

X-ray photoelectron spectroscopy and corrosion studies of zinc phosphate coated on 7075-T6 aluminium alloy

Part II: *Effect of coating pH*

W. F. HEUNG, Y. P. YANG, M. Y. ZHOU, P. C. WONG, K. A. R. MITCHELL
Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

T. FOSTER
Chemistry Group, Defence Research Establishment Pacific, FMO Victoria, British Columbia, Canada V0S 1B0

Coated layers which formed on 7075-T6 aluminium alloy surfaces after treatment in zinc phosphate (ZPO) suspensions adjusted to different pH values (3.5, 5.0, 6.6, 10.5 and 13.0) were characterized by X-ray photoelectron spectroscopy (XPS). Comparative XPS tests were also made after the treated surfaces were exposed to a 3.5% NaCl solution for 5 h. The processes of coating from solution, oxidation, etching and bulk diffusion were all involved, although in different proportions, in the different treatments. The amounts of zinc and phosphorus in the uppermost layers were enhanced when the coating was at pH values of 5.0, 10.5 and 13.0, and in each case a mixed ZnO_x - AlO_x -ZPO structure was apparently formed. The coating prepared at pH = 13.0 appeared to provide the best corrosion protection.

1. Introduction

Zinc chromate has been widely used in chemical conversion coatings, and as a pigment in anticorrosive primers, to improve the corrosion resistance of aluminium surfaces, but concerns about its carcinogenic nature are forcing the development and evaluation of replacement materials. In Part I, we explored the chemical composition and morphology of the surface layers which formed when a 7075-T6 aluminium alloy was treated with a zinc phosphate solution at the natural pH [1]. X-ray photoelectron spectroscopy (XPS) showed that two forms of zinc are bonded to the surface; one is weakly bound, and can be removed by ultrasonic washing, but the other is strongly bound and appears to correspond to an oxide, ZnO_x , which is distributed reasonably homogeneously within the aluminium-oxide film above the metal. Corrosion tests indicated that this treatment increases the alloy stability in a corrosive Cl^- environment.

This work, part II, aims to extend Part I [1] and to characterize the corrosion stability and coating mechanism in this system when the zinc-phosphate coating is performed at different values of the solution pH. XPS is again the main characterization technique.

2. Experimental procedure

Square test panels of 7075-T6 aluminium alloy were prepared in the way described in Part I. The zinc-

phosphate (ZPO) coating process was performed by suspending the test panels for 1 h at room temperature in 10 wt % ZPO suspensions adjusted to different pH values (from 13.0 to 3.5) with sodium hydroxide (NaOH) or acetic acid (HOAc). After coating, the panels were ultrasonically rinsed in distilled water for 1 min, and then they were rinsed with absolute ethanol and air dried. Corrosion tests were performed on these treated samples by immersing in a 3.5% sodium chloride (NaCl) solution for 5 h at room temperature. After this treatment, the panels were rinsed with distilled water, to remove any NaCl solution from the surface, and then air dried. Table I summarizes the different preparations and treatments used in this study. XPS spectra were measured in a Leybold MAX200 spectrometer following the procedures detailed in Part I.

3. Results and discussion

3.1. Coating process

The initial samples (Table I) are designated A1 to F1. In brief, they are the polished 7075-T6 alloy surface without coating (A1), the polished alloy surface treated with the ZPO suspension at pH = 3.5 (B1), pH = 5.0 (C1), pH = 6.6 (D1), pH = 10.5 (E1) and pH = 13.0 (F1). After the ZPO treatments, all the samples retained a mirror-like appearance (whereas at pH values of 10.5 and 13.0 the surfaces had visible signs of

TABLE I Identification of the samples studied with XPS

Letter code	Sample identification
A	Polished 7075-T6 aluminium panel
B	Sample A after treatment for 1 h with a 10% ZPO suspension adjusted to pH = 3.5 with acetic acid
C	Sample A after treatment for 1 h with a 10% ZPO suspension adjusted to pH = 5.0 with acetic acid
D	Sample A after treatment for 1 h with a 10% ZPO suspension (with the natural pH of 6.6)
E	Sample A after treatment for 1 h with a 10% ZPO suspension adjusted to pH = 10.5 by sodium hydroxide
F	Sample A after treatment for 1 h with a 10% ZPO suspension adjusted to pH = 13.0 by sodium hydroxide

In the text, the letter code is followed either by a 1 (to indicate a sample prepared as described here) or a 2 (corresponding surface after immersion for 5 h in a 3.5% NaCl solution).

