Environmental-friendly electrolyzed water and its application for metal surface treatment

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Abstract

Anode water (acidic electrolyzed water, AcEW) and cathode water (alkaline electrolyzed water, AlEW), which are produced from dilute electrolyte solutions by electrolysis, are referred to as electrolyzed water (EW). In this review, the principles of generation of EW and characteristics of AcEW and AlEW are described; and its use and application for surface treatment of metals are introduced. AlEW can be used for degreasing and rinsing metal surfaces, which shows equal precision cleaning performances compared to conventional methods that use detergents. AcEW can be used for removing and etching oxidized layers of metal surfaces and roughing of metal surfaces. The use and application of EW for surface treatment of metallic materials are promising.

1. Introduction

Electrolyzed water (EW) is a generic name for aqueous solutions produced from dilute electrolyte solutions by electrolysis [1]. EW has been used in the medical and hygiene fields and has been increasingly used in the industrial fields in recent years. In the past, organic solvents were used for degreasing metal parts; however, recently aqueous cleaning agents consisting primarily of surfactants replaced them. Furthermore environmental-friendly alkaline electrolyzed water (AlEW) is used as non-toxic and easy-to-use cleaning agents instead of surfactants. Meanwhile inorganic acids, such as hydrochloric acid and sulfuric acid, have been used for the removal of rust on the metal surfaces; and acidic electrolyzed water (AcEW) is used as an alternative. In this review, I illustrate the characteristics of EW and describe its application for metal surface treatments, such as degreasing, rinsing, removal of oxidized layers and etching metallic materials, using its characteristics.

2. The generating principles and characteristics of EW

Anode water and cathode water are generated from an electrolyte solution in an anode chamber and a cathode chamber, respectively, by electrolysis using a diaphragm type electrolytic device. Sodium chloride (NaCl) is commonly used as an electrolyte for the generation of electrolyzed water. In the anode chamber, oxygen and hydrogen ions are generated by the oxidation of water, and chlorine by oxidation of chloride ions. Chlorine reacts with water to yield hypochlorous acid (HOCl) and hydrochloric acid (HCl). As a result, anode water is acidified; and its oxidation reduction (redox) potential (ORP) increases significantly. Meanwhile, in a cathode chamber, water and dissolved oxygen are reduced to yield hydrogen and hydroxide ions; and cathode water becomes alkaline. Cathode water shows an increased dissolved hydrogen concentration and a decreased dissolved oxygen concentration simultaneously; and its ORP decreases significantly. Reactions that occur at the anode and the cathode during electrolysis are shown as equations (1) – (5). When sodium sulfate (Na_2SO_4) is used as an electrolyte, chlorine is not generated in the anode chamber; and only equation (1) occurs, resulting in an elevated dissolved oxygen concentration.

[Anode] $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ ··· (1)

$2Cl^- \rightarrow Cl_2 + 2e^-$ ···(2)

$Cl_2\ (aq) + H_2O \leftrightarrow HCl + HClO$ ···(3)

[Cathode] $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ ···(4)

$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ ···(5)

The characteristics of AcEW and AlEW were obtained using NaCl or Na_2SO_4 as electrolytes (referred to as NaCl AlEW, AlEW or Na_2SO_4 AcEW, AlEW) and are shown in Table 1. The ORPs of AcEW are higher than those of acid solution at the same pH; and those of AlEW are lower than those of the alkaline solution at the same pH. NaCl AcEW shows an elevated ORP because of the formation of chlorine and hypochlorous acid. Na_2SO_4 AcEW, which consists of no chlorine, shows an elevated ORP because of an increased dissolved oxygen concentration. AlEW shows a negative ORP that is lower than that of sodium hydroxide (NaOH) solution at the same pH. The characteristics of EW are as follows: HOCl, which is thermodynamically unstable in aqueous solutions, can be formed by electrolysis; acidic and alkaline solution can be formed electrochemically without using dangerous acids or alkaline; and therefore the work procedure is safe.

