Effects of Alloying Elements in Aluminum Alloys and Activations on Zincate Treatment and Electroless Nickel-Phosphorus Plating

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Zincate treatment and electroless nickel-phosphorus plating for aluminum alloys of A1100, A2017, A5052 and A7075 were researched from the viewpoints of alloying elements and activation conducted prior to zincate treatment. Surface morphologies of zincated surfaces, electrochemical properties during zincate treatment and depth profiles on activated and zincated surfaces were investigated by microscopy and measurement of temporal changes of electrode potential.

Adhesion strengths of the plated films were measured by 90° peeling test, which showed that double zincate treatment improved adhesion strength especially when ferric ion was added into the zincate solution except for the case of A7075. Temporal changes of electrode potential during zincate treatments and morphologies of the zincated surfaces showed that copper and zinc promoted uniform precipitation of zinc and resulting rapid termination of conversion reaction. Excess zinc was shown to dissolve into the plating solution and cause the formation of low-density area or gaps between plated films and substrates.

Activation for A1100 by various conditions showed that formation of oxide film had a remarkable effect on precipitation of zinc during zincate treatment. When a mixture of nitric and hydrofluoric acid was used for activation, finer particles of zinc were formed near etch pits compared with the cases of hydrochloric or nitric acid. On the other hand, the surface was uniformly covered with fine zinc particles in the case of the activation with a solution of sodium hydroxide. This indicates that uniformity of oxide film on substrate before zincate treatment is thought to bring about uniform precipitation of zinc. [doi:10.2320/matertrans.L-M2009830]

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1. Introduction

Industrial application of aluminum alloys has been expanding for advantages of their light weight, workability, and excellent corrosion resistance. In order to improve their surface properties such as wear resistance, corrosion resistance or ornamentation, platings on aluminum alloys are commonly adopted. As one of the measures to improve surface properties of aluminum alloys, electroless nickel-phosphorus plating¹–⁴ is promising for its excellent corrosion resistance as well as high hardness of ~HV600 and wear resistance. Recently, corrosion of aluminum by bio-fue尔斯５–⁸ has become of interest in automotive applications, which is hopefully suppressed by nickel-based platings.

Since aluminum is such an active element as to be oxidized and passivated in water⁹ as well as in air, poor adhesion of plated films to substrates is one of the problems in the process.¹⁰ The most common solution for ensuring good adhesion of plated films is the ‘double zincate treatment’¹¹ in which a conversion treatment is repeated twice in an alkaline zincate solution prior to plating. Electroless nickel-phosphorus plating also requires the double zincate treatment for improvement of adhesion strength. Although behavior of alloying elements in aluminum alloys has been considered to be important for understanding adhesion of plated films to substrates, the detailed nature remains unknown which affects the interfacial structure between electroless nickel-phosphorus plated films and substrates.

In this research, adhesion strengths of electroless nickel-phosphorus plated films to commercial aluminum alloys were quantified for various zincate treatment conditions. Also, morphologies of zincate films and their formation process were related to activation conducted prior to zincate treatment and to adhesion strengths of plated films by microscopy and electrochemical measurement. Here, electroless nickel-phosphorus plating and electroless nickel-phosphorus plated film are expressed as ‘plating’ and ‘plated film’ in the following sentences unless otherwise noted.

2. Experimental

Rolled sheets of commercial aluminum alloys (Japan Industrial Standard, JIS A1100P (99 mass%Al), A2017P (3.9Cu), A5052P (2.5Mg), A7075P (5.8Zn-2.7Mg-1.6Cu)) were used as substrate. Chemical composition of each alloy is shown in Table 1. Adhesion strengths of plated films were evaluated according to the previous reports.¹²,¹³ The substrates were cut into platelets of a dimension of 35 × 10 mm², then, each platelet was polished to a mirror finish by buffing to eliminate anchoring effect on adhesion of the plated films to the substrates and also to enhance the changes of adhesion strength with respect to the condition of zincate treatment. Prior to plating, pretreatments (alkaline degreasing, activation and zincate treatment) were carried out as shown in

<table>
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<th>Alloy</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
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<td>0.57</td>
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<td>A2017P T3</td>
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<td>0.27</td>
<td>3.93</td>
<td>0.6</td>
<td>0.53</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
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<tr>
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<td>0.27</td>
<td>0.04</td>
<td>0.08</td>
<td>2.47</td>
<td>0.22</td>
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<tr>
<td>A7075P T651</td>
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<td>1.6</td>
<td>0.04</td>
<td>2.07</td>
<td>0.20</td>
<td>5.8</td>
<td>0.02</td>
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</table>
Table 2. Here, a mixed solution of nitric acid and hydrofluoric acid (volume ratio HNO$_3$ : HF = 3 : 1) was used for activation in the measurement of adhesion strength of the plated films. This mixed solution, which is standard pretreatment, is expressed as ‘nitric-hydrofluoric acid’ in the following sentences.

