Formation of Zincate Films on Binary Aluminum Alloys and Adhesion of Electroless Nickel-Phosphorus Plated Films

Koji Murakami¹, Makoto Hino¹, Masashi Ushio², Daichi Yokomizo²,³ and Teruto Kanadani²

¹Industrial Technology Research Institute of Okayama Prefectural Government, Okayama 701-1296, Japan
²Faculty of Engineering, Okayama University of Science, Okayama 700-0005, Japan

The formation of zincate films and the adhesion of electroless nickel-phosphorus plated films on binary aluminum alloys of Al–2 at% Mn, Al–2 at% Fe, Al–2 at% Cu, Al–2 at% Zn and high-purity aluminum (99.999 mass%) were studied. The precipitation mode of zinc during the zincate treatments significantly varied according to the alloying elements in the substrates. For the first and second zincate treatments of Al–Mn, Al–Fe and high-purity aluminum, the zinc excessively precipitated, then porous films of zinc repeatedly fell off the substrate. The surfaces of the Al–Cu and Al–Zn alloys were immediately coated by uniform zincate films during the first and the second zincate treatments. The precipitation of zinc is considered to be uniform if the oxide film on a substrate uniformly and rapidly dissolves in the zincate solution. When an electroless nickel-phosphorus plating was conducted after the second zincate treatment of the Al–Mn and Al–Fe alloys, the plated films easily peeled off. Those on the Al–Cu and Al–Zn alloys showed excellent adhesion, and dimple patterns of the substrates were observed on the partly peeled areas. The poor adhesion is thought to be caused due to the fact that the excess zinc dissolves at the beginning of the plating and generates hydrogen gas, then gaps are formed between the plated films and the substrates.

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1. Introduction

Aluminum alloys are indispensable in reducing the weight of automobiles and electronic equipment due to their excellent specific strength, heat conductivity, electric conductivity and workability. These applications often require surface modifications in order to improve their tribological properties and corrosion resistance as well as to form magnetic recording layers. For these purposes, electroless nickel-phosphorus plating¹,² is commonly used. Since plated surfaces have to maintain their functions during practical use, a strong adhesion of the plated films must be obtained on the active surface of the substrates. However, the surface of aluminum alloys are protected by stable oxide films which cause peeling or blistering of the plated films.³ This is due to the low adhesion between the plated films and the substrates, therefore, appropriate pretreatments are required for improving the adhesion. The surfaces are typically activated by acid or alkaline etching, then the zincate treatment is performed before electroplating or electroless plating.

Based on the previous reports,⁴,⁵ zinc particles, which excessively precipitate on commercial aluminum alloys, vigorously dissolve into the solution of the electroless nickel-phosphorus plating as soon as the zincated surface is immersed. The electrons generated by the dissolution of zinc are consumed by the formation of the plated films and by hydrogen gas which leaves voids between the plated films and the substrates. Since the voids initiate the fracture, the excess zinc causes poor adhesion of the plated films. Based on these results, the surfaces of aluminum alloys must be kept active by preventing oxidation or passivation in order to obtain an adequate adhesion between the plated films and the substrates. It is also necessary to avoid any excess precipitation of the zinc since the generation of hydrogen gas during the initiation of plating causes defects at the interface.

Thin and uniform zincate films are successfully formed by the second zincate treatment⁶ after removing the first zincate films in a solution of nitric acid. According to previous reports,⁴,⁵ thin and uniform zincate films are formed by both the first and the second zincate treatments for commercial aluminum alloys which contain copper or zinc (A2017, A7075). On the other hand, coarse zinc particles are formed only by the first zincate treatment on the aluminum alloys which contain no meaningful amount of copper or zinc (A1100, A5052), then uniform zincate films are obtained by the second zincate treatment. Since the alloying elements significantly change the formation mode of the zincate films, and the phases (Al–Fe, Al–Si–Fe intermetallic compounds), which originate from the impurities, exist in commercial alloys, the detailed effects of the elements in alloys on the zincate treatments and electroless nickel-phosphorus plating need to be evaluated in simpler systems. For A7075, on which thin and uniform zincate films are formed, the adhesion between the plated films and the substrates is poor compared to the other aluminum alloys. Therefore, the effect of coexisting alloying elements must be discussed after clarifying the exact nature of each element in aluminum. In this article, binary aluminum alloys made of high-purity materials are used as the substrates onto which the zincate treatment and electroless nickel-phosphorus plating are conducted. Unless otherwise specified, the electroless nickel-phosphorus plating and electroless nickel-phosphorus plated films are expressed as ‘plating’ and ‘plated film’, respectively, in the following sections.