Table 1 Characteristics of electrolyzed water

	pH	Redox Potential mV vs.SHE	Dissolved Oxygen mg/dm^3	Dissolved Hydrogen mg/dm^3	Free chlorine mg/dm^3
Na_2SO_4-AcEW	2.5	850	>20	0	0
NaCl-AcEW	2.5	1300	15	0	20-60
Sulfuric acid Hydrochloric acid	2.5	750	8	0	0
Na_2SO_4-AlEW	11.5	-450	4	1.5	0
NaCl-AlEW	11.5	-450	4	1.5	0
Sodium hydroxide	11.5	290	8	0	0

An electrolytic cell to generate EW consists of an anode chamber and a cathode chamber, which are separated by means of a diaphragm (diaphragm type electrolytic cell). Electrodes are made of titanium coated with platinum. In the industrial field, the diaphragm and flow type electrolytic apparatuses that have a generation capacity of 2 – 3 L/min are commonly used. The appearance of the apparatus [2] is shown in Figure 1; and the conceptual diagram of flow type electrolysis in Figure 2. AcEW generated from a typical electrolytic apparatus has a free chlorine concentration of 30 – 50 mg/L. Demerits of AcEW are a generation of chlorine gas at anode during electrolysis which causes metal to corrode and a deterioration of working environment by smell of chlorine. Improvement of these demerits is accomplished by high-voltage electrolysis [3]. It adapted an increased current density so that the NaCl concentration can be decreased to as low as 0.01 %, resulting in a free chlorine concentration of 5 mg/L. Because chlorine gas is not generated, the corrosion of metal and the working environment are improved, so this electrolytic apparatuses are frequently used for degreasing, rinsing and surface treatment of metallic materials for precise electrical parts [4, 5].

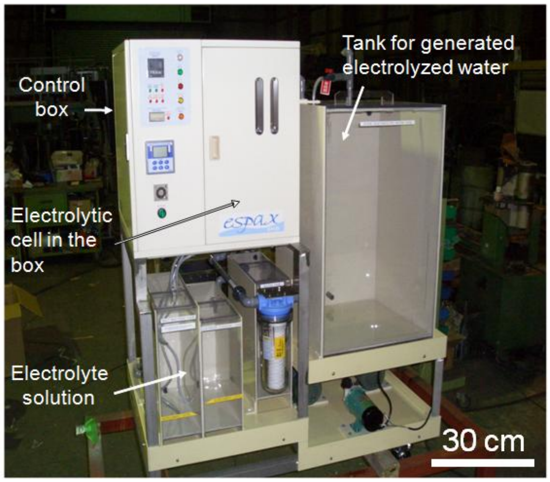

Fig. 1 EW generating system (Espax, JIPCM [2])

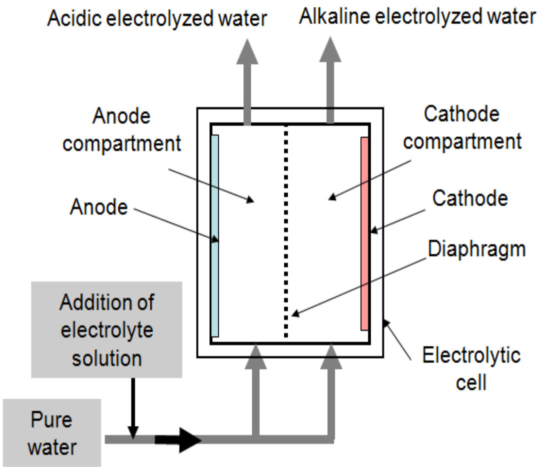

Fig. 2 Conceptual diagram of flow type electrolysis

3. Potential-pH diagram for the Fe-H_2O system

Regarding the stability of metal in pure water, Pourbaix diagrams [6] are useful. Potential-pH for the six solutions (shown in Table 1) is superposed on a potential-pH diagram for the Fe-H_2O system (Figure 3).

A dashed line *a* represents an equilibrium potential for oxygen generation, which is expressed as $EO_2 = 1.23 - 0.059\text{pH}$. A dashed line *b* represents an equilibrium potential for hydrogen generation, which is expressed as $EH_2 = -0.059\text{pH}$. Water is stable within a region between line *a* and line *b*; oxygen is generated at a higher potential than line *a*; and hydrogen is generated at a lower potential than line *b*. 1 in Figure 1 represents potential-pH for the NaCl AcEW, 2 for Na_2SO_4 AcEW, 3 for hydrochloric acid and sulfuric acid at pH 2.5, 4 for NaOH solution at pH 11.5, 5 for NaCl AlEW, and 6 for Na_2SO_4 AlEW, respectively (for the potential-pH for 1 – 6, refer Table 1).

The potential-pH for AcEW lies on the corrosion region for iron, therefore iron dissolves. Meanwhile the potential-pH for AlEW lies on the passivity region for iron, therefore iron does not corrode. Even though ORP is low, corrosion occurs at a pH above 14. NaCl and Na_2SO_4 AlEW consist of chloride ions and sulfate ions, respectively; and when iron is immersed in those solutions at low ion concentrations corrosion is less likely to occur. When iron is immersed in Na_2CO_3 AlEW corrosion does not occur.

