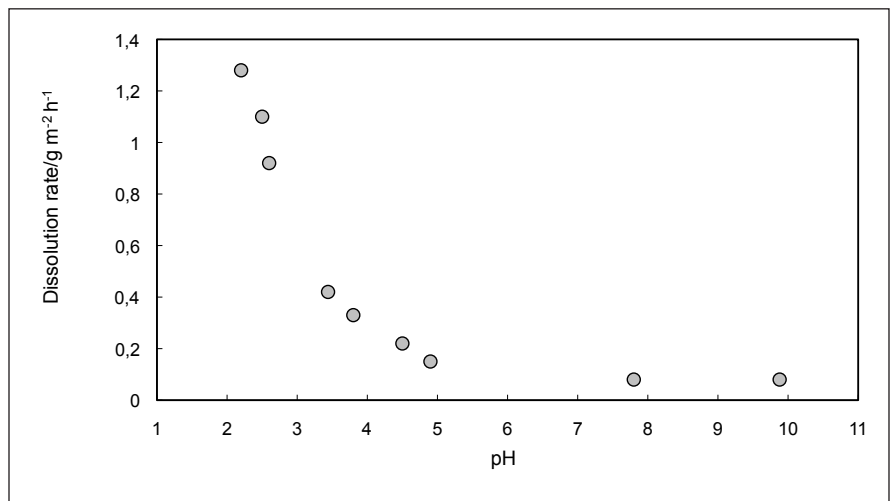

Fig.7 Effect of pH of NaCl-AEW on the dissolution rate of oxygen-free copper.

surface was polished with sandpaper (#4000) to remove natural-oxide film. Then the specimen was immersed in 200 dm^3 of NaCl-AEW or Na_2SO_4-AEW, as well as HCl (3.3 x 10^{-3} mol/dm^3) or H_2SO_4 solution (1.7 x 10^{-3} mol/dm^3) at the same pH of 2.4, for 1 hour. The dissolution rate was calculated from the weight loss of oxygen-free copper before and after immersion by equation (6). Simultaneously, it was calculated from the copper ion concen-

tration in the solution determined through a ICP analysis by equation (7).

Dissolution rate (g/m² h) =
$[w_b (g) - w_a (g)]/[S (m^2) \times 1 (h)]$ $\cdots$ (6)

Dissolution rate (g/m² h) =
$w_d (g) /[S (m^2) \times 1 (h)]$ $\cdots$ (7)

where w_b is weight of the specimen before immersion, w_a is weight of the specimen after immersion, S is total surface area of the specimen and w_d is weight of dissolved copper in the solution.

2.4 Evaluation of the effect of free chlorine

The following tests were performed to evaluate the effect of free chlorine on the dissolution and morphology of the oxygen-free copper surface in NaCl-AEW. NaCl solutions that having concentrations of 1.0×10^{-2}, 2.5×10^{-2}, and 1.0×10^{-1} mol/dm³ were electrolyzed under the same condition described in section 2.2 to yield NaCl-AEWs with free chlorine concetrations of 8.6×10^{-4}, 1.6×10^{-3} and 3.9×10^{-3} mol/dm³, respectively. All the NaCl-AEWs had the same pH of 2.48. The surface roughness of specimens were measured after they were immersed in the AEWs for 15 min. Also the dissolution rates were evaluated by an immersion of the specimens in the AEWs for 1 hour. The correlation between free chlorine concentrations and the roughness of the oxygen-free copper surface was investigated, as well as free chlorine concentrations and the dissolution rates.

Furthermore, the following tests were performed to investigate the effect of pH of NaCl-AEWs on the rate of copper dissolution. NaCl solutions of concentrations of 2.5×10^{-2} mol/dm³ was electrolyzed under the same condition described in section 2.2 to yield NaCl-AEWs (pH 2.48) with free chlorine concentrations of 1.6×10^{-3} mol/dm³, which were mod-
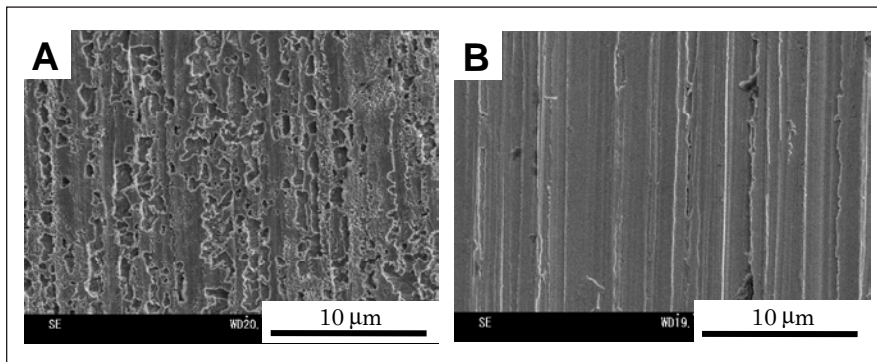