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²Undergraduate Student, Okayama University of Science. Present address: Hiroshima Aluminum Industry Co., Ltd., Hiroshima 733-0011, Japan
³Graduate Student, Okayama University of Science. Present address: Yamashin Giken Co., Ltd., Kasaoka 714-0098, Japan
### 2. Experimental

The binary aluminum alloys were made by casting into metallic molds in which aluminum, manganese, iron, copper and zinc of 99.999 mass% were used as the raw materials. The chemical composition of each alloy was 2 at%, and the shape of the cast alloys was a cylinder whose diameter and length were 15.5 mm and 90 mm, respectively. In the following sections, each alloy is expressed as ‘Al–Mn alloy’, ‘Al–Fe alloy’, ‘Al–Cu alloy’ and ‘Al–Zn alloy’ for simplicity. After casting, the alloys were quenched in water, then the alloys were homogenized in air for 173 ks. The temperatures for the homogenization were 873, 873, 823 and 723 K for the Al–Mn, Al–Fe, Al–Cu and Al–Zn alloys, respectively. After homogenization, each alloy was quenched in water. The purpose of the homogenizations for the Al–Mn and Al–Fe alloys was the fine particle coarsening of the intermetallic compounds. That for the Al–Cu alloy was to obtain aluminum matrices supersaturated by copper into which most of the nonuniformly dispersed phase of the intermetallic compound dissolves. The homogenization temperature for the Al–Zn alloy was chosen to obtain a uniform distribution of zinc in the aluminum matrix. All the alloys showed the intended microstructures by the homogenization for 173 ks. The 2-mm-thick substrates were obtained from the homogenized cast bars by cutting with a steel knife, then the bars of 1-µm diamond abrasive. The bars of high-purity aluminum used as a raw material for the casting were machined to have a cross section of 10 mm x 15 mm, then cut and polished as described above. The substrate is expressed as ‘5N-Al’ in the following section.

The pretreatment conditions are shown in Table 1, previously used for the degreasing, activation and zincate treatment of commercial aluminum alloys. The activation was conducted in a solution of nitric acid (69 mass%) and hydrofluoric acid (46 mass%) whose mixing ratio was HNO₃ : HF = 3 : 1 in volume. The solution for the zincate treatment was either the basic solution or the ferric ion-added one. The former was prepared by dissolving zinc oxide (40 kg/m³ solution) into a solution of sodium hydroxide (240 kg/m³ solution), and the concentration of the ferric ion in the latter was Zn : Fe = 40 : 1 in atomic ratio. The substrates underwent the zincate treatments for 30 s at 298 K, and the second zincate treatment was conducted after removing the zincate film obtained by the first zincate treatment with the solution of 5 vol% nitric acid. The zincated substrates were immediately immersed into the solution for plating (nickel(II) sulfate 26 kg/m³ solution, sodium acetate 26 kg/m³ solution, trisodium citrate 15 kg/m³ solution, sodium hypophosphite 16 kg/m³ solution, thiourea 0.8 x 10⁻³ kg/m³ solution, 363 ± 3 K). The averaged thickness of the plated film was 20 µm for the 5.4 ks plating.