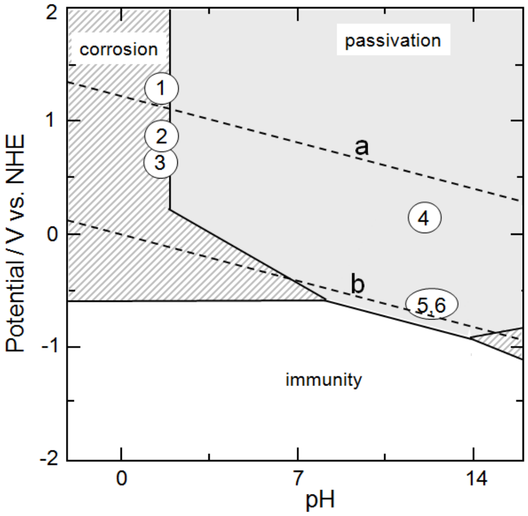

Fig. 3 Pourbaix diagrams of iron superposed with potential-pH for the six solutions.

Refer the number 1 – 6 to table 1.

4. Characteristics of AlEW and its use

4.1. Degreasing

One of the characteristics of AlEW is degreasing action. Degreasing oxygen-free copper which was contaminated with machine oil was tested. AlEW, NaOH solution at the same pH as AlEW (11.5), and pure water were used as cleaning liquids; and the metal was spray-washed with heated cleaning liquids followed by a rinsing with pure water then drying. The cleaning properties of those cleaning liquids are compared with that of organic solvent and surfactant, which are used in conventional specifications. The results are shown in Figure 4. Degreasing with AlEW shows that the residual oil content and residual ion content are equal to those of conventional specifications, suggesting it is able to apply precision cleaning [7]. The result of surface analysis shows that oxidation of oxygen-free copper does not occur by degreasing with AlEW.

The mechanism of degreasing metal with machine oil by AlEW appears to be the following: grease is hydrolyzed by alkaline to yield soap, which acts as a surfactant and form micelles to emulsify mineral oil that is hydrocarbons. Furthermore spraying heated AlEW plausibly removes oil layer by the pressure of spraying because of lowered oil viscosity by heat, resulting in an increased cleaning property. In comparison with NaOH solution to AlEW at the same pH, the latter shows an increased cleaning property. The degreasing mechanisms of AlEW appear to consist of saponification by alkaline and pressure of spraying, as well as hydrogen nano-bubbles [8] generated by electrolysis, which may increase the degreasing efficiency.

The higher the pH of AlEW, the more efficacious is its' degreasing effect; and therefore a generation device of AlEW at pH of more than 12 is commercially available. However, such AlEW is associated with some risks due to a high pH, so AlEW may be used at a pH of less than 12 in light of safety. Alternatively, there can be a method to use diluted AlEW at a pH of 13, which is stored in a plastic container, and used as needed; however, stored AlEW, in which hydrogen nano-bubbles disappear, has the same characteristics with the NaOH solution at the same pH; and therefore the effect of hydrogen nano-bubbles cannot be expected. Furthermore, AlEW at a pH of 13 is also associated with some risks due to a high pH.

