

Effects of zincate treatment on adhesion of electroless Ni-P coating onto various aluminum alloys

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Abstract: The effects of alloying elements on zincate treatment and adhesion of electroless Ni-P coating onto various aluminum alloy substrates were examined. Surface morphology of zinc deposits in the 1st zincate treatment and its adhesion were changed depending on the alloying element. The zinc deposits in the 2nd zincate treatment became thinly uniform, and the adhesion between aluminum alloy substrate and Ni-P coating was improved irrespective of the alloying element. XPS analysis revealed the existence of zinc on the surface of each aluminum alloy substrate after the pickling in 5% nitric acid. This zinc on the surface should be an important factor influencing the morphology of zinc deposit at the 2nd zincate treatment and its adhesion.

Key words: electroless Ni-P coating; aluminum alloy; zincate treatment; adhesion

1 Introduction

Aluminum alloys are increasingly utilized recently to improve fuel consumption of vehicles by reducing their mass, because of their excellent workability and corrosion resistance[1–2]. In surface modifications of aluminum alloys for improving their hardness, wear resistivity, or for decorative purposes, appropriate pretreatment is indispensable to obtain high adhesive strengths of the films, since the surfaces of aluminum alloys are passivated by oxidation in water as well as in air[3]. For this purpose, zincate treatment is commonly adopted which covers surface of substrate with zinc film by displacement reaction of aluminum and zinc. Especially, the double zincate treatment[4] which repeats a conversion treatment twice shows remarkable increase in adhesive strength of the electroless Ni-P coating onto aluminum alloy substrates.

In a few previous researches[5–7] on zincate treatment for aluminum alloy substrates, morphology of zinc particles and anchoring effect due to roughening brought by dissolution of the substrate have been reported to affect adhesion of the electroless Ni-P coating to the substrate. Although behavior of zinc has been

considered to be important for understanding adhesion of the coating to the substrate, its detailed mechanism remains unknown.

In this study, the effects of alloying element and pretreatment such as the number of zincate treatment and the kind of acid after the 1st zincate treatment on adhesion of electroless Ni-P coating onto various aluminum alloys substrates were investigated by using peeling test, field-emission scanning electron microscope (FE-SEM) and XPS.

2 Experimental

Rolled aluminum alloys were used as substrate whose chemical compositions were shown in Table 1. These sheets were cut to platelets (35 mm×10 mm), then polished to mirror finish by buffing for eliminating anchoring effect. Preceding to the electroless Ni-P platings, various pretreatments were carried out according to Table 2. A commercial zincate solution (Japan KANIGEN Co. Ltd., SUMER K-102) and an electroless Ni-P plating solution (Japan KANIGEN Co. Ltd., S-754) were used for the treatments. Each zincate treatment was carried out at 298 K for 30 s, and the electroless Ni-P plating at (363±3) K for 7.2 ks. The

Table 1 Chemical compositions of various aluminum alloys (mass fraction, %)

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others	Al
A1100P	0.23	0.93	0	0	0	0	0	0	0.05	Bal.
A2017P	0.54	0.27	3.33	0.6	0.53	0.02	0.12	0.03	0.01	Bal.
A5052P	0.09	0.27	0.04	0.1	2.47	0.22	0.01	0	0.03	Bal.

Table 2 Various pretreatments and zincate procedures

Without zincate	1st zincate	2nd zincate	2nd zincate (pickling)	2nd zincate (pickling)+ zincate
Alkaline cleaning	Alkaline cleaning	1st zincate	1st zincate	1st zincate (pickling)
↓	↓	↓	↓	↓
Washing	Washing	5% HNO ₃ dipping (Dipping for 10 s)	Pickling (1HF+3HNO ₃) (Dipping for 10 s)	5% HNO ₃ dipping (Dipping for 10 s)
↓	↓	↓	↓	↓
Pickling (1HF+3HNO ₃) (Dipping for 10 s)	Pickling (1HF+3HNO ₃) (Dipping for 10 s)	Washing	Washing	Washing
↓	↓	↓	↓	↓
Washing	Washing	Zincate treatment (30 s)	Zincate treatment (30 s)	Zincate treatment (30 s)
	↓	↓	↓	↓
	Zincate treatment (30 s)	Washing	Washing	Washing
	↓			
	Washing			

content of phosphorus and the averaged thickness of the Ni-P coating obtained under the above conditions were (9±0.5)% and 20 μm, respectively.