The electrode potential was measured for electrochemical evaluation of the surface state of the substrates during the zincate treatments. The electrodes for the potential measurement were prepared by sealing the non-polished areas on the substrates with epoxy resin, then immersed into the basic solution after the activations with nitric-hydrofluoric acid. A salt bridge of saturated potassium chloride and a reference electrode of saturated calomel (SCE) were used for the measurement. Field emission scanning electron microscopy (FE-SEM) and field emission Auger electron spectroscopy (FE-AES) were used for observing the morphology and elemental analysis on the zincated surfaces. Adhesion of the plated films was evaluated as follows. The plated film and a part of the substrate were cut with a steel knife, then the film was partly peeled from the substrate. The peeled surfaces were subsequently evaluated by scanning electron microscopy with elemental analysis. Observations and elemental analysis of the peeled surfaces were conducted by a field emission electron probe microanalysis (FE-EPMA).

According to previous reports, the amount of zinc which precipitates in the basic solution is greater than that of the ferric ion-added one, and adhesion of the plated films was shown to be improved when the ferric ion-added solution was used because of the appropriately suppressed precipitation of zinc. In this study, the basic solution was used in the cases of observation and analysis of the zincated surfaces and measurement of the electrode potential in order to enhance the behavior of the zinc precipitation. On the other hand, the specimens, which underwent the plating, were zincated in the ferric ion-added solution, since the solution improves the adhesion of the plated films. Unless otherwise noted, the zincate treatment with the basic solution is expressed as ‘the zincate treatment’, and when the zincate treatment was conducted with the ferric-ion added solution, the treatment is expressed as ‘the zincate treatment with the ferric ion-added solution’ in the following section.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Pretreatment conditions.</th>
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<td>Degreasing</td>
<td>Activation</td>
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<tr>
<td>Water rinse</td>
<td>5 s</td>
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<tr>
<td>Alkaline degreasing</td>
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<tr>
<td>(Na₂CO₃ 20 kg/m³ + Na₂SiO₃ 10 kg/m³)</td>
<td>150 s</td>
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<td>Water rinse</td>
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3. Experimental Results

3.1 Morphology of activated and zincated surface

Figure 1 shows the backscattered electron images (compositional mode) of the activated or zincated surfaces of the Al–Mn alloy. The images are expressed as ‘BEIs’ in the following section. From Fig. 1(a), the Al–Mn intermetallic compounds, indicated by the arrow in the figure, dissolves faster than the matrix during activation by the nitric-hydrofluoric acid, and zinc preferentially precipitates on the intermetallic compound in Fig. 1(b). Excess zinc precipitated on the surface of the Al–Mn alloy during both the first and the second zincate treatments, and generation of a gas and spalling of the excess zinc continued. Figures 1(c) and 1(d) show the surface after removing the excess zinc by ultrasonic cleaning in acetone. The surfaces after the first and the second zincate treatment showed almost the same morphology in which coarse zinc particles precipitated on the Al–Mn intermetallic compound and no film of zinc is observed on the matrix.

Figure 2 shows the BEIs of the activated or zincated surfaces of the Al–Fe alloy. As in the case of Fig. 1(a), the Al–Fe intermetallic compounds are preferentially etched during the activation, then the surfaces of the compounds are covered with zinc, and coarse particles of zinc begin to precipitate near the etch pits (Fig. 2(b)). Since an excess precipitation of zinc occurred, the zincated specimens underwent ultrasonic cleaning after the zincate treatments. While coarse zinc particles exist only near the etch pits on the surface after the first zincate treatment, the surface of the matrix is not covered with zinc particles (Fig. 2(c)). Although zinc particles of less than 1 µm are observed on the surface after the second zincate treatment (Fig. 2(d)), the particles do not cover the entire surface of the matrix.