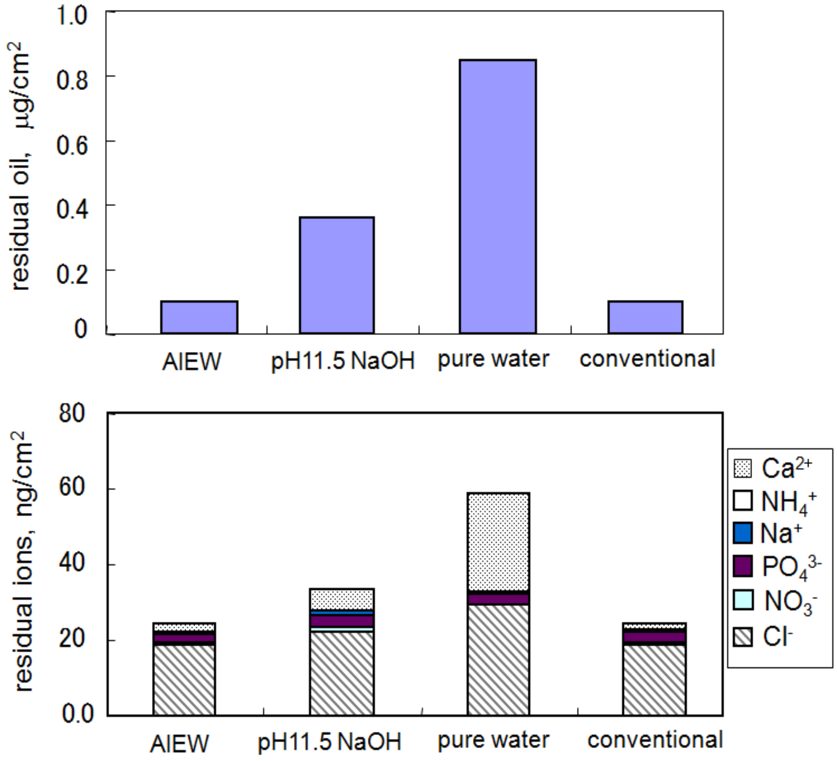

Fig. 4 Comparison of residual oil content and residual ion content on the copper surface by several cleaning liquids

4.2. Rinsing

In addition to the degreasing effect, AlEW has a rinsing effect, that is, an effect to remove fine particles and surfactants from the surface of cleansed objects [9]. The rinsing effect is attributed to the alkalinity of AlEW, as well as hydrogen nano-bubbles that enhance the cleansing effect on the cleansed objects and the fine particles on their surface. It is explained that hydrogen nano-bubbles in AlEW adhere onto the fine particles, resulting in an induction of a physical peel force to separate them from the cleansed objects [10]. Furthermore, the surface potential of fine particles has a large negative value in alkaline solutions, so it is explained that detached fine particles repel each other, as well as to the cleansed objects, and disturb re-adherence to the surface [11]. It is explained that the effect of AlEW on removal of anion surfactants is attributed to hydrogen nano-bubbles by the same mechanism as the removal of fine particles. It is speculated that when cleansed objects with remaining anion surfactants are immersed in AlEW, hydroxyl ions adhering on hydrogen nano-bubbles surfaces are selectively substituted to anion surfactants via an ion exchange reaction, as a result, anion surfactants on the cleansed objects are detached. It is explained that detached anion surfactants repel to negatively charged hydrogen nano-bubbles, and thus do not re-adhere to the surface of cleansed objects, resulting in the efficient rinsing and washing. A pattern diagram of rinsing is shown in Figure 5. In this way, it is reported that the use of AlEW significantly reduces the amount of pure water usage for rinsing when surfactants are rinsed [12]. In case of degreasing, AlEW can be re-used until its pH decreases; however, in case of rinsing, AlEW is effective without recycling because the effect is due to hydrogen nano-bubbles. A similar phenomenon occurs when rinsing sulfuric ions, which tend to remain on the electro-plated surfaces.

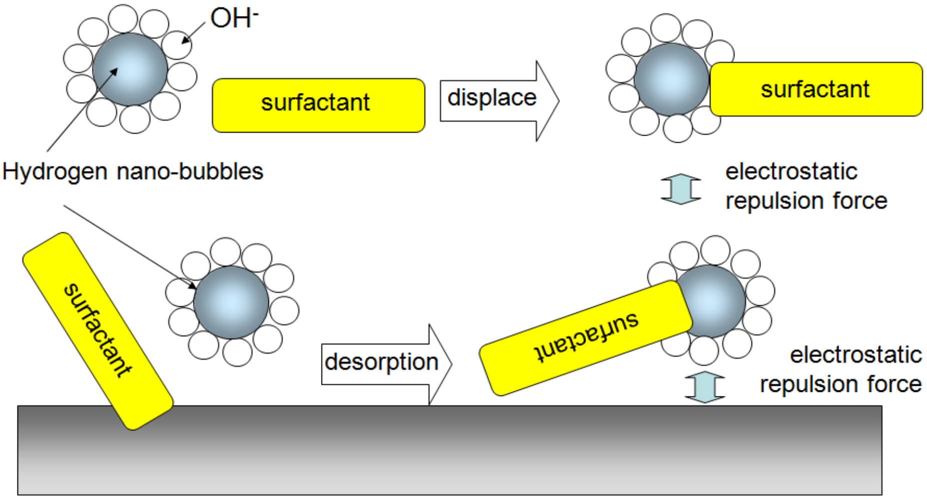

Fig. 5 A pattern diagram of rinsing surfactants by hydrogen nano-bubbles.

