Effect of Zincate Treatment on Adhesion of Electroless Nickel-Phosphorus Coating for Commercial Pure Aluminum

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The present authors have conducted characterization of zincate films formed as a pretreatment for electroless nickel-phosphorus coatings on commercial pure aluminum substrate (JIS A1050P-H24, 99.5 mass% Al). By using a basic solution which consisted of sodium hydroxide and zinc oxide, a zincate film formed by single zincate treatment showed coarse zinc grains of 1–2 μm in size whose (0001) planes were mainly parallel to the surface of the substrate. A double zincate treatment by using the basic solution reduced the coarse grains, and the thickness of the uniform zincate film was 30–40 nm. A commercial zincate solution which contained iron decreased the number and the size of coarse zinc grains for the single zincate treatment compared with the case of the basic solution, and the double zincate treatment formed a further thin zincate film of 10–20 nm in thickness.

The single zincate treatment by using the basic zincate solution resulted in such poor adhesive strength of the electroless nickel-phosphorus plated film as to peel off the substrate due to its residual stress. Quantification of adhesive strength by 90° peeling test showed the double zincate treatment increased the adhesive strength of the plated film up to 30 N/m. In the case of the commercial zincate solution, the adhesive strength obtained by the single zincate treatment was 125 N/m. Furthermore, the adhesive strength of the plated nickel-phosphorus film was too high to conduct the peeling test in the case of the double zincate treatment by the commercial solution, where dimple patterns were observed due to ductile fracture of the substrate.

Observation by transmission electron microscopy of the interface between the nickel-phosphorus plated film and the substrate showed gaps in the case of the double zincate treatment by the basic zincate solution. On the other hand, the double zincate treatment by the commercial solution eliminated gaps and a strong interface was obtained. [doi:10.2320/matertrans.47.2518]

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1. Introduction

Aluminum alloys are increasingly utilized recently to improve fuel consumption of vehicles by reducing their weight, and their excellent workability, corrosion resistance, and recyclability are also advantages in electronic and electric equipment as well as in automotive applications. In surface modifications of aluminum alloys for improving its hardness, wear resistivity, or decorative purposes, appropriate pretreatments are indispensable to obtain high adhesion strengths of the films, since the surfaces of aluminum alloys are passivated by oxidation in water as well as in air.¹ For this purpose, zincate treatment is commonly adopted which covers surfaces of substrates with zinc film by substitution reaction of aluminum and zinc. Especially the double zincate treatment² which repeats a conversion treatment twice shows remarkable increase in adhesive strength of electroless plated films onto substrates.

The authors have pointed out in the previous reports³⁵ that thinner zincate films on which aluminum is detected by X-ray photoelectron spectroscopy and Auger electron spectroscopy, as well as heat aftertreatment, lead to higher adhesive strength of nickel-phosphorus plated films in the case of aluminum-copper alloy (JIS A2017P-T3) substrate. Although some reports have already shown that the addition of iron and nickel in a zincate solution is effective in improving adhesive strength of the subsequently obtained films,⁶⁷ the role of the additions in zincate solutions and resulting interfacial structure have not adequately been researched. In this study, relation between adhesive strengths of electroless nickel-phosphorus plated films and the properties of zincate films on commercial pure aluminum substrate is discussed from the viewpoint of the existence of iron in the zincate solutions by analysis of the surface and the interface of the zincate and the plated films.

2. Experimental Procedure

A rolled aluminum alloy (JIS A1050P-H24) of 1.5 mm-thick was used as substrate whose chemical composition is shown in Table 1. The rolled sheet was cut to platelets of a dimension of 35 × 10 mm², then polished to a mirror finish by buffing for eliminating anchoring effect on adhesion of the nickel-phosphorus plated film to the substrate and for enhancing the changes of the adhesive strength with respect to the zincate treatment condition. Preceding to the electroless nickel-phosphorus platings, pretreatments were carried out according to Table 2.³⁵ As zincate solutions, a basic solution and a commercial solution (Japan KANIGEN Co., Ltd., SUMER K-102) which contains iron were used for investigating the difference in thickness of zincate films and adhesive strength of electroless nickel-phosphorus plated films onto substrates. Here, the basic zincate solution consists of zinc oxide (50 kg/m³-solution) and sodium hydroxide (250 kg/m³-solution).⁸⁻¹⁰

<table>
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<th>element</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>V</th>
<th>Ti</th>
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<td>0.04</td>
<td>0.37</td>
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Table 1 Chemical composition of substrate.
Each substrate was immersed in an electroless nickel-phosphorus plating solution (Japan KANIGEN Co. Ltd., SD-200) immediately after the pretreatment, and the plating was conducted at 363°C for 5.4 ks. The content of phosphorus and the averaged thickness of the nickel-phosphorus plated film obtained under the above conditions were 9.0 mass% and 20 μm, respectively.