Fig. 8 SEM images of surface of oxygen-free copper which was immersed for 900 s in NaCl-AEW at a free chlorine concentration of 1.0×10^{-3} mol/dm³ and at pH 2.20 (A) or pH 4.60 (B).

ified by adding either water and HCl (1.0×10^{-2} mol/dm³) or water and NaOH solution (1.0×10^{-2} mol/dm³) to shift pH to 2.2 – 9.9 and free chlorine concentration to 1.0×10^{-3} mol/dm³. Next the dissolution rate was evaluated by the immersion of specimens in these solutions.

2.5 Evaluation of the effect of dissolved oxygen

Oxygen generated by electrolysis is dissolved in AEW in oversaturated conditions. AEW releases excessively dissolved oxygen gradually and reach a saturated concentration of 2.5×10^{-4} mol/dm³ (25 °C) in 3 hours. So AEW from Na_2SO_4 solution (1.0×10^{-2} mol/dm³) was generated by electrolysis and was left for 24 hours at room temperature. And then a dissolution rate was evaluated by immersion of a specimen in the resulting AEW with a saturated oxygen concentration for 1 hour. In addition, a dissolution rate was evaluated by immersion of specimens in H_2SO_4 solution, whose oxygen concentration was enriched over the saturated concentration by blowing oxygen, at pH of 2.48.

2.6 Surface analysis and observation of the specimens with thermal-oxide film immersed in AEW

The surface analysis and observation of specimens with thermal-oxide film immersed in AEWs were performed to investigate the changes in their surfaces when the thermal-oxide film and underlaying copper were simultaneously dissolved.

Specimens were oxidized by heat in the air at 200°C for 1 hour to form thermal-oxide film on the surface. Specimens exhibited a brass color after the heat treatment. When the thermally-oxidized specimens were immersed in NaCl-AEW, Na_2SO_4-AEW, HCl or H_2SO_4 solution with a pH of 2.48 for 2 min, the brass color faded gradually followed by the appearance of a lusterless surface of copper in each case. Then these specimens were immersed in each solution for 10 min, washed with water, and dried by nitrogen gas. Auger electron spectroscopy analysis was performed for conducting a surface analysis of these specimens, as well as specimens immediately after dry-polishing with sandpaper (#4000) for comparison.

Furthermore, surface analysis by SEM was performed with specimens with thermal-oxide film after immersion in each solution for 15 min. The immersion time was extended in order to accelerate the change in surface morphology because there was no difference in surface appearance when the immersion time was short.