More than ordinary rinsing using pure water, AlEW of dilute potassium carbonate aqueous solution exhibits a stronger rinse effect for elimination of remaining sulfate ions when rinsing nickel-plated surfaces. This rinse effect was recognized even for AlEW that was used 24 h after it was produced, but not 1 week after. Behaviors of hydrogen nanobubbles observed by dynamic light scattering revealed nanobubbles of about 128-nm diameter even 24 h after generation. The Ostwald ripening phenomenon was observed. Hydrogen nanobubbles in an open system changed: some shrank because of ripening, later dissolving in the aqueous solution and disappearing; others showed swelling and expansion. One week later, few nanobubbles smaller than 300 nm were observed. Rinse effects by AlEW, which are attributable to the actions of hydrogen nanobubbles generated in AlEW, occur because sulfate ions are cleaned and removed from the nickel-plated surface [13].

4.3. Cutting

When metal materials are cut, cutting fluids are generally used. However, because cutting fluids consist of various ingredients they are collected and disposed by waste disposal companies. And cut surfaces are contaminated with cutting fluids, so the metal materials should be cleansed with organic solvents. However, organic solvents are highly volatile and have adverse effects on environmental health, so a reduction in use of organic solvents is required. Recently, in order to resolve these problems, AlEW has been used as an alternative to cutting fluids [14 – 16]. AlEW has a superior cooling effect compared to oil; and thus the cutting temperature can be kept low. Furthermore, AlEW can prevent high-temperature oxidation and corrosion of cutting surfaces, and has a distinct advantage of not corroding the cutting facility. In addition, AlEW has a degreasing effect as described in the section 4.1., so the cutting surface that is cut with AlEW has an unadulterated surface. AlEW used for cutting is generated from potassium carbonate as an electrolyte and does not consists of corrosive ions, so metal does not corrode even when left unwashed. Waste of AlEW after use can be disposed of as it is after oil-water separation, suggesting that it may reduce the production costs and enhance the production efficiency.

Occasionally, grease can be added to AlEW to improve the lubricating effect. Grease is saponified by AlEW to yield soap and glycerin, which enhance the lubricating effect. A cutting fluid based on AlEW added with grease has a less greasy content than conventional aqueous cutting fluids and does not consist of other ingredients like anti-corrosion agents, suggesting that it makes the waste water treatment easier. It is expected that AlEW will be used as a cutting fluid from the viewpoints of improvement of cleanliness of cutting surfaces and a reduced cost of liquid waste treatment for cutting fluids. In addition, AlEW at a pH of 12 – 13 is sometimes used in mixtures to prevent cutting fluids from emitting a putrefactive odor. It is due to the death of microorganisms that cause the putrefactive smell at a pH of more than 12. AlEW of sodium silicate is used for processing and degreasing aluminum materials [17]. Aluminum is an amphoteric metal and corrodes in both acidic and alkaline solutions; however, it does not corrode in AlEW of sodium silicate. It may be attributed to the formation of passive layers of silicate salts on the aluminum surface.

5. The characteristics of AcEW and its application

5.1. Removing oxidized metal layers

AcEW, which has the same effects of acid, is able to dissolve and remove oxidized layers of metal and to etch the under layers of metal surfaces. Oxygen free copper was heated in the atmosphere to form thermally-oxidized layers and used as test specimens, followed by the immersion in NaCl AcEW and hydrochloric acid solution at the same pH; and then the change of their surfaces was studied by Auger electron stereoscopy depth-profile elemental analysis. As a result, both specimens showed a significantly reduced intensity of oxygen, suggesting that thermally-oxidized layers were removed. The oxidation state of the underlying surface of treated oxygen free copper whose thermally-oxidized layers were dissolved and removed is nearly equal to that of surface of oxygen free copper that has naturally-oxidized layers.

Iron specimens were prepared as the same way, immersed in NaCl AcEW and surface analysis was performed [18]. The result showed that thermally-oxidized layers were dissolved and removed and the oxidation state of surface of treated iron is nearly equal to that of surface of iron without thermal treatment. The SEM (Scanning Electron Microscopy) images of iron specimens before and after the immersion of NaCl AcEW are shown in Figure 6. The result confirmed that the surface of iron whose thermally-oxidized layers were removed is finely roughened.