As zincate solutions, a basic solution and a ferric ion-added one were used for investigating the difference in properties of zincate films as well as adhesion strengths of plated films. The basic solution consists of zinc oxide (40 kg/m$^3$ solution) and sodium hydroxide (240 kg/m$^3$ solution), and the concentration of iron in the ferric ion-added solution was set as Zn : Fe = 40 : 1 in atomic ratio. For adding ferric ion into the basic zincate solution, a solution of iron(III) chloride and a complexing agent for zinc-iron plating (Nippon Hyoumen Kagaku, Co., Ltd., Stronzinc) was used. Zincate treatment was conducted at 298 K for 30 s, and double zincate films were obtained by zincate treatment after removing single zincate films with a solution of 5 vol% nitric acid. Immediately after the pretreatments, each substrate was immersed in an electroless nickel-phosphorus plating solution (Japan KANIGEN Co., Ltd., SD200), and the plating was conducted at 363 K for 5.4 ks. The averaged thickness of the plated films obtained under the above conditions was 200 μm.

After plating, a 90° peeling test was carried out for quantification of adhesion strength of the plated films. Before the peeling test, the specimens were coated with copper film of 30μm-thick by electroplating in copper sulfate solution for reinforcement of the electroless nickel-phosphorus plated films. After the side planes of the copper-coated substrates were polished by abrasive papers (#1200), the plated films were peeled with the cross head speed of 0.5 mm/s. Adhesion strength was conveniently determined here as the value of the maximum load divided by the width of the peeled film (10 mm).

Electrochemical properties of the surfaces of the substrates during zincate treatment were investigated by measuring electrode potential. The polished substrates were covered with epoxy resin, leaving square windows of 10 $\times$ 10mm$^2$ which contact the zincate solutions. After degreasing and pickling, each substrate was immersed into the basic zincate solution or the ferric ion-added one, and the potential was measured by using a salt bridge of saturated potassium chloride and a standard calomel electrode (SCE) as a reference.

The surfaces of the substrates after zincate treatments were observed by field emission scanning electron microscopy (FE-SEM). Element analysis on the activated or zincated surfaces were obtained by using argon ion etching whose acceleration voltage and sputtering rate were 3 kV and 0.68 nm/cycle, respectively.

3. Experimental Results

3.1 Adhesion strength of plated film

Figure 1 shows adhesion strengths of the plated films. Although adhesion strengths are generally low in the case of the basic zincate solution (Fig. 1(a)), that of 5052 (double
zincate treatment) is remarkably higher than other substrates. By using the ferric ion-added zincate solution (Fig. 1(b)), adhesion strengths were improved for all substrates. Here, for a plated film which ruptured during the peeling tests, ‘Film ruptured’ is denoted in the corresponding bar. On the other hand, for a specimen whose plated film peeled off before the peeling test, ‘Film peeled off’ is denoted.

On the other hand, adhesion strengths were generally poor in the case of A7075 compared with other substrates. The plated films could be peeled continuously even for the specimens which underwent the double zincate treatment with the ferric ion-added solution.

3.2 Temporal change of electrode potential during zincate treatment

Figure 2 shows the temporal changes of electrode potential during zincate treatments. The curves during the single zincate treatments of A1100 and A5052 with the basic solution (Fig. 2(a),(c)) show almost the same tendency, in which rather slow rises of electrode potential at the beginning are observed. The electrode potentials of A1100 and A5052 are rapidly stabilized for the double zincate treatments.

On the other hand, the potential curves of A2017 and A7075 in the case of the basic zincate solution (Fig. 2(b),(d)) are almost the same for both the single and the double zincate treatments, and the potentials are stabilized in a few seconds after the substrates are immersed into the solution. By using the ferric ion-added zincate solution (Fig. 2(e)–(h)), the initial potentials are shifted to less-noble side compared with the cases of the basic solution, but the tendency is almost the same as that of Fig. 2(a)–(d).