2.7 Dissolution loss of thermal-oxide film

Specimens were oxidized by heat in the air at 200°C for 3 hours to form a thicker thermal-oxide film. These specimens were immersed in NaCl-AEW, Na_2SO_4-AEW, HCl or H_2SO_4 with a pH of 2.48 for 10 min. The dissolution loss of thermal-oxide film was evaluated by the change in weight of a specimen before and after immersion.
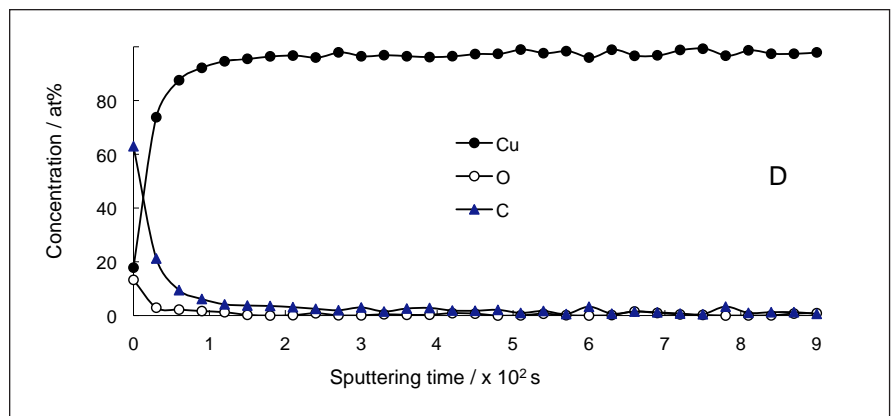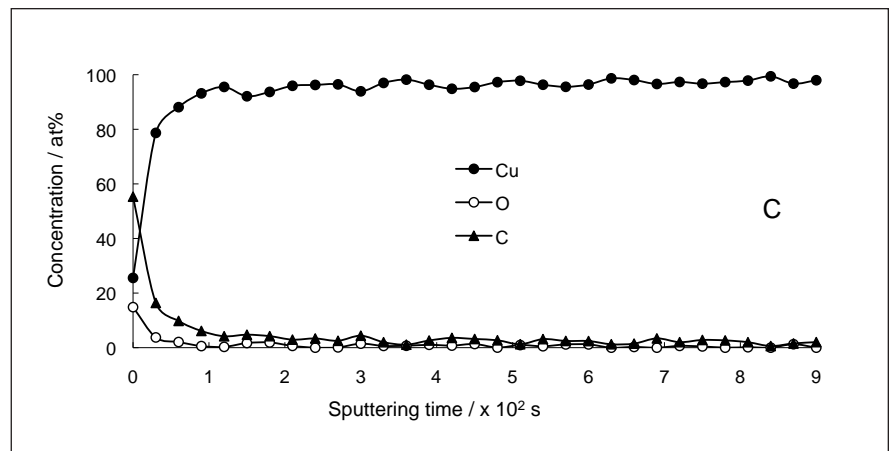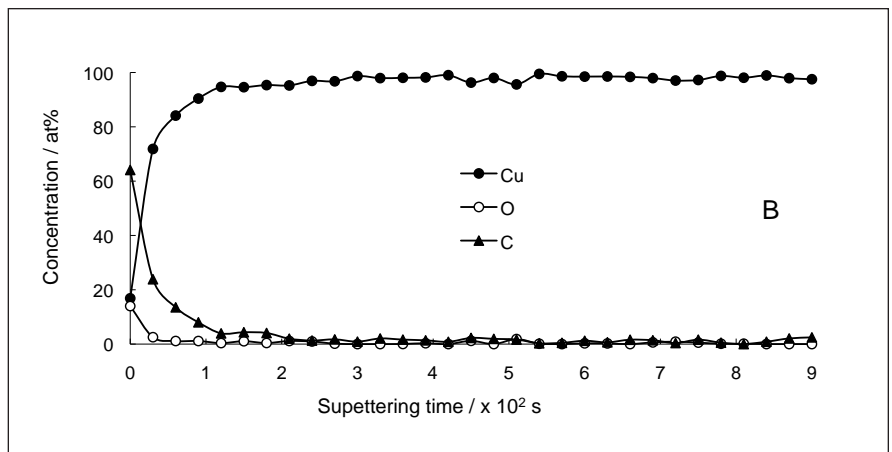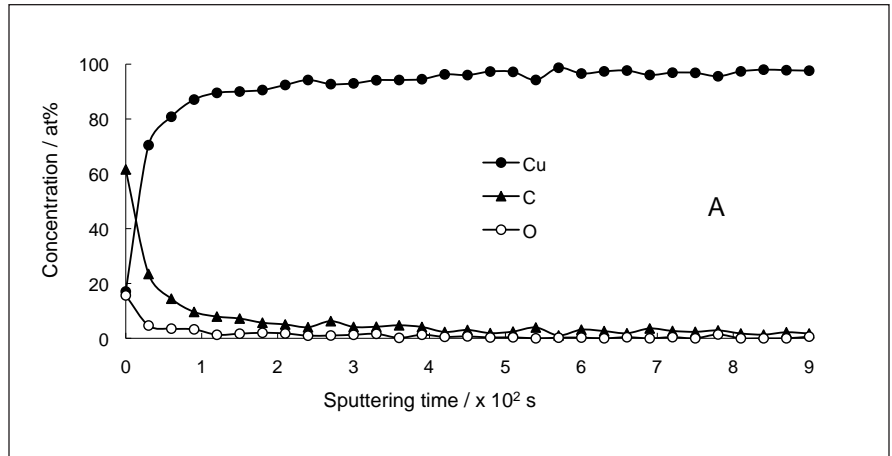