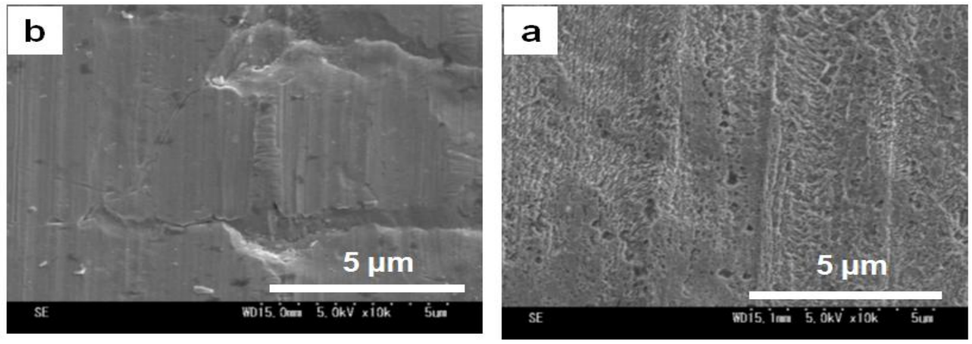

Fig. 6 SEM images of iron surface as sintered before immersion (b),
and dissolved oxidized film after immersion in NaCl AcEW (a).

The dissolution and removal of oxidized layers were also observed using Na_2SO_4 AcEW, as well as hydrochloric acid and sulfuric acid at the same pH. Because the oxidation state of the surface of underlying copper and iron whose thermally-oxidized layers were dissolved and removed by AcEW is nearly equal to that of surface of copper and iron that have naturally-oxidized layers, it is suggested that AcEW can be used for pretreatment, such as scaling and removing rusts, as an alternative to hydrochloric acid and sulfuric acid.

5.2.Metal etching

Copper foils were electro-plated with copper 1 µm in thickness and used as test specimens. They were immersed in NaCl AcEW and hydrochloric acid at pH of 2.5; and their appearances were studied by SEM [19]. The results are shown in Figure 7.

When specimens were immersed in hydrochloric acid, dissolution was observed from the crystal grain boundary, however in NaCl AcEW a significant pitting corrosion occurred. Nickel plates were studied as the same way, and as shown in Figure 8 a significant pitting corrosion occurred in NaCl AcEW.

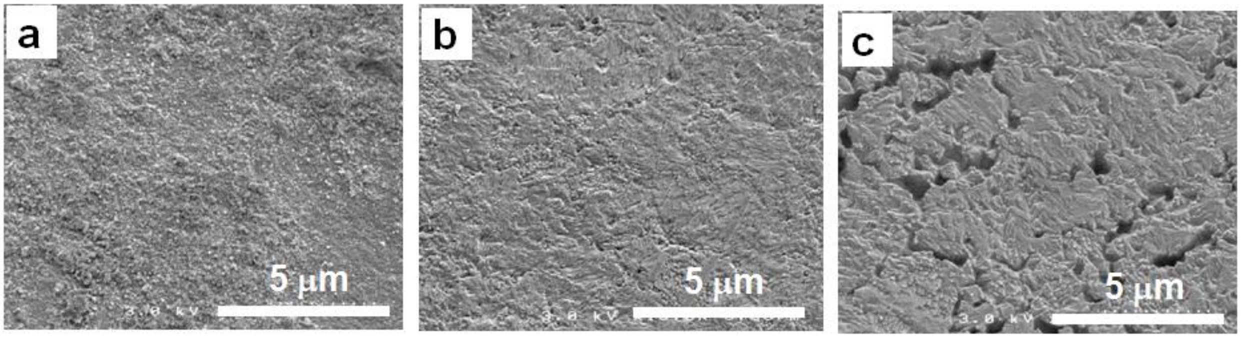

Fig. 7 SEM images of copper electro-plated surface before immersion (a), immersed in pH 2.5 HCl solution (b), and in NaCl AcEW (c).

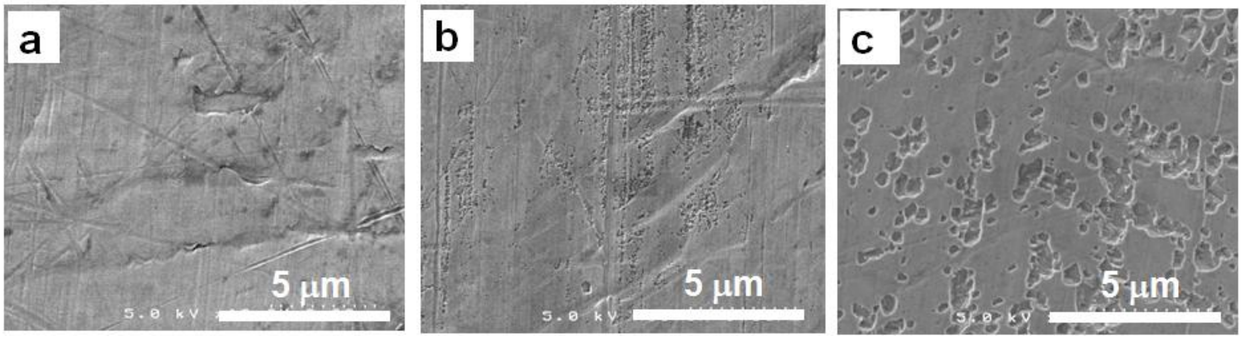

Fig. 8 SEM images of nickel plate surface before immersion (a), immersed in pH 2.5 HCl solution (b), and in NaCl AcEW (c).