After the electroless Ni-P coating, a 90° peeling test was carried out for quantification of adhesive strength of the plated films to the substrates[8]. Before the peeling test, the specimens were coated with 30 μm-thick copper film by electro plating in copper sulfate solution for reinforcement of the electroless Ni-P coating. The sides of the copper-coated substrates were polished to remove unnecessary films for the peeling test, and then a part of the coating 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 various pretreated substrates was observed by FE-SEM. Chemical analysis on the surface dipped into various acids after the 1st zincate treatment was conducted by XPS.

3 Results and discussion

Table 3 shows the adhesive strengths obtained by 90° peeling test. Here, an adhesive strength is defined as the maximum value of the load in a load—displacement curve[7]. Without zincate treatment, Ni-P coatings on

Table 3 Adhesion strength for Ni-P coatings after 90° peeling test

Zincate treatment	Adhesion strength/(kN·m ⁻¹)		
	A1100P	A2017P	A5052P
Without zincate	No deposition	0.07	0.04
1st zincate	0.52	0.13	0.06
2nd zincate	Film rupture	1.12	1.16
2nd zincate (Pickling)	0.75	0.67	0.16
2nd zincate (Pickling)+ zincate	Film rupture	Film rupture	Film rupture

A1100P are not thin and nonuniform, which are inapplicable for the 90° peeling test. On the other hand, the coatings on A2017P and A5052P formed. It seems that the Ni-P coating cannot form on A1100P alloy, which may be caused by the change of oxide film in state. The adhesive strengths of both A2017P and A5052P are poor.

The adhesive strength of each specimen was slightly improved by the 1st zincate treatment; however, the 2nd zincate treatment caused drastic improvement in adhesive strength for each specimen. In particular, the adherence in which Ni-P coating on A1100P ruptured for the 90° peeling test is shown. On the adhesion between the aluminum alloys substrate and electroless Ni-P

coating, it is found that the 2nd zincate treatment is much effective.

As mixed acid ($1\text{HF}+3\text{HNO}_3$) shown in Table 2 was used instead of 5% nitric acid for the pickling after the 1st zincate treatment, the adhesive strength of each specimen after the 2nd zincate treatment was lowered. And the 10% hydrochloric acid instead of the mixed acid for the pickling was also made to lower the adhesive strength for each specimen. In addition, as these specimens whose adhesive strength was lowered by using the mixed acid were again dipped in 5% nitric acid for the pickling, adhesive strength after the zincate treatment was improved further than that after the 2nd zincate treatment. These results suggest that adhesive strength after the 2nd zincate treatment is affected by the type of acid for the pickling after the 1st zincate treatment.

Fig.1 shows SEM images of the surface after zincate treatment with various pretreatments shown in Table 2. Although the morphology of zinc deposits after the 1st zincate treatment is different depending on the alloy type, the nonuniformly rough deposits are observed besides A2017P. In previous report[9], it was shown that this uniform and fine zinc deposit on A2017P after the 1st zincate treatment was attributed to Cu-rich on the substrate surface after the pickling ($1\text{HF}+3\text{HNO}_3$). On the other hand, the surface of each substrate by the 2nd zincate treatment with dipping in 5% nitric acid was uniformly covered by fine deposits. From these results of Table 3 and Fig.1, the adhesive strength is closely

associated with the morphology of zinc deposits treated by the zincate treatment.

The surfaces of each aluminum alloy substrate after the different pretreatments were investigated by XPS in order to clarify the factor in which the zinc deposits by the same zincate treatment changed. Fig.2 shows XPS wide spectra for each substrate surface after the different pickling. After pickling by the $1\text{HF}+3\text{HNO}_3$ solution, aluminum, oxygen, carbon and fluorine derived from alloy elements and reaction between the aluminum substrate and HF were detected for each specimen, and copper was detected for only A2017P. The uniform and fine zinc deposit on A2017P after the 1st zincate treatment as shown in Fig.1 was attributed to Cu-rich on the substrate surface[9]. On the other hand, after the pickling by 5% HNO_3 solution, zinc was detected together with the foregoing elements for each specimen. This zinc existing on the surface should affect the morphology of zinc deposit in the next zincate treatment, because zinc was not detected in the surface, as the mixed acid ($1\text{HF}+3\text{HNO}_3$) was used instead of 5% nitric acid for the pickling. And the morphology of zinc deposit obtained by zincate treatment as shown in Fig.1 becomes thick and nonuniform. This zinc on the surface can be attributed to the diffusion of zinc and aluminum between the zinc deposit from the 1st zincate and the aluminum alloy substrate.