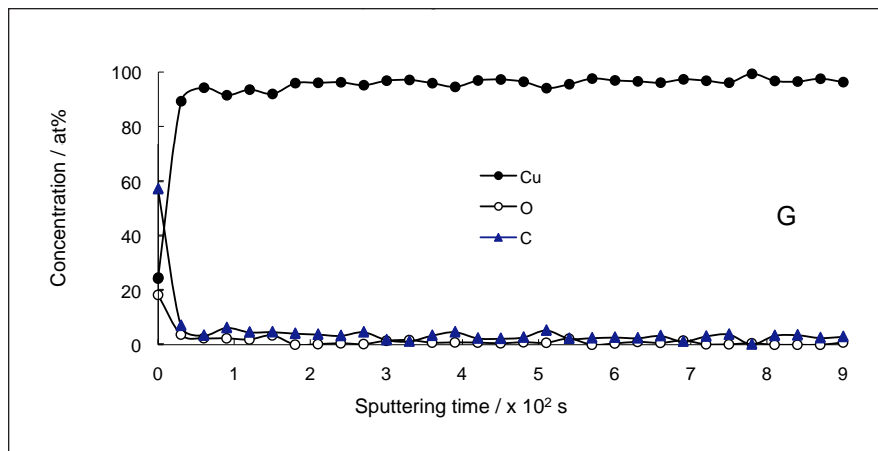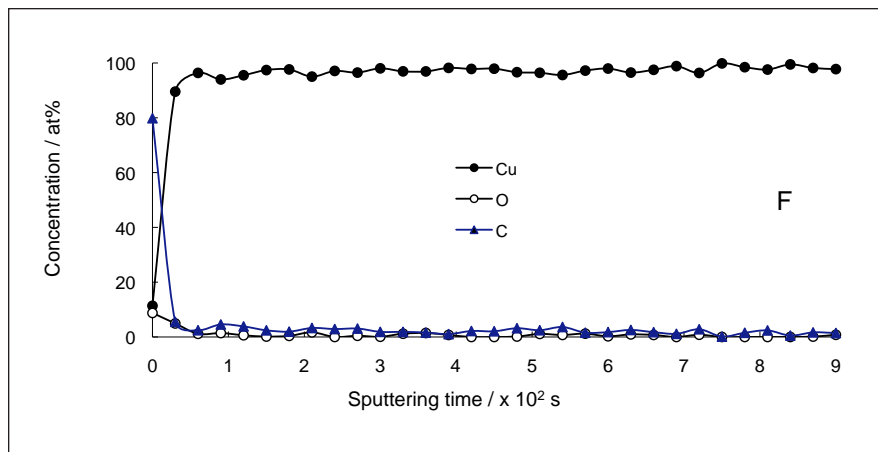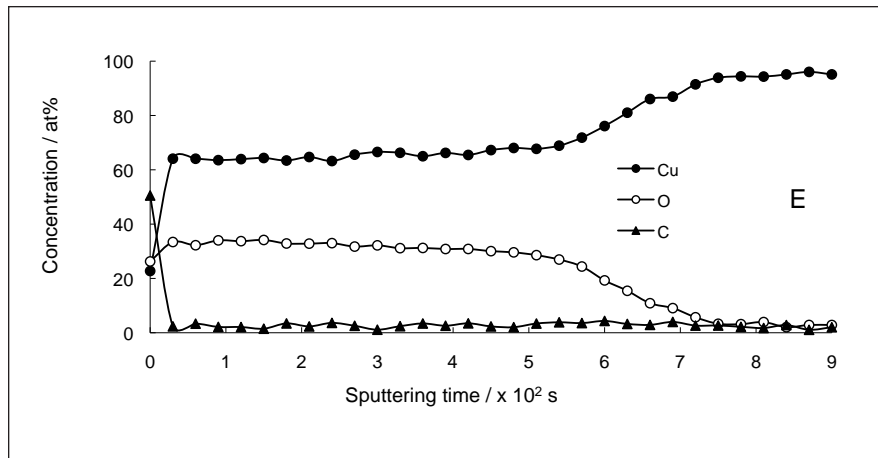
Fig.9 Depth profile of specimens by Auger electron spectrometry. Oxygen-free copper with thermal-which were heated in the air at 200ºC for 1 h and immersed in NaCl-AEW (A), HCl of pH 2.48 (B), Na$_2$SO$_4$-AEW H$_2$SO$_4$ of pH 2.48 (D) for 600 s, without immersion (E), oxygen-free copper degreased with acetone and ethanol copper degreased with acetone and ethanol and polished by sandpaper #4000 (G).