As just described, when NaCl is used as an electrolyte, free chlorine generated in anode etches metal surfaces to form convex-concave surfaces (pitting corrosion). Roughening metal surfaces is possible using pitting corrosion by free chlorine in NaCl AcEW. SEM images of electrolytic copper plating surfaces that is sprayed with NaCl AcEW are shown as examples, in Figure 9. The images show that convex-concave surfaces are uniformly formed. The increase in adhesiveness of electro-plated films coated on the surface may be attributed to roughening metal surface.

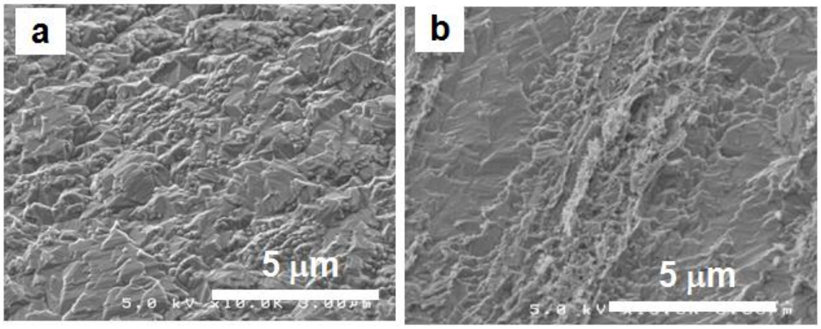

Fig. 9 Surface morphology of electro-plated copper (a) and copper plate (b) etched with NaCl AcEW of 40℃ by spraying.

Although Na_2SO_4 AcEW does not roughen a metal surface like NaCl AcEW, it shows a higher metal dissolution rate than sulfuric acid at the same pH. Figure 10 shows that the dissolution rate of copper in Na_2SO_4 AcEW is three times more than those in sulfuric acid and hydrochloric acid. This phenomenon may be due to the oxidation by dissolved oxygen, which is oversaturated in Na_2SO_4 AcEW.

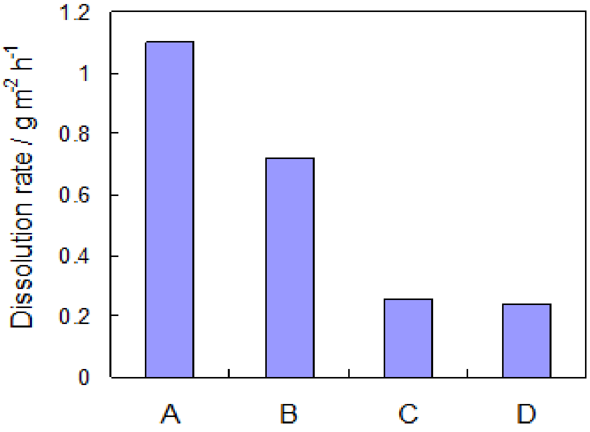

Fig. 10 Dissolution rate of copper immersed in (a) NaCl AcEW,
(b) Na_2SO_4 AcEW, (c) pH 2.5 HCl, or (d) pH 2.5 H_2SO_4.

As discussed above, AcEW is more oxidative solution and has a higher dissolution rate of copper compared to hydrochloric acid and sulfuric acid at the same pH. This characteristic suggests that AcEW has a possibility of the use for etching metal surface.

5.3. Application for circuit boards

AcEW has functions described in sections 5.1 and 5.2. Because of those functions, it is used in the manufacturing processes of circuit boards (substrates for electronic components with copper circuit wiring) and copper clad laminated boards (substrates without copper circuit wiring) as described below, and has an effect on their cleaning.

1) dissolution and removal of ground copper fine powder after mechanical polishing of copper clad laminated board surfaces
2) dissolution and removal of finger prints and oxide films on copper clad laminated board surfaces
3) rinsing residual chemicals after chemical polishing with a mixture of sulfuric acid and hydrogen peroxide solution
4) minute roughening for copper surface alternative to conventional mixture of sulfuric acid and hydrogen peroxide solution
5) removal of development residues of photopolymer for copper circuit wiring formation
6) cleaning electro-plated surfaces

The use of AcEW in the process of photopolymer development residue is shown in Figure 11 and the treatment tank for AcEW in Figure 12. Recently, an apparatus with AcEW in the copper circuit wiring formation process of the circuit board [20] has been achieved.