After the electroless nickel-phosphorus plating, a 90° peeling test was carried out for quantification of adhesive strength of the plated films to the substrates as shown in Fig. 1. Before the peeling test, the specimens were coated with copper film of 30 μm-thick by electro plating (current density 0.04 A/m²) in copper sulfate solution (copper sulfate (240 kg/m³-solution) + sulfuric acid (6.0 × 10⁻² m³/m³-solution)) for reinforcement of the electroless nickel-phosphorus plated films. The sides of the copper-coated substrates were polished to remove unnecessary films for the peeling test as shown in Fig. 1, then a part of the plated film was peeled from the edge of the substrate for chucking. Then, the tensile test was carried out for the substrate fixed on the slider where the cross head speed was 0.5 mm/s.

The morphology of the surfaces of the substrates after the zincate treatments were observed by field emission scanning electron microscopy (FE-SEM), then X-ray diffraction patterns were measured by 2θ-θ scan geometry with a parallel beam optics. Quantitative analysis by electron probe microanalysis (EPMA) was conducted at arbitrary 10 points on each zincated surface with probe diameter of 100 μm for measuring the amount of zinc which precipitated on the substrate. Depth profiles were obtained by Auger electron spectrometry (AES) with argon ion etching (8 nm/ks for silicon dioxide). Line analysis by EPMA was conducted on the cross sections of the electroless nickel-phosphorus plated substrates for measuring distribution of oxygen and zinc at the interface of the substrate and the plated film. The interface was observed by transmission electron microscopy (TEM) for which the thin films were prepared by focused ion beam (FIB) of gallium with in-situ micro-manipulator.

### 3. Experimental Results

#### 3.1 Adhesive strength of electroless nickel-phosphorus plated film to substrate

Figure 2 shows the adhesive strengths obtained by peeling test. Here, an adhesive strength is defined as the maximum value of the load in a load-displacement curve. Without zincate treatment, the plated films were thin and nonuniform, which were inapplicable for the peeling test. Since the adhesive strength was still poor for the single zincate treatment by the basic solution, the plated film peeled off from the substrate when the sides were polished for the peeling test. The adhesive strength was improved to 127 N/m by the single zincate treatment with the commercial solution.

The double zincate treatment by the basic solution improved the adhesive strength to 36 N/m, and the triple zincate treatment showed almost the same adhesive strength (39 N/m). Figure 3(a) shows the surface of the substrate after peeling of the nickel-phosphorus plated film obtained by the double zincate treatment with the basic solution. In Fig. 3(a), grain boundaries, pits, and scratches can be observed, and nickel was detected in the circled areas. On the other hand, the double and the triple zincate treatment caused drastic improvement in adhesive strength in the case of the
commercial zincate solution. Since the plated film could not be peeled off the substrate continuously, its adhesive strength was not quantified. Figure 3(b) shows the partly peeled region, where dimple patterns are observed on the substrate.

3.2 Surface observation and analysis of zincate film

Figure 4 shows X-ray diffraction patterns of the zincated surfaces. In Fig. 4(a), the $d$-spacings of zinc agree with those of the powder diffraction, but intensity of (0002)$_{Zn}$ is about 40% of that of (0002)$_{Zn}$. In the case of the commercial solution (Fig. 4(b)), the diffraction of zinc becomes weaker, and the peak position of (0002)$_{Zn}$ shifts to high angle by $\pm 1.1^\circ$ compared with that obtained by the basic solution. On the other hand, the peak position of (1010)$_{Zn}$ shifts to low angle by $-0.42^\circ$, and that of (1011)$_{Zn}$ is almost the same with that obtained by the basic solution.

Figure 5 shows secondary electron images of the surfaces after zincate treatments. In Fig. 5(a), coarse particles of 1–2 $\mu$m in its size and underlying fine particles of 200–300 nm are observed. In Fig. 5(b), the surface of the substrate is uniformly covered by fine particles which are similar to the fine ones observed in Fig. 5(a). On the other hand, the surface of the substrate treated by the commercial zincate solution was covered by finer particles (Figs. 5(c)(d)) when compared with the case of the basic solution (Figs. 5(a)(b)), and the shape of the particles also differed between the two solutions.