Figure 3 shows the BEIs of the activated or zincated surfaces of the Al–Cu alloy. From Fig. 3(a), Al–Cu intermetallic compounds are observed on the activated surface. The surfaces of the compounds are covered with zinc immediately during the first zincate treatment, and zinc particles of a few hundred nanometers nonhomogeneously precipitate on certain grains in the matrix. The former zinc is indicated as ‘Zn(1)’ in Fig. 3(b), and the latter ‘Zn(2)’. While the surfaces of the Al–Cu intermetallic compounds are covered with a uniform film of Zn(1), particles of Zn(2) do not form a uniform film, and the morphology of the etched substrate can be observed. Unlike the results of the Al–Fe and Al–Mn alloys (Figs. 1 and 2), no coarse zinc particle exists on the surfaces of the Al–Cu alloy after the first and second zincate treatments. The amount of zinc, which precipitates on the surface of the matrix, varies according to the crystal orientation of the matrix. In Figs. 3(c) and 3(d), particles of Zn(2) cannot be observed on some grains in the matrix, but many particles of Zn(2) exist on other grains.
Figure 4 shows the BEIs of the activated or zincated surfaces of the Al–Zn alloy. From Fig. 4(a), the second phase is not observed in the Al–Zn alloy in which each grain was strongly etched and became uneven depending on its crystal orientation. The precipitation of zinc in the first zincate treatment was uniform (Fig. 4(b)), and the reaction immediately finished when the entire surface was covered with zinc. The surface was covered with finer particles of zinc after the second zincate treatment (Fig. 4(d)) compared to the case of the Al–Zn alloy, but the particles only slightly adhere to the substrate. While the flat surface of the Al–Cu alloy is covered with a uniform zincate film whose thickness is a few tens of nanometers (Fig. 4(c)), an ~500 nm-thick zincate film developed following the surface shape formed by the activation in the case of the Al–Zn alloy.

3.2 Cross-sectional microstructure after zincate treatment

Figure 6 shows the cross-sectional BEIs of the specimens after the first zincate treatment for 30 s. For the Al–Mn alloy, the surfaces of the Al–Mn intermetallic compounds are covered with a plate-shaped substance on which the zinc precipitates (Fig. 6(a)). Oxygen and manganese were detected at the plate-shaped substance on the surface of the Al–Mn intermetallic compound by FE-EPMA elemental analysis. From Fig. 6(b), coarse zinc particles precipitate on the Al–Fe alloy, but the particles only slightly adhere to the substrate. While the flat surface of the Al–Cu alloy is covered with a uniform zincate film whose thickness is a few tens of nanometers (Fig. 6(c)), an ~500 nm-thick zincate film developed following the surface shape formed by the activation in the case of the Al–Zn alloy.

3.3 Elemental analysis on zincated surface

Figure 7 shows the Auger electron spectra obtained on the zincated surfaces. The measurement points on the matrix correspond to the broken circles in Figs. 1–5. From Fig. 7(a), aluminum and zinc were detected in the matrix of the Al–Mn alloy after the first zincate treatment (Fig. 1(c)), and the same result was obtained for the second zincate treatment. On the other hand, Fig. 7(b) does not show the zinc peak after the first zincate treatment of the Al–Fe alloy (Fig. 2(c)), but aluminum and zinc were detected after the second one as in the case of the Al–Mn alloy (Fig. 7(a)). From Figs. 7(d) and 7(e), aluminum and zinc were detected after the first zincate treatment of the Al–Cu alloy and the second one of the Al–Zn alloy, but the aluminum intensity is lower when compared to that of the Al–Mn and Al–Fe alloys, and the shape of the
Auger peak differs. Figure 7(f) only shows the aluminum peak on the surface of the 5N-Al after the second zincate treatment (Fig. 5(d)) similar to the first one for the Al–Fe alloy (Fig. 7(b)).

3.4 Temporal change in electrode potential during zincate treatment

Figure 8 shows the temporal change in the electrode potential during the zincate treatment. For the Al–Mn (Fig. 8(a)) and Al–Fe (Fig. 8(b)) alloys, the electrode potentials during the first zincate treatment continued to vary, and those during the second one were shifted to the noble side by 0.05 V. On the other hand, the temporal change in the electrode potentials for the Al–Cu (Fig. 8(c)) and Al–Zn (Fig. 8(d)) alloys were almost the same, showing a constant value immediately after immersion. For the 5N-Al (Fig. 8(e)), the temporal changes in the potentials for the first and the second zincate treatments equally continued to vary in the less noble direction.