## 3. RESULTS AND DISCUSSION

3.1 Characteristics of AEW

The time course of free chlorine concentrations and dissolved oxygen concentrations in the solutions is shown in Fig.1. The concentrations of free chlorine and dissolved oxygen decreased markedly within 15 min immediately after the end of electrolysis, and stabilized relatively around 1 hour after the end of electrolysis. However, since in a manufacturing setting AEW is used immediately after its generation because of efficiency, AEW immediately after its generation was used in this study.

The properties of NaCl-AEW, Na$_2$SO$_4$-AEW, HCl and H$_2$SO$_4$ solution used in this study are shown in Table 1. Free chlorine concentrations and dissolved oxygen concentrations of AEWs are measured values 5 min after the end of electrolysis because it takes 5 min to get AEW out and to measure. Na$_2$SO$_4$-AEW exhibited high dissolved oxygen concentration and redox potential. This result shows that the increased redox potential is attributed to the high dissolved oxygen concentration. Meanwhile chlorine was generated in NaCl-AEW in concurrence with oxygen. It appears to be due to the lower chlorine overpotential compared to the oxygen overpotential in electrolysis of NaCl solution. The standard electrode potentials ($E°$, vs. SHE) for generated chlorine (1.36 V) and HOCl (1.63 V) are high, suggesting that the higher redox potential of NaCl-AEW compared to Na$_2$SO$_4$-AEW is attributed to the hybrid potential of generated chlorine and HOCl. Regarding the difference in concentrations of cations and anions, it is due to that Cl$^-$ or sulfate ions (SO$_4^{2-}$) were electrophoresed to an anode during electrolysis, resulting in the elevated concentrations of these ions in the anode chamber.

The equilibrium composition of free chlorine in NaCl-AEW shifts dependent on the pH of solution. At acidic pH a part of Cl$_2$ (aq) becomes gaseous chlorine (Cl$_2$ (g)) to yield chlorine gas. At weakly acidic to neutral pH, undissociated HOCl is formed. At weakly alkaline pH, ClO$^-$ is formed. The dissociation equilibrium is shown as equation (8). The acid dissociation constant of HOCl (pKa) is 7.5 at 25 °C [3].

$$Cl_2\ (aq) + H_2O \leftrightarrows HOCl +$$
$$Cl^- + H^+ \leftrightarrows ClO^- + Cl^- + 2H^+ \qquad \cdots (8)$$
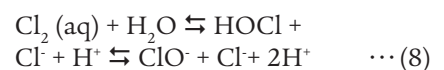
The molar concentration ratios of Cl$_2$ (aq), HOCl and ClO$^-$ at each pH are shown in Fig.2 [4]. Cl$_2$ (aq), HOCl and ClO$^-$ are held in equilibrium in NaCl-AEW. The lower the Cl$^-$ concen-

tration is, the larger the region of existence for HOCl is [5]. Since the Cl_2 (aq) concentration fulfill the equilibrium with the Cl_2 (g) concentration, the higher the Cl_2 (aq) concentration is, the higher the Cl_2 (g) concentration is. That is, the Cl_2 (aq) concentration is equilibrated with H^+ concentration in solution, while the Cl_2 (g) concentration is dependent on the Cl^- concentration and pH. Cl_2 (g) in NaCl-AEW is released to the air so that free chlorine concentration shifts to the equilibrium concentration.

3.2 Dissolution rate

The dissolution rate (n = 5) of oxygen-free copper is shown in Fig.3. The dissolution rate was 1.10 g/m² h (SD = 0.18) and 0.26 g/m² h (SD = 0.08) when oxygen-free copper was immersed in NaCl-AEW and in HCl solution, respectively. The dissolution rate in NaCl-AEW was 4.2 times faster than that in HCl solution. It is considered that free chlorine in NaCl-AEW accelerated the dissolution of oxygen-free copper, which is investigated further in section 3.3. The dissolution rate was 0.72 g/m² h (SD = 0.21) and 0.24 g/m² h (SD = 0.11) when oxygen-free copper was immersed in Na_2SO_4-AEW and in H_2SO_4 solution, respectively. The dissolution rate in Na_2SO_4-AEW is 3.0 times faster than that in H_2SO_4 solution.

The solutions, which were used for immersion of specimens and shown in Table 1, have no buffering effect, suggesting the pH of the solutions shift after immersion. Therefore the pH of the solutions was measured after specimens were immersed for 1 hour. As a result, there was no change in the pH of HCl or H_2SO_4 solution, while it was observed that the pH of NaCl-AEW and in Na_2SO_4-AEW was elevated to 2.52.