Figure 6 shows the concentration on the zincated surface of the substrate obtained by EPMA. The amount of oxygen was comparable with that of zinc in each zincated substrate. By the double zincate treatment, the amount of zinc and oxygen became about half for the basic zincate solution, and that for the commercial solution became one-fourth. Iron was detected on the surface of the substrate zincated by the commercial solution, and its amount was almost the same for the single and the double zincate treatments.

Figure 7 shows the depth profiles of the double zincate films obtained by AES. From Fig. 7(a), aluminum and oxygen exist in the zincate film, and thickness of the double zincate film obtained by the basic solution is 30–40 nm, calculated by the etching rate of silicon dioxide (8 nm/ks). On the other hand, the double zincate film obtained by the commercial solution contains iron in it, and intensity of aluminum rapidly increases with respect to etching time compared with the case of the basic solution. Intensity of iron shows its maximum at 10–15 nm in silicon dioxide rate, then gradually decreases.

Figure 8 shows the cross-sectional line profiles at the interface between the nickel-phosphorus plated films and the substrates. In the case of the basic solution (Fig. 8(a)), the double zincate treatment lowered the amount of oxygen detected at the interface by about 50% of that obtained by the single zincate treatment. By the use of the commercial zincate solution, the amount of oxygen for the double zincate treatment is almost the same for that of the single zincate solution. Figures 8(c) and (d) show zinc exists at the interface between the substrate and the plated film for the single zincate treatment by the commercial solution as well as the basic one. The retained zinc is not detected in the case of the double zincate treatment (the broken curves in Figs. 8(c),(d)).

Figure 9 shows the bright field images of the interfaces between the electroless nickel-phosphorus plated films and the substrates. In Fig. 9(a), gaps of 100–300 nm in their widths exist along the interface, and the plated film has only a few contacts with the substrate. Although the widths of the gaps at the interface decreases to about 50 nm as shown in Fig. 9(b), the plated film is still poorly bonded. In the magnified bright field images of Fig. 9(b), part of the interface contains a bubble-like structure whose selected area diffraction patterns showed Debye rings. However, the rings did not agree with either those of aluminum, zinc, oxide
or hydroxide of aluminum or zinc. On the other hand, Fig. 9(c) shows no gaps at the interface between the plated film and the substrate except a few regions where the electroless nickel-phosphorus plated film showed intrusion into the etch pits on the substrate. The magnified bright field images in Fig. 9(c) show strongly bonded interfaces which contain no intermediate layer between the plated film and the substrate.

4. Discussion

From Figs. 2, 6, 7, adhesive strength of an electroless nickel-phosphorus plated film on the substrate is improved by lowering thickness of zincate films. Here, oxygen detected in Fig. 6 is thought to exist in the zincate films from Fig. 7,
and the signal of aluminum in Fig. 6 is mainly from the substrate, since the volume from which characteristic X-rays are emitted is thought to be larger than that of the overlying zincate films. The previous reports 3–5) about adhesive strength of electroless nickel-phosphorus plated films on an aluminum-copper alloy (JIS A2017) substrate show the same tendency where the plated film obtained by the triple zincate treatment, which forms a thicker zincate film than the double zincate treatment, showed poorer adhesive strength than that obtained by the double zincate treatment. The depth profiles of the triple and the quadruple zincate films obtained by the basic solution are not shown here, but they showed almost the same profiles as the double zincate film which well correspond with the adhesive strength in Fig. 2.

The circled nickel-detected spots in Fig. 3(a) are considered to correspond with the bonds in Fig. 9(b), and the peeling takes place at the weak interface between the plated film and the substrate shown as the gaps or the intermediate layer with bubble-like structure in Fig. 9(b). In the case of the commercial zincate solution, the interface between the plated film and the substrate become stronger than the substrate which showed ductile fracture and resulting dimple patterns when the plated film was peeled off the substrate.

Although the thickness of each zincate film is not precisely observed, the order of the width of the gap in Fig. 9(b) (50 nm) agree with that estimated by Fig. 7(a) (30–40 nm) in its order. Fig. 7(b) does not show a distinct zincate film, but rapid increase in aluminum concentration with respect to etching time and the maximum of iron concentration suggest its thickness is 10–15 nm. The gradual increase of aluminum and the decrease of zinc and oxygen concentration are thought to be due to the roughened surface of the substrate. The difference in thickness of the two zincate films is due to the existence of iron in the commercial zincate solution, and the concentration of iron has its maximum at the interface between the zincate film and the substrate. Precipitation of iron by substitution of aluminum is considered to precede that of zinc, then the iron particles which cover the surface of the substrate are considered cause to work as precipitation sites for zinc.