3.3 Morphology of zincated surface

Figure 3 shows secondary electron images of the surfaces after zincate treatment with the basic solution. The surface morphologies of A1100 and A5052 after zincate treatment (Fig. 3(a)–(c) and (g)–(i)), whose temporal changes of electrode potential showed almost the same tendency, were similar, showing rather coarse zinc particles of ~500 nm around the etch pits at the beginning of the single zincate
treatment. Other flat areas were covered with fine zinc particles after the formation of the coarse ones. Coarse zinc particles were not observed in the cases of the double zincate treatment as shown in Fig. 3(c),(i).

On the other hand, in the case of A2017 and A7075, the coarse zinc particles were not observed near the etch pits even after the single zincate treatment. For these substrates, surfaces after the single and the double zincate treatment showed almost the same morphologies where no distinguishable zinc particle could be seen. Although the data is not shown here, the morphologies of the zincated surfaces obtained by the ferric ion-added solution showed almost the same tendency as those obtained by the basic solution.

3.4 Effect of activation

Figure 4 shows secondary electron images of the zincated surfaces of A1100 for various activation conditions. In the cases where nitric or hydrochloric acid was used (Fig. 4(b),(c)) for activation, coarser grains of zinc (~1 μm) were formed near the etch pits compared with the case of the nitric-hydrofluoric acid (Fig. 4(a)). On the other hand, the surface activated by the solution of sodium hydroxide was uniformly covered with fine particles of zinc. In this case, neither etch pits nor coarse particles of zinc were observed, but surfaces of intermetallic compound which did not dissolve into the solution for activation were also coated by zinc.

Figure 5 shows the depth profiles of oxygen on the surfaces of A1100 before and after activation. Oxide film became thinner for all activation conditions than that on the as-polished surface. In the cases of nitric-hydrofluoric acid and sodium hydroxide, where fine particles of zinc coated the surfaces of the substrate (Fig. 4(a),(d)), oxide films are thinner compared with the cases of nitric and hydrochloric acid.

Figure 6 shows the depth profiles of oxygen, copper, aluminum and zinc on the surfaces of A2017 which underwent polishing, activation with the nitric-hydrofluoric acid, and single zincate treatment with the basic solution. While the thickness of oxide film is reduced by activation, enrichment of copper is observed at ~10 nm from the surface (Fig. 6(b)). This behavior of copper in activation was also confirmed in the case of A7075. The copper-rich layer still exists at the depth of ~20 nm after single zincate treatment (Fig. 6(c)), and the zincate layer contains oxygen up to 50 at%. Similar profiles were obtained in the case of A7075.

Fig. 7 shows the secondary electron image on the surface of A1100 after activation with the nitric-hydrofluoric acid. Here, the surface was slightly (~1 nm) etched by argon ion beam, whose acceleration voltage was 3 kV, before taking the micrograph in the ultra high vacuum chamber of AES. A number of brighter areas (indicated by broken curves in Fig. 7) are observed which surround the etch pits on the activated surface. This brightness change appeared after the argon ion etching mentioned above.

3.5 Structure of the interface between plated film and substrate

Figure 8 shows the cross-sectional microstructures of the interfaces between the substrates and the plated films after single zincate treatment with the basic solution and subse-
sequent plating. In Fig. 8(a),(b),(c), the zincated surface of A1100 is covered with the layer (i) which consists of zinc and nickel after immersion in the plating solution for 5 s. The surface also showed a low-density part (iii) compared with the outer layer (ii), and low-densisy parts were observed partly at the interface between the substrate and the zinc-nickel layer (i). When the zincated specimen was immersed in the plating solution for 30 s, many pores of \( \sim 100 \text{ nm} \) in size were found at the interface by cross-sectional SEM observation.20

On the other hand, those pores at the interface can hardly be found in the case of A2017 by SEM (Fig. 8(d)). However, a continuous gap or a low-density layer whose width is \( \sim 10 \text{ nm} \) lies between the plated film and the substrate as observed by TEM (Fig. 8(e)). Such defects at the interface were also observed in the case of A7075.

4. Discussions

4.1 Adhesion strength and zincate treatment

In the previous research for a commercial pure aluminum,16 thickness of zincate film and adhesion strength of plated film became thinner and higher, respectively, when concentration of ferric ion in zincate solution was increased. From Fig. 1, similar effect is thought to occur in each alloy, where precipitation of iron precedes that of zinc, then the surfaces of the substrates are covered with thin zincate film. Here, the reason for remarkably low adhesion strengths in the case of A7075 will be discussed later, which contains rather large amount of zinc (5.8 mass%).