Regarding the dissolution behavior of oxygen-free copper in electrolyzed water, the measurements of the corrosion potential and the polarizing potential remain to be solved for a comprehensive discussion.
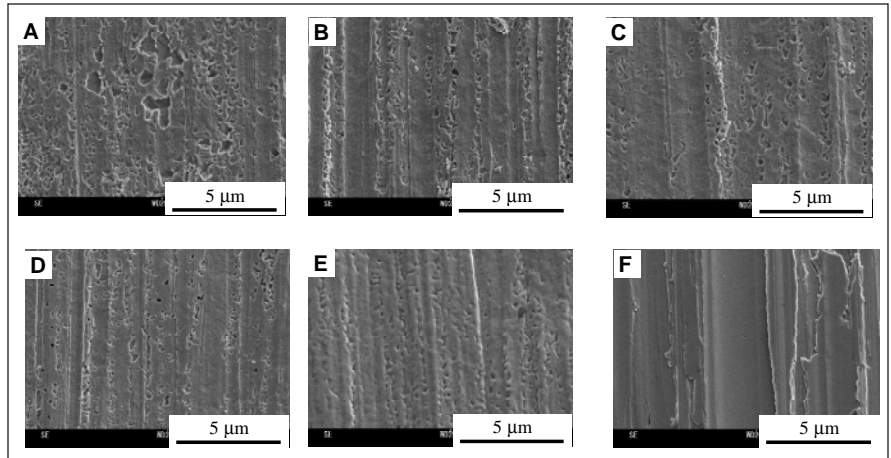

Fig. 10 SEM images of surfaces of specimens. Oxygen-free copper with thermal-oxide film, which were heated in the air at 200ºC for 1 h and were immersed in NaCl-AEW (A), HCl of pH 2.48 (B), Na_2SO_4-AEW (C) or H_2SO_4 of pH 2.48 (D) for 900 s, without immersion (E), or without heat treatment (F).
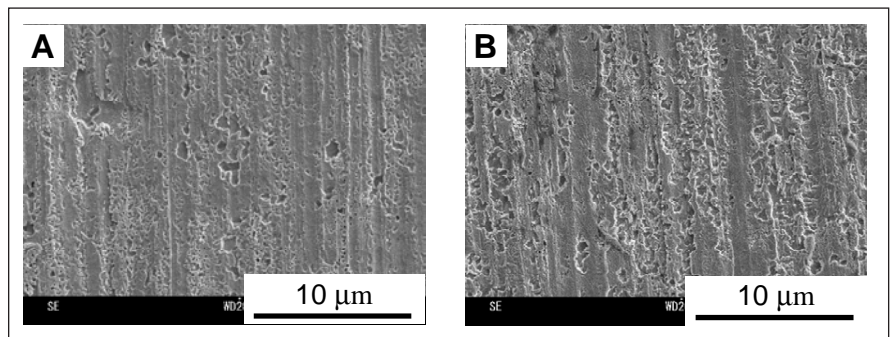

Fig. 11 Comparison of surface morphology of specimens. Oxygen-free copper with thermal-oxide film, heated in the air at 200ºC for 1 h (A) , or oxygen-free copper without heat treatment (B) was immersed in NaCl-AEW for 900 s, respectively.
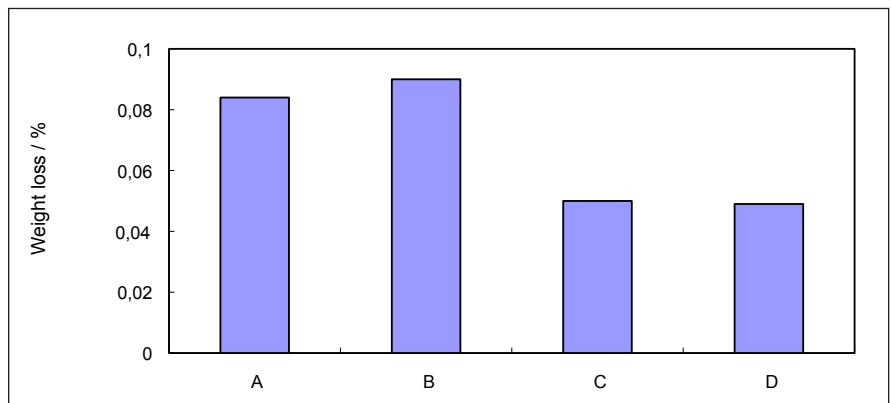
Fig. 12 Weight loss of copper with thermal oxide film, which was immersed in NaCl-AEW (A), Na_2SO_4-AEW (B), 2.48 (C) or H_2SO_4 of pH 2.48 (D) for 600 s.

3.3 Effect of free chlorine

The surface SEM images of the specimen immersed in NaCl-AEWs, when the free chlorine concentrations were prepared at 1.6×10^{-3} and 3.9×10^{-3} mol/dm³, for 15 min are shown in Fig.4. The specimen surface was roughened in a more concavo-convex shape with an increase in the free chlorine concentration.

The relationship between free chlorine concentration and dissolution rate of oxygen-free copper in NaCl-AEW is shown in Fig. 5. The dissolution rate increased with increase in the free chlorine concentration. The relationship

between free chlorine concentration and the surface roughness of the specimen in NaCl-AEW is shown in Fig. 6. The surface roughness increased along with the increase in free chlorine concentration. These results show that free chlorine dissolves oxygen-free copper surface in a concavo-convex shape and elevates the dissolution rate and surface roughness.