3.5 Adhesion of plated film

Figure 9 shows the BEIs on the surfaces of the substrates and the plated films after peeling. Although many pits were formed by the preferential dissolution of the Al–Mn intermetallic compounds on the surface of the Al–Mn alloy (Fig. 9(a)), and corresponding convex points were observed on the peeled surface of the plated film (Fig. 9(b)), the plated film was easily peeled. For the Al–Fe alloy, the peeled surface of the substrate showed a remarkable unevenness (Fig. 9(c)), and nickel was detected at the convex points.
However, the morphology of the peeled surface of the plated film (Fig. 9(d)) was almost the same as that of the substrate, and the adhesion of the plated film was as poor as that of the Al–Mn alloy. On the other hand, the plated films on the Al–Cu (Fig. 9(e)) and Al–Zn (Fig. 9(f)) alloys could not be continuously peeled. Dimple patterns on the substrates were observed at the areas where the plated films were only partly peeled by twisting the steel knife when the cuts reached the substrates from the plated films.

4. Discussion

4.1 Microstructure of alloys

For the Al–Mn and Al–Fe alloys, primary crystals of the intermetallic compounds are formed, then the liquid phase of the eutectic compositions decompose into aluminum and intermetallic compounds when the molten alloy is cooled according to the equilibrium phase diagrams.16,17) The intermetallic compounds, which exist in the Al–Mn and Al–Fe alloys (Figs. 1 and 2), are Al6Mn and Al13Fe, respectively. Since the alloys were quenched in water after the homogenization, the matrices of the alloys are supersaturated with the alloying elements of manganese and iron. The as-cast microstructure of the Al–Cu alloy consists of primary crystals of aluminum and the eutectic domain, and the intermetallic compound, which precipitates during the solidification, is Al12Cu. Although most of the copper in the alloy dissolves into the matrix during the homogenization, some particles of the slightly retained Al12Cu are observed in Fig. 3. On the other hand, for the Al–Zn alloy,18) all the zinc dissolves into the matrix during the homogenization, therefore, no precipitate is observed in Fig. 4. These intermetallic compounds were identified by FE-EPMA using a wavelength-dispersive spectrometer, and each compound corresponds to what the equilibrium phase diagrams16,17,19) suggest.

4.2 Change in surface state by activation and formation of zincate film

From Fig. 1, the surface of Al6Mn in the Al–Mn alloy, which preferentially dissolves during the activation, becomes the preferred precipitation site of zinc. Electrons consumed by the precipitation of zinc (reductive reaction) is supplied by the dissolution of the matrix and Al6Mn. Since Al6Mn is remarkably etched compared to the matrix (Fig. 6(a)), the main oxidation reaction is thought to be the dissolution of aluminum and manganese in the Al6Mn. The plate-like substance on the surface of Al6Mn, which is shown to consist of oxygen and manganese by the FE-EPMA, is considered to be originally manganese(II) hydroxide based on the electrode potential during the zincate treatment and the pH of the zincate solution.20) Although the data are not shown here, the manganese hydroxide dissolved into the solution of the 5% nitric acid after the first zincate treatment, and the surface of Al6Mn was observed again.

Continued dissolution of the Al6Mn during the zincate treatments is suggested by the continued precipitation of zinc and the generation of gas, and also by the fact that the electrode potential does not reach the value which zinc shows (Fig. 8(a)). The excess precipitation of zinc corresponds to the nucleation on the surface of the alloy and the following precipitation in the areas from the surface. Based on the electrode potential during the zincate treatments, the generated gas is considered to be hydrogen. When zinc precipitates, the concentration of zinc ions in the solution locally decreases near the zinc particles, therefore, the precipitation is controlled by the supply rate of zincate ion or the reaction rate during the oxidation of aluminum or manganese. Since the surface of Al6Mn is not thoroughly covered with the precipitated zinc (Fig. 6(a)), hydroxide ions continue to be supplied to the surface of the Al6Mn. Thus, the pH at the surface remains high, and the dissolution of aluminum and manganese, or the generation of electrons, does not stop.