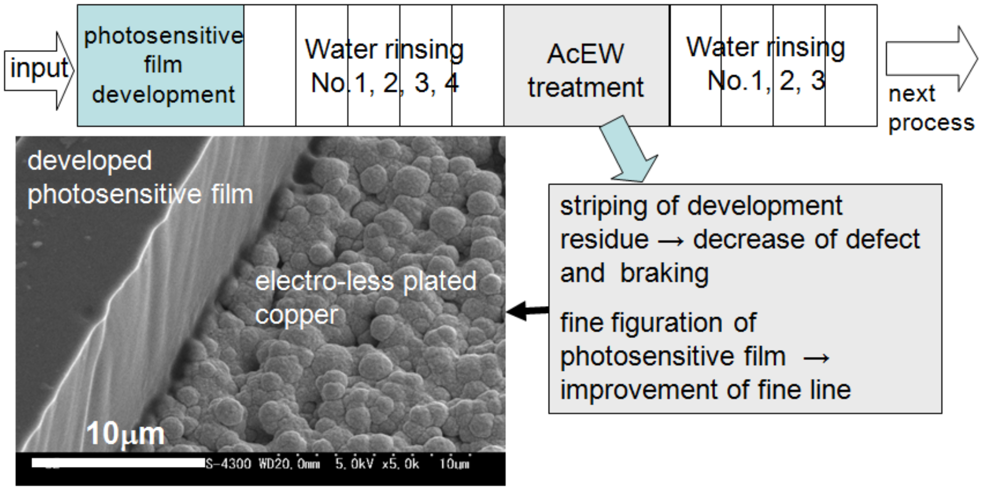

Fig. 11 Process of photopolymer development used by AcEW.

Fig. 12 A treatment tank for AcEW in the process of photopolymer development residue.

6. Conclusions

In the degreasing process for metal materials, degreasing with AlEW achieve the same cleanness equal to other conventional methods with cleansing agents and can be applied to precision cleaning. Furthermore, AlEW is able to rinse surfactants and fine particles, and this rinsing activity is due to hydrogen nano-bubbles in AlEW. Meanwhile, AcEW is able to remove oxidized layers and etching and can be used as an alternative for pretreatments using inorganic acid and is applicable to other surface treatments. In addition, Na_2SO_4 AcEW has a higher dissolution rate than sulfuric acid at the same pH; and NaCl AcEW roughens metal surfaces by free chlorine. Using the forgoing characteristics, AcEW achieved satisfactory results in the application of circuit boards. AcEW and AlEW is promising in a wide variety of use and application in manufacturing processes for precision electronic parts as in Figure 13.

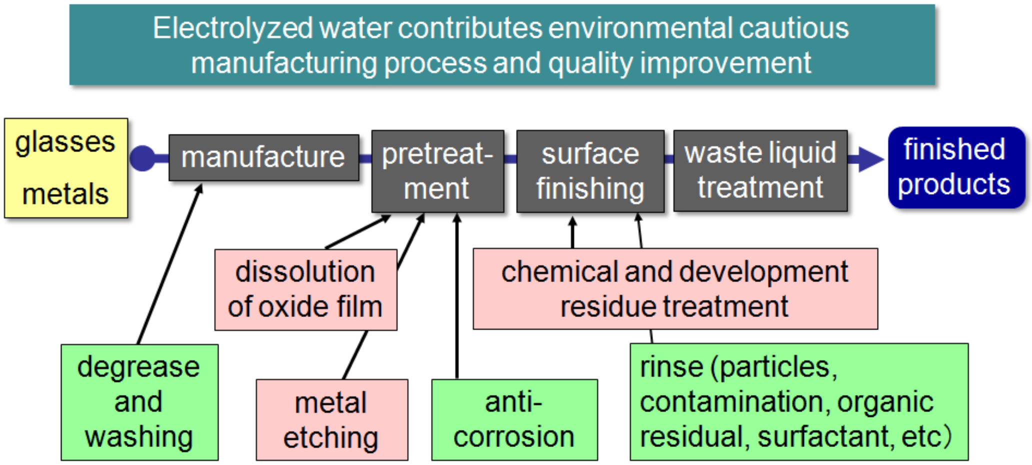

Fig. 13 Utilization and application of electrolyzed water for manufacturing process.

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