The effect of the pH on the dissolution rate of oxygen-free copper when free chlorine exists in the NaCl-AEWs is shown in Fig. 7. The free chlorine concentration was 1.0×10^{-3} mol/dm³ for each AEW. The dissolution rate increased with a decrease in the pH of AEW and maintained nearly constant when AEW was in neutral and alkaline regions. It was found that oxygen-free copper dissolved even in these regions.

The surface appearances of the specimens immersed in NaCl-AEWs at pH of 2.20 and 4.60, when the respective dissolution rates were 1.28 and 0.22 g/m² h, for 15 min were observed. The surface SEM images of the specimens are shown in Fig.8. When a specimen was immersed in the former, the roughening of the surface in a concavo-convex shape increased compared to that in NaCl-AEWs at pH of 2.48 (refer to Fig.4A). The hydrogen ion concentration was elevated by the added HCl to lower the pH value, resulting in the increase in the concentration of Cl_2(aq) (refer to the equation (6)). As a result, roughening of the surface was accelerated. The pH of NaCl-AEW shifted from 2.20 to 2.30 after immersion, suggesting that it is due to the progress of dissolution. Meanwhile, when a specimen was immersed in the latter with a pH of 4.60, nearly all of free chlorine existed as HOCl. The roughening of the surface in a concavo-convex shape did not occur significantly, nor was found the shift of the pH.

Moreover, when free chlorine in the generated NaCl-AEW was removed by the addition of ascorbic acid (50

mmol/dm³), the appearance of oxygen-free copper immersed in the solution was similar to that in the HCl as previously described (not shown). The dissolution rate was 0.23 g/m² h, which is almost the same as that in the HCl.

From these results, it was found that free chlorine in NaCl-AEW increased the dissolution rate and had an effect on oxygen-free copper to metamorphose its surface in a concavo-convex shape. This phenomenon is also observed when iron or nickel are immersed in NaCl-AEW [6, 7].

3.4 Effect of sulfate ions

To investigate the effect of the total sulfate ions on the dissolution rate of oxygen-free copper, H_2SO_4 at pH 2.48 with a sulfate ions concentration of 0.1 mol/dm³ was prepared by adding Na_2SO_4 to the solution, and then the dissolution rate was measured in the resulting solution. As a result, the dissolution rate was 0.24 g/m² h, which is identical to that in the H_2SO_4 at pH 2.48. Therefore the result shows that sulfate ions do not have an effect on the dissolution rate.

3.5 Effect of dissolved oxygen

The dissolution rates of oxygen-free copper in Na_2SO_4-AEW and H_2SO_4 solution with the same pH and different dissolved oxygen concentrations are shown in Table 2. The dissolution rates were equal for Na_2SO_4-AEW and H_2SO_4 solution with a dissolved oxygen concentration nearly equal to the saturation concentration. The dissolution rates were equal for Na_2SO_4-AEW immediately after generation and H_2SO_4 solution with an increased dissolved oxygen concentration of 6.3×10^{-4} mol/dm³. Moreover, the dissolution rate decreased with the decrease in dissolved oxygen with the progress of time in Na_2SO_4-AEW, and increased with the increase in dissolved oxygen in the H_2SO_4 solution (not shown). The $E°$(vs. SHE) for copper and oxygen are 0.34 V and 1.23 V, respectively, so oxygen-free copper is dissolved with the consumption of oxygen in acidic solutions. The results show that the increased dissolution rate in Na_2SO_4-AEW is due to dissolved oxygen.
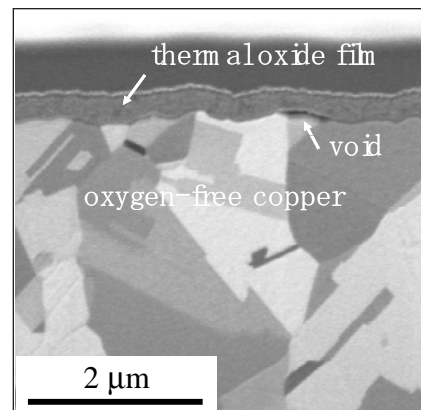

Fig. 13. SIM of thermal-oxide film milled by FIB.