In general, the deposited film by displacement plating such as gold plating becomes thinly uniform, because the electron is discharged as the less noble metal

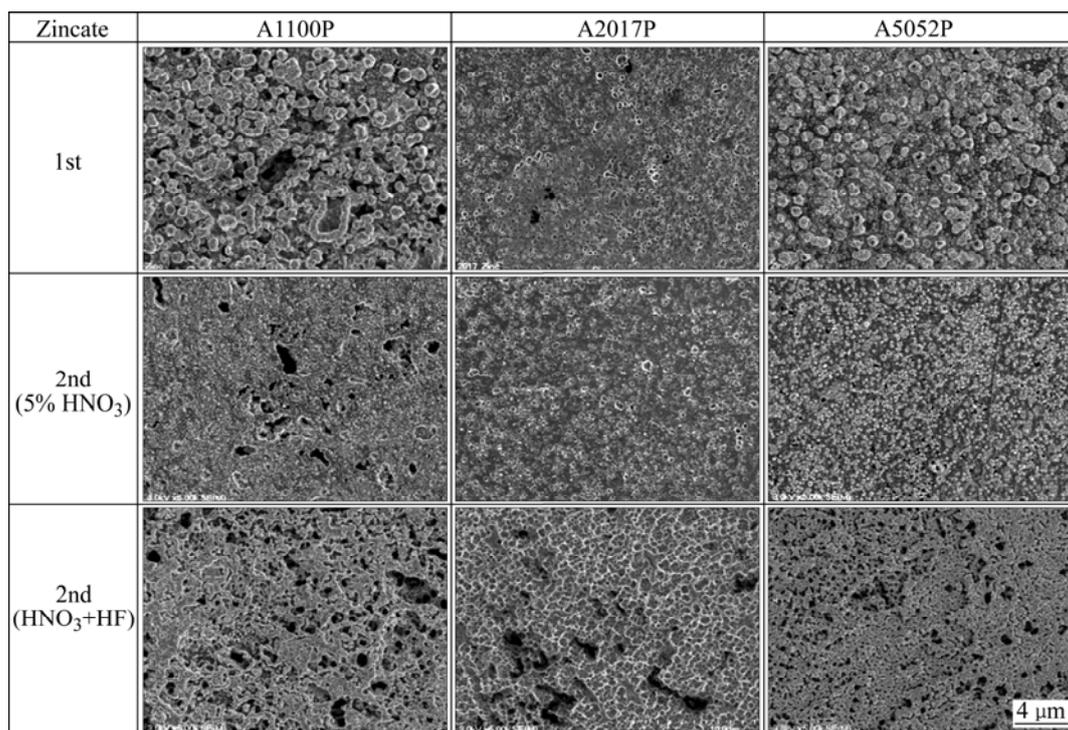


Fig.1 SEM images of specimens showing zincate treated surface on various aluminum alloys