While a part of the electrons are considered to be consumed by the generation of hydrogen gas, the other ones move toward the points, where the supply rate of zincate ions is higher, through the precipitated particles of zinc, then zinc particles further precipitate. Therefore, porous films of zinc are excessively formed, the generation of hydrogen gas continues on the surface of the Al6Mn, and the films of zinc spall from the substrate. After the water rinse and the ultrasonic cleaning of the zincated specimens, most of the coarse zinc particles, which weakly adhered to the substrate, are removed, and only the zinc particles, which well adhered on the manganese hydroxide, remained. Since manganese hydroxide does not have a good electrical conductivity, the electrons generated by the dissolution of Al6Mn first move to the substrate, migrate to the zinc particles which contact the matrix, then are consumed by the reduction of zincate ions or the precipitation of zinc at the locations off the surface of the substrate as already mentioned. Regarding the surface of the matrix, zinc and aluminum are detected on the areas where no zinc particle is observed after the first zincate treatment (Fig. 7(a)). This suggests that the surface is covered with a zincate film whose thickness is a few nanometers or that some areas are imperfectly covered.

For the Al–Fe alloy, Fig. 2 shows that Al17Fe preferentially dissolves during the activation, and the etched areas become preferred precipitation sites of the zinc particles during the first and the second zincate treatments (Figs. 2(b)–2(d)). Although the precipitation mode of zinc is similar to that of the Al–Mn alloy, Al17Fe is uniformly covered with zinc (Fig. 2(b)), and the surface of the matrix becomes uneven (Fig. 6(b)). Based on these results, the electrons consumed by the reductive reactions (precipitation of zinc and generation of hydrogen gas) are supposed to be generated by the dissolution of the aluminum matrix. While the films of zinc on Al17Fe well adhere as in the case of the Al–Mn alloy, the zinc particles, which excessively precipitate and poorly adhere, fall off the substrate during the ultrasonic cleaning, and the surface of the matrix is exposed. Regarding the exposed matrix, zinc is not detected after the first zincate treatment (Fig. 7(b)), but the surface shows the existence of zinc after the second zincate treatment (Fig. 7(c)). This means that the surface of the matrix is locally covered with zinc during the second zincate treatment. Since the electrode potential of the Al–Fe alloy during the first and second zincate treatments (Fig. 7(b)) are shifted in the noble direction compared to those of the Al–Mn alloy (Fig. 7(a)),
it is suggested that the generation of hydrogen gas is suppressed and the coating by zinc proceeds in the case of the Al–Fe alloy.

For the AI–Cu alloy, no meaningful roughening occurs during the activation (Fig. 3(a)) compared to that of the alloys of Al–Mn and Al–Fe. After AI₂Cu dissolves at a higher rate than the matrix, AI₂Cu becomes the preferred precipitation site of zinc during the zinctate treatments as in the case of AI₃Fe. Regarding the matrix, although the amount of precipitated zinc differs according to the crystal orientation of the aluminum grains, the surface is covered with fine particles of zinc after the first and second zinctate treatments (Figs. 3(c) and 3(d)). Since the electrode potential rapidly shows a constant value in Fig. 8(c), the dissolution of the passivation film on the matrix and subsequent coating by zinc are thought to be immediately finished. This mode of precipitation and the temporal changes in the electrode potential are similar to that of A2017 in previous reports. Copper in the alloy is suggested to accelerate the dissolution of the passivation film, and affect the uniform precipitation of zinc. The thickness of the zinctate film is a few tens of nanometers based on the cross-sectional observation (Fig. 6(c)), and the layer is thought to correspond to the bright areas in Fig. 3(c). Since the Auger electron spectrum of aluminum in Fig. 7(d) differs from those in Figs. 7(a)–7(c) and 7(f), the properties of the zinctate films are thought to change according to the chemical state of the aluminum in the films. Chemical analyses by Auger spectroscopy will be conducted in a future study.