3.6 Surface analysis of underlaying copper after dissolved thermal-oxide film

The result of the Auger electron spectroscopy analysis of the surface of underlaying copper after a thermal-oxide film was dissolved is shown in Fig. 9. It was found that copper oxide was thickly-formed on the specimen with thermal-oxide film (E). Formation of natural-oxide film was observed on the top of the specimen degreased with acetone and ethanol (F). Oxygen was observed on the top of the specimen (G), which was prepared from specimen (F) by polishing with sandpaper to remove natural-oxide film, suggesting that the natural-oxide film was formed immediately after polishing. The thickness of the natural-oxide film was equal for specimens (F) and (G), so specimens with natural-oxide film used in this study were substantially reproducible.

When specimens were immersed in NaCl-AEW (A) and in HCl (B), the oxygen concentration decreased from the topmost surface to the bulk layer and the copper concentration increased contrastingly. A strong peak of oxygen appeared on the uppermost surface in either case, which is assigned to natural-oxide film formed on the undelaying copper surface after removal of thermal-oxide film. Also, the significant peak of oxygen was attenuated by the sputtering time of about 60 seconds in each case. The etching speed of copper by Argon sputtering in Auger electron spectroscopy analysis is 88 nm/min [9], suggesting that oxygen

diffused as deep as 88 nm. The profiles of oxygen concentration for specimens (A) and (B) are similar to those for specimens (F) and (G), suggesting that the oxidation states of specimens (A) and (B), when the thermal-oxide film was removed, are similar to those of specimens (F) and (G) with the natural-oxide film. The results of specimens (C) and (D), which were immersed in Na_2SO_4-AEW and H_2SO_4 solution, were similar to those of specimens (A) and (B).

3.7 Surface observation of underlaying copper after dissolved thermal-oxide film

SEM images of the specimen are shown in Fig. 10. Because the brass color of thermal-oxide film was not observed to the naked eye, the SEM images are the bulk surface of the specimens after both the thermal-oxide film and the underlaying copper were dissolved and removed by the immersion. When a specimen was immersed in NaCl-AEW (A), its surface morphology undergoes a change in a significant concavo-convex shape. When specimens were immersed in HCl (B), Na_2SO_4-AEW (C) and H_2SO_4 solution (D), smaller concave dissolutions (pitting corrosion), compared to (A), were found in each case. The difference in surface morphology of specimens with and without thermal-oxide film after immersed in NaCl-AEW is shown in Fig.11.

3.8 Dissolution loss of thermal-oxide film

The dissolution loss in NaCl-AEW and Na_2SO_4-AEW was approximately 1.7 times larger that that in HCl and H_2SO_4 solutions at the same pH (Fig. 12). AEW may easily dissolves thermal-oxide film. To examine this phenomenon, thermal-oxide film was milled by FIB and then the SIM image of its cross-section surface was observed. As shown in Fig. 13, it was found that thermal-oxide film was not a dense coat. In addition, a void on the boundary of copper was observed, suggesting that the adhesiveness between the thermal-oxide film and copper is weak. It is demonstrated that oxygen nanobubbles with a diameter of several dozen nm exist stably in AEW[10]. Moreover, it is also shown that hydrogen ions tend to concentrate on the gas-liquid interface of oxygen nanobubbles [11]. The dissolution and removal of thermal-oxide film is due to the dissolution of copper oxide by hydrogen ions and etching of underlaying copper.

3.9 Use of AEW alt. to HCl and H_2SO_4

These results show that AEW is a more oxidative solution than HCl and H_2SO_4 solutions at the same pH and dissolution rate for AEW is larger than those for HCl and H_2SO_4 solutions. It is proposed that AEW is likely to be used for etching of oxygen-free copper surface. Furthermore, the oxidative state of the surface of underlaying copper after removal of thermal-oxide film is identical to that of copper with natural-oxide film. This suggests that AEW is likely to be used for pretreatment, such as scaling and rust removal, as an alternative to HCl and H_2SO_4 solutions. In addition, it would appear that roughening of the oxygen-free copper surface treated with NaCl-AEW, as shown in Fig. 11, may improve the adhesiveness of plated films.

Cathodically electrolyzed water, which is simultaneously generated on electrolysis, exhibits a redox potential of -700 mV (vs. SHE) and a pH of approximately 11.5. Cpper under the above-mentioned condition appears in the region of immunity in the Pourbaix Diagram [12], and is not eroded unless corrosive ions coexist. Although cathodically electrolyzed water of NaCl or Na_2SO_4 contains chloride ions or sulfate ions, when the concentrations of these ions are low, copper almost never erodes by the immersion of these solutions. It was shown that corrosion did not occur when iron was immersed in cathodically electrolyzed water of sodium carbonate [13]. Therefore, it is thought that a stepwise method, which consists of acid treatment using AEW followed by anti-corrosive treatment by the immersion in cathodically electrolyzed water, may be possible.

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