In Fig. 2, the slow rises of electrode potential during the single zincate treatments for A1100 and A5052 are thought to correspond to nonuniform dissolution of oxide film on the substrates and resulting precipitation of zinc. Those zinc particles, observed in Fig. 3(a),(g), are rather coarse supposedly as a result of the elongated dissolution of aluminum in the etch pits where the supply rate of zincate ion is low. That is, the anode and the cathode sites in the early stage of the single zincate treatment are thought to be the inside of the etch pits and their edges, respectively. Precipitation of zinc stops when the solution in the etch pits is saturated with aluminate ion or concentration of zincate ion decreases.

Here, the amount of zinc in an etch pit is estimated by the concentration of zinc in the zincate solution (32 kg/m³) and the volume of an etch pit whose shape is assumed to be a cube of \( a^3 \mu \text{m}^3 \). The corresponding thickness of the zincate film formed inside the etch pit is given as \( t \sim 9 \times 10^{-4} \mu \text{m} \), if a uniform film covers the inside. Since the averaged size...
of etch pits is $a \sim 5 \mu m$, thickness of zinc is $t \sim 4\text{--}5$ nm. From this estimation, the inside of the etch pits become reasonable anode sites if precipitation of zinc occurs nonuniformly and aluminum continue to dissolve into the zincate solution in the etch pits.

After the nonuniform precipitation of zinc for a few seconds, the remaining flat areas are covered with finer zinc particles within $\sim 10$ s. This is thought to be the result of uniform dissolution of oxide film and aluminum, followed by immediate precipitation of zinc. When the surface is totally covered with zinc particles, the conversion reaction of aluminum and zinc stops, and the electrode potential curve shows the steady state. Here, the potential rise in the single zincate treatment of A5052 (aluminum-magnesium alloy) is the slowest in Fig. 2. Since magnesium is known to improve corrosion resistance of aluminum,21,22) the slow rise (alkaline) is the slowest in Fig. 2. Since magnesium is known to improve corrosion resistance of aluminum,21,22) the slow rise in potential is thought to be because of the stable or thick oxide film and its resulting low dissolving rate or long duration before metallic aluminum is exposed to the zincate solution.

### 4.2 Effect of activation

In the case of the activation with the nitric-hydrofluoric acid (Fig. 4(a)), finer zinc particles are found near the etch pits compared with the case of nitric or hydrochloric acid (Fig. 4(b),(c)). As discussed in the temporal changes of electrode potential, the coarse zinc particles indicate nonuniform disappearance of oxide film, therefore, the surfaces activated with the nitric or hydrochloric acid (Fig. 4(b),(c)) are thought to be nonuniformly oxidized compared with the case of nitric-hydrofluoric acid (Fig. 4(a)). On contrary, the surface activated by the solution of sodium hydroxide was uniformly covered with fine zinc particles (Fig. 4(d)) which precipitated at once immediately after the immersion into the zincate solution. This is because oxide film is not formed during the activation and the zincate treatment,93 between which the specimen is not rinsed in water.

The depth profiles of oxygen (Fig. 5) on the activated surfaces of A1100 show that the activation with the nitric-hydrofluoric acid suppresses the development of oxide film. Since fluorine is detected at the surface after the activation with the nitric-hydrofluoric acid, the surface after the activation is thought to partly consist of aluminum fluoride, which suppresses oxidation compared with the case of hydrochloric and nitric acid. The complex film may easily dissolve into the zincate solution, then, the exposed aluminum is covered with zinc particles by conversion reaction.

Here, the nonuniformity of the activated surface is shown in Fig. 7, where the brighter areas near the etch pits (indicated by broken curves) suggest that the areas are covered with thinner oxide film or metallic aluminum is exposed by the slight etching in the ultra high vacuum chamber. Thus, the brighter areas near the etch pits are thought to be the preferred precipitation sites of zinc particles which become rather coarse at the early stage of zincate treatment.