For the AI–Zn alloy, the etched surface (Fig. 4(a)) shows an unevenness with directionality which reflects the crystal orientation. This means that the etching rate of the AI–Zn alloy is higher than those of the other alloys, and the preferentially etched planes are thought to correspond to certain crystal planes. The precipitation mode of zinc is as uniform and rapid as that of the AI–Cu alloy (Fig. 4(b)), and the temporal changes in the electrode potential (Fig. 8(e)) are almost the same as that for the AI–Cu alloy. These points suggest that the passivation film on the AI–Zn alloy rapidly and uniformly dissolves, and that almost the entire surface is covered with zinc. However, since the precipitation of zinc lasts longer than that of the AI–Cu alloy, the amount of precipitated zinc is more than ten times greater when compared to that of the AI–Cu alloy (Fig. 6(d)). The electrons required for the higher amount of precipitated zinc, compared to that of the AI–Cu alloy, are considered to be supplied by the dissolution of aluminum through the pinholes in the zinctate film where hydroxide ions diffuse to the substrate. The dissolution process of the passivation films and the surface state of the precipitated zinc determine the profiles of the electrode potential during the zinctate treatments, therefore, the minor anodic reaction is not considered to bring about meaningful changes in the profiles of the electrode potential. The size of the zinc particles is reduced to 100 nm for the second zinctate treatment, and the thickness of the zinctate film is considered to have almost the same particle size. Based on the fact that aluminum is detected on the second zinctated surface by Auger electron spectroscopy (Fig. 7(e)) and the thickness of the zinctate film is far greater than the analyzed depth, the detected aluminum is not from the substrate, but means that aluminum atoms diffused from the substrate to the surface of the zinctate film. Previous papers have reported that aluminum is detected only on the second zinctated surfaces. Although the aluminum atoms are supposed to diffuse through the grain boundaries of the zinc, the diffusion coefficient has not been measured, and the diffusion speed and length cannot be precisely predicted. However, since films obtained in aqueous solutions contain a high number of hydrogen atoms and vacancies, the diffusion coefficient of aluminum in zinctate solutions can be much greater than the value for the high-purity metals, and aluminum atoms can diffuse to the surface of the zinctate film by bulk diffusion. One of the reasons that aluminum is not detected on the first zinctated surface can be the thicker zinctate film which results in a lower driving force or smaller gradient of the aluminum concentration. Another reason may be the coarse zinc particles which produce smaller areas of grain boundaries required for the diffusion of the aluminum atoms.

For the 5N-Al, Fig. 5 shows a slight etching of the surface by the activation. This may be because the passivation of aluminum by nitric acid precedes dissolution of the passivation film and aluminum by hydrofluoric acid for 5N-Al. After dissolution of the passivation film in the zinctate solution, electrons are generated by the dissolution of aluminum, then coarse zinc particles are formed (Figs. 5(b) and 5(c)). The precipitation mode is the same as those for the AI–Mn and AI–Fe alloys, when hydrogen gas is generated, zinc excessively precipitates and the porous film of zinc continue to spall from the substrate. These phenomena were observed during the first and second zinctate treatments, and Fig. 8(e) shows the electrode potential which mainly reflects the aluminum dissolution. From Fig. 5(d), fine zinc particles are observed on the second zinctated surface, but the flat areas are not covered with zinc (Fig. 7(f)). This is due to the continued dissolution of aluminum during the second zinctate treatment. The fine zinc particles precipitated on the scratch (Fig. 5(d), in the broken rectangle) where the passivation film is supposed to be poorly developed due to the damage. Therefore, the surface may rapidly dissolve compared to the other flat areas, and the preferential precipitation of zinc is thought to occur.