A zincate film formed by this process is thought to be thin since the cathodic reaction (precipitation of zinc) and the anodic one (dissolution of aluminum into the zincate solution) immediately stop when the surface of the substrate is uniformly covered with zinc film. On the other hand, the zincate film becomes thicker in the case of the basic solution because of spatially nonuniform coverage with zinc film where anodic and resulting cathodic reactions last longer. The coarse zinc particles are thought to form when supply of zinc to certain part on the surface of the substrate is not adequate to cover with zinc, where dissolution of aluminum continues until the chemical potential of aluminum in the solution which faces the anodic site reaches its maximum or the solution is locally saturated with aluminum.

The amount of oxygen, comparable with that of zinc from Fig. 6, is not condensed at the interface of the zincate film and the substrate, but oxygen is detected in the zincate films as shown in Fig. 7. Since Fig. 4 does not show the existence of either zinc oxide or zinc hydroxide, the chemical state of oxygen in the zincate films is not clear at this point. Oxygen might be contained in the zincate films as fine or amorphous oxide particles which do not form meaningful diffraction peak, or exist as water molecules.

The 2θ-values of the diffraction peaks in Fig. 4(a) agree with the reported powder diffraction data, 13,14 but the intensity of the (0002) diffraction is higher than that of (1010) which shows the most intense peak in the case of powder diffraction. The highly textured precipitation of zinc is also observed in Fig. 5 where (0001) planes with 6-fold symmetry of the coarse particles seems to be parallel to the surface of the substrate. This texture is considered to be due to the minimization of the surface energy of the zinc particles which contact the zincate solution. In Fig. 4(b), the broader diffraction peaks of zinc and the shifts of the peaks from those of Fig. 4(a) suggest solubility of iron in the matrix of zinc and resulting changes in the lattice constants. An estimation of the lattice constants by (0002) and (1010) planes shows $a = 0.2691$ and $c = 0.4803$ nm for the single
zincate film by the commercial zincate solution, while those of powder diffraction data \(^{13,14}\) are \(a = 0.2666\) and \(c = 0.4949\) nm.

Although the iron particles cover the surface of the substrate in the single zincate treatment, there still remain rather passive areas and pits where conversion reaction is delayed. Those areas are considered to be anodic sites where aluminum continues to dissolve into the solution, and the electrons generated by the anodic reaction are consumed by the growth of the coarse zinc particles near the anodic sites. Figure 10 shows schematic illustration of the formation of zincate films for each condition. Coarse zinc particles are precipitate by the single zincate treatment because of the nonuniformity of anodic sites and cathodic ones where dissolution of aluminum and precipitation of zinc take place, respectively. The nonuniformity might be due to pits on the surface of the substrate where zinc ions are not supplied adequately and dissolution of aluminum continues until the chemical potential of aluminum in the solution reaches its maximum.

5. Conclusion

In this study, adhesive strength of electroless nickel-phosphorus platings was quantified on a commercial pure aluminum substrate (JIS A1050), and properties of zincate films formed as their pretreatment were investigated by electron microscopy and X-ray diffraction measurements. The main results obtained can be summarized as follows.

1. Adhesive strength of electroless nickel-phosphorus films to a commercial pure aluminum substrate is improved by double zincate treatment where a uniform zincate film is obtained. Coarse zinc particles formed by single zincate treatment is thought to be due to spatially nonuniform anodic (dissolution of aluminum) and cathodic (precipitation of zinc) reactions.

2. Uniform zincate films are obtained by double zincate treatment both for the basic and the commercial zincate solutions as a result of spatially uniform conversion reaction of aluminum and zinc. The thickness of the double zincate film obtained by the basic solution is 30–40 nm, while that by the commercial solution is 10–15 nm estimated by the depth profile of iron.

3. Electroless nickel-phosphorus plated films show poor adhesive strength for thicker zincate films. In those cases, zinc and oxygen are detected at the interface between the plated film and the substrate, and gaps are observed by transmission electron microscopy.

4. A thinner zincate film is considered to form on a layer of iron which precedingly forms in the commercial zincate solution to be preferred precipitation sites of zinc particles.

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REFERENCES

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