In the cases of A2017 and A7075, copper-rich layers were formed by activation as shown in Fig. 6. Enrichment of copper is thought to occur due to its nobleness compared with that of aluminum in the nitric-hydrofluoric acid. Since adsorption of copper on aluminum is reported to promote uniform precipitation of zinc,23) copper may act as preferred nucleation sites of zinc or to increase dissolution rate of oxide film into the zincate solution. Concerning the zincate film formed on A2017 or A7075, oxygen and aluminum are contained up to 30 and 50 at%, respectively. Since aluminum is oxidized more easily than zinc, the zincate film may be regarded as a layer of zinc which contains aluminum oxide. The structure might be analogous to the oxide film formed by immersion in nitric acid after the single zincate treatment, as previously proposed by Morikawa.19)

### 4.3 Initial reaction in plating

Figure 9 schematically shows the cross sections of the zincated surfaces and the plated ones at the initial state of plating. In Fig. 8(a)--(c), the part (i) is thought to have been a flat zinc layer in Fig. 4(a), and the parts (ii) (iii) were originally a coarse zinc particle (Fig. 9(a)). Since the original zinc layer is alloyed with nickel in 5 s after immersion into the plating solution, zinc is thought to once dissolve into the plating solution, then, precipitate with nickel and phosphorus to form the initial plated layer (Fig. 9(b)). The low-density part (iii) is thought to be formed also as a result of dissolution of zinc, but deposition of nickel is not clearly observed. This is supposedly because the supply of nickel ion is suppressed by the porous shell of nickel-zinc alloy (ii) which has been formed immediately after immersion into the plating solution.

These low-density parts or voids which lie between the substrate and the plated film cause poor adhesion, therefore, lowering the amount or thickness of zincate film is effective as far as the layer suppresses oxidation of aluminum. Since dissolution of zinc in electroless nickel-phosphorous plating solution is reported to induce precipitation of nickel on aluminum,24) uniformity of zincate film and its rapid dissolution are necessary for ensuring good adhesion of plated films.

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Fig. 9 Cross-sectional schematic illustration of the surfaces after zincate treatment with the basic solution and electroless nickel-phosphorus plating. (a) A1100, after the single zincate treatment, (b) After plating for 5 s of (a), (c) A2017, after the single zincate treatment, (d) After plating for 30 s of (c).
The zincate film of A2017 (Fig. 9(c)) is uniform (Fig. 3(e)) and its thickness is \( \sim 20 \) nm (Fig. 6(c)), considering the position of the copper-rich layer which suggests the position of the original surface after activation with the nitric-hydrofluoric acid. The amount of zinc needs to be further lowered for obtaining better adhesion strength of plated films, since the gap in Fig. 8(d) is thought to be formed in the lower layers or gaps at the interfaces between the substrate and plated film, which can cause poor adhesion.

(3) While nonuniform oxide film is thought to be formed on A1100 and A5052 corresponded to the nonuniform formation of coarse zinc particles. Nucleation and growth of zinc occurred near etch pits formed by dissolution of intermetallic compounds in substrate during activation with nitric-hydrofluoric acid. The coarse zinc particles dissolved into the plating solution immediately after immersion, leaving low-density layers or gaps at the interfaces between the substrate and plated film which can cause poor adhesion.

(4) Adhesion strengths of plated films were greatly improved by the double zincate treatment with ferric ion-added solution, during which electrode potential rapidly reached the steady state. In the case of A7075, however, improvement by the double zincate treatment was quite small compared with the other alloys supposedly because of zinc as an alloying element in the substrate.

(5) Uniform zincate films on A2017 and A7075 contained oxygen up to \( 50 \) at% which might consist of aluminum oxide and metallic zinc. The copper-rich layer formed on the substrates by activation with the nitric-hydrofluoric acid is thought to have an effect to promote uniform precipitation of zinc.

5. Summary

In this paper, reactions in zincate treatment and subsequent electroless nickel-phosphorus plating were researched by electrochemical measurement and microscopy. Morphology of zincated surfaces and adhesion strengths of plated films were largely changed by conditions of activation, those of zincate treatment and alloying elements. The results are summarized as follows.

(1) Temporal changes of electrode potential of aluminum alloys during zincate treatment were categorized into two types. While the alloys which contain copper and/or zinc (A2017, A7075) showed rapid changes of electrode potential both in single and double zincate treatment, the other alloys (A1100, A5052), which do not contain meaningful amount of copper or zinc, showed rather slow changes during single zincate treatment.

(2) The slow temporal changes of electrode potential in the cases of A1100 and A5052 corresponded to the uniform precipitation of coarse zinc. Nucleation and growth of zinc occurred near etch pits formed by dissolution of intermetallic compounds in substrate during activation with nitric-hydrofluoric acid. The coarse zinc particles dissolved into the plating solution immediately after immersion, leaving low-density layers or gaps at the interfaces between the substrate and plated film which can cause poor adhesion.

REFERENCES