4.3 Relation between zinctate film and adhesion of plated film

Based on previous reports, the second zinctate treatments for commercial aluminum alloys significantly improves the adhesion of the plated films. While the plated films cannot be peeled off the A1100 (99 mass% Al), A2017 (3.9Cu), A5052 (2.5Mg), the adhesion of the plated films on the Al–Mn and Al–Fe alloys was poor. The peeled surfaces of the plated films show the morphology of the substrates with etch pits (Figs. 9(b) and 9(d)). In these cases, the unevenness of the surfaces does not properly function to improve the adhesion by an anchoring effect. Therefore, improvement of the adhesion of the plated films should be based on the reduction of voids between the plated films and the substrates, and a metallurgical bond is necessary. In order to achieve this strong bond, plating via a zinctate film of ~10 nm-thick must be conducted, but thicker zinctate
films are formed on the Al–Mn and Al–Fe alloys even when the ferric ion-added zincate solution is used. It is postulated that hydrogen gas is then generated during the initiation of plating, and there exist a number of gaps between the plated films and the substrates. Although observations by transmission electron microscopy\textsuperscript{4,5} and measuring the electrode potential\textsuperscript{26} are appropriate to examine the reaction at the initiation of the plating, these will be future studies. In Fig. 9(c), nickel is detected in the convex areas on the peeled surface of the Al–Fe alloy substrate. This suggests that the zincate film is thin on these areas, and the plated film began to immediately form after the precipitation of nickel by the conversion reaction of zinc and nickel.

From Figs. 9(e) and 9(f), the dimple patterns, observed for the Al–Cu and Al–Zn alloys which underwent the second zincate treatment, suggest that the adhesion strengths between the plated films and the substrates exceed the strengths of the substrates. That is, copper and zinc in the aluminum alloy appropriately control the amount of precipitated zinc to improve the adhesion strength. In previous reports,\textsuperscript{4,5} the plated films on the A7075 (5.8 mass\%Zn–2.7Mg–1.6Cu) alloy showed a poorer adhesion compared to those of the other commercial alloys. On the other hand, since the adhesion strengths for the Al–Cu and Al–Zn alloys in this paper were quite high, copper and zinc in the A7075 may not be the main factor for the poor adhesion. Magnesium is another major alloying element in A7075, but A5052, which contains a comparable amount of magnesium, shows a high adhesion strength. Therefore, the coexistence of magnesium with copper or zinc might produce a poor adhesion, whose mechanism should be clarified by detailed studies on the formation process of the zincate film and the initial behavior during plating on the substrates of aluminum–magnesium and aluminum–magnesium–zinc alloys. These studies will be reported in the future.

5. Summary

In this paper, formation of zincate films and adhesion of plated films were described using binary aluminum alloys of high-purity raw materials. Each alloying element had a characteristic effect on the zincate treatments and plating, and the results are summarized as follows:

1. Manganese in an aluminum alloy forms Al\textsubscript{5}Mn which preferentially dissolves during the zincate treatments and generates electrons. The electrons are consumed by precipitation of the zinc and generation of hydrogen gas, but the substrate is not totally covered with the precipitated zinc. Therefore, the reaction continues and excess precipitation of the zinc occurs during the first and second zincate treatments. Since the excess zinc dissolves and hydrogen gas is generated during the initiation of plating, gaps are formed between the plated film and the substrate which cause poor adhesion.

2. Iron in an aluminum alloy forms Al\textsubscript{3}Fe which is immediately covered with zinc during the zincate treatments. The dissolution of the matrix, generation of hydrogen gas and precipitation of zinc then continue.

Although a part of the substrate is covered with zinc after the second zincate treatment, the adhesion of the plated film is poor because of the excess zinc. Nickel is detected only on part of the peeled surface of the substrate.

3. When copper or zinc exists in an aluminum alloy, the passivation film on the substrate immediately dissolves into the zincate solution. The precipitation of zinc then begins, and the surface is instantly covered with zinc. The adhesion strength of the plated films is significantly improved by the second zincate treatment which produces thin and uniform zincate films. In this case, the surfaces of the substrates undergo ductile fracture when the plated films are peeled.

REFERENCES