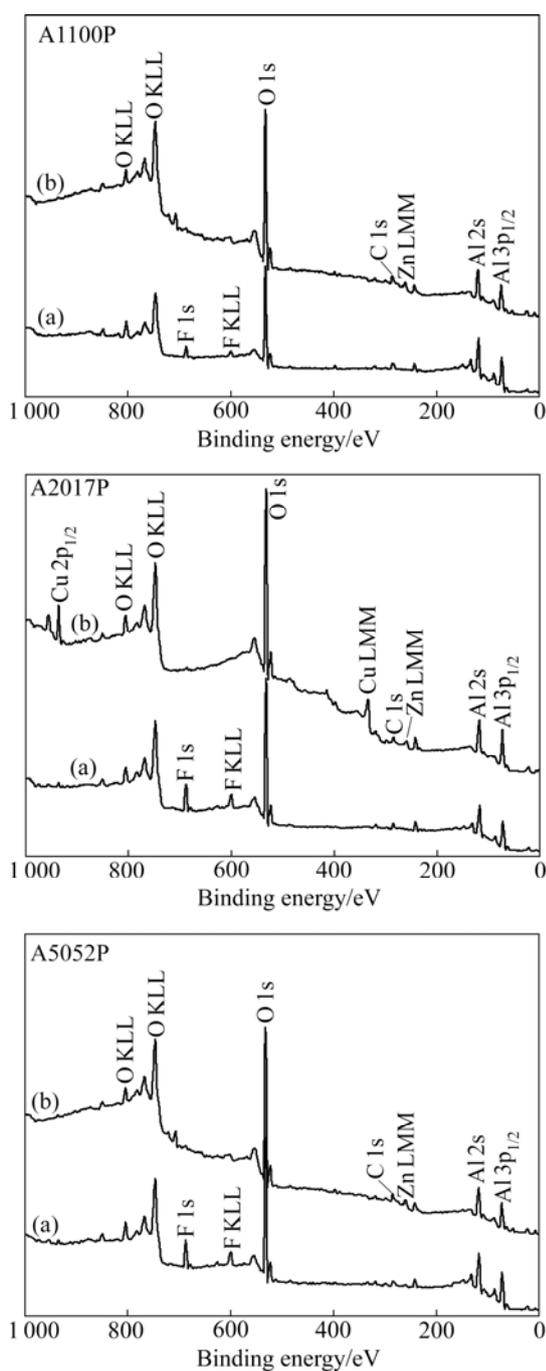


Fig.2 XPS wide spectra on various aluminum alloys after pickling (1HF+3HNO₃) against substrate (a) and pickling (5% HNO₃) against the 1st zincate treatment (b)

substrate dissolves. Subsequently, metal ion in the solution is reduced by the electron, and this reaction is finished instantly when deposited film perfectly covers the substrate. Fig.3 shows the cross-sectional SEM images of specimens after the 1st and the 2nd zincate treatment on A1100P aluminum alloy. As shown in Fig.3(b), zinc deposit on the surface is rarely observed after the 2nd zincate treatment, and this fact is explainable in term of the idea of displacement plating.

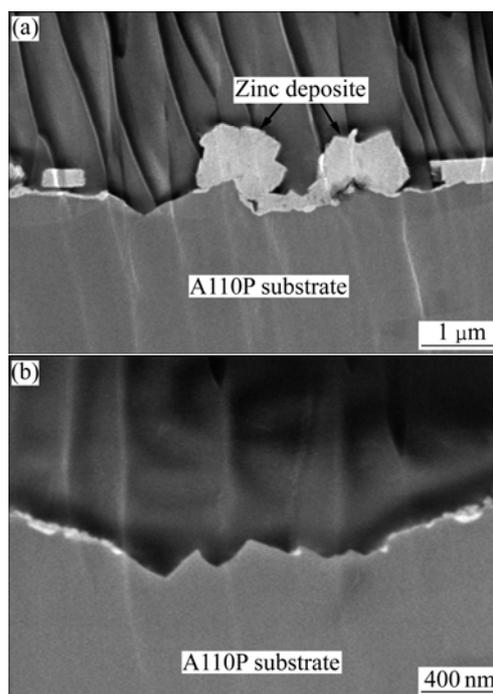


Fig.3 Cross-sectional SEM images of specimens showing zincate treatment on A1100P aluminum alloy: (a) The 1st zincate treatment; (b) The 2nd zincate treatment

On the other hand, after the 1st zincate treatment, zinc deposit with the remarkable ruggedness is observed, as shown in Fig.3(a), and these results well agreed with the surface morphology shown in Fig.1. This fact is not compatible with the idea of displacement plating. This morphology of zinc deposit in the 1st zincate treatment can occur, as different sites between the anodic dissolution and the deposit by reduction exist, and the behavior of this deposit is based on the formation of the nonuniform oxide film on aluminum substrate[10]. After the pickling by 5% HNO₃ solution, Al-Zn alloy layer on the surface, which is formed by the diffusion between zinc deposit and aluminum substrate, seems to suppress the passivation of aluminum substrate, and thus the oxide film dissolves immediately. Subsequently, displacement reaction of aluminum and zinc occurs uniformly on the substrate surface. The morphology of zinc deposit in the 2nd zincate treatment shall become thinly uniform in this manner.

4 Conclusions

The effects of alloying elements on zincate treatment and adhesion of electroless Ni-P coating onto various aluminum alloy substrates were examined. Surface morphology of zinc deposit in the 1st zincate treatment and its adhesive strength are changed depending on the alloying element. The zinc deposit in

the 2nd zincate treatment becomes thinly uniform, and its adhesive strength is improved irrespective of the alloying element. The zinc existing on the surface after the pickling in the 5% HNO₃ solution shall affect the morphology of zinc deposit in the next zincate treatment and its adhesion. It seems that this zinc on the surface can be attributed to the diffusion of zinc and aluminum between the zinc deposit in the 1st zincate and the aluminum alloy substrate.

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