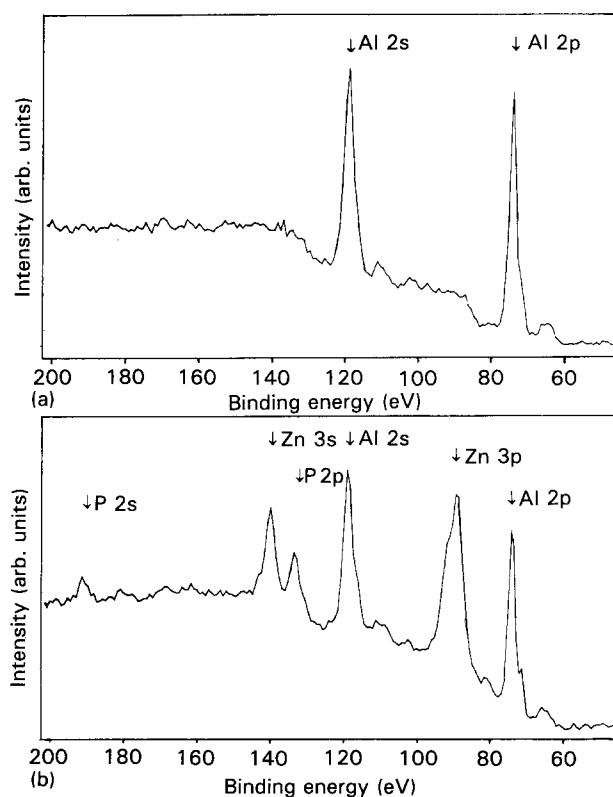


Figure 1 XPS survey spectra for: (a) sample A1 and (b) sample F1.

reaction in the absence of ZPO). Survey XPS spectra for samples A1 and F1 are shown in Fig. 1. Oxygen, carbon and aluminium (including both the oxide and the metallic form) were detected on these surfaces; zinc was found on the surfaces B1 to F1, but not on A1, even though the 7076-T6 aluminium alloy contained around 5–6% zinc [2]. Phosphorus was not detected on samples A1 and D1, whereas it was seen on samples B1, C1, E1 and F1.

It quickly became apparent that the processes involved are quite complex in that coating from solution, oxidation, etching and bulk diffusion can occur concurrently, but in different proportions, for the different samples. Attempts were made to gain information from XPS by measuring binding energies and the coating-to-substrate composition ratios, both for the normal take-off angle ($\theta = 90^\circ$) and for smaller values of θ , which can give some initial guidance on the surface morphology and the composition with depth [3, 4].

Binding energies for the Zn $2p_{3/2}$ peaks from coated samples were measured in the range 1023.1–

1023.6 eV, while corresponding values of the sum of the Auger parameter and the X-ray excitation energy turned out to be in the range 2010.1–2010.6 eV. These values are consistent with a ZnO_x oxide [5], although very similar values (1023.7 and 2010.3 eV, for the binding energy and Auger parameter, respectively) were measured for a ZPO reference compound. Therefore, it was not possible to discriminate between these forms in relation to zinc (that is, this metal is present in the +2 oxidation state), nevertheless the measured P_{2p} peaks from coated material (between 133.5 and 133.9 eV) matched the value (133.7 eV) measured for the ZPO reference compound. This supports the view that phosphorus exists on these surfaces as a phosphate (that is, in the +5 oxidation state).

Fig. 2a shows how the amounts of zinc and phosphorus on the alloy surface vary with the coating pH; the relative Zn/Al and P/Al ratios were obtained from the Zn_{2p}, P_{2p} and Al_{2p} peak areas, measured at high resolution, for photoelectrons emitted normal to the surface to emphasize the maximum probe depth.

TABLE II The atomic ratios of zinc and phosphorus to aluminium^a on ZPO-treated surfaces measured for different take-off angles, θ

Sample	θ	Zn/Al	P/Al	Zn/P
B1 (pH = 3.5)	30°	0.03	0.10	0.3
	45°	0.03	0.06	0.5
	60°	0.04	0.06	0.7
	90°	0.04	0.05	0.8
C1 (pH = 5.0)	30°	0.55	0.19	2.9
	45°	0.53	0.19	2.8
	60°	0.44	0.11	4.0
	90°	0.35	0.07	5.0
D1 (pH = 6.6)	30°	0.05	0.00	–
	45°	0.06	0.00	–
	60°	0.07	0.00	–
	90°	0.07	0.00	–
E1 (pH = 10.5)	30°	0.39	0.09	4.3
	45°	0.37	0.08	4.6
	60°	0.34	0.06	5.7
	90°	0.30	0.07	4.3
F1 (pH = 13.0)	30°	0.42	0.10	4.2
	45°	0.49	0.15	3.3
	60°	0.53	0.09	5.9
	90°	0.52	0.08	6.5

^a For these ratios, Al is the total of the oxide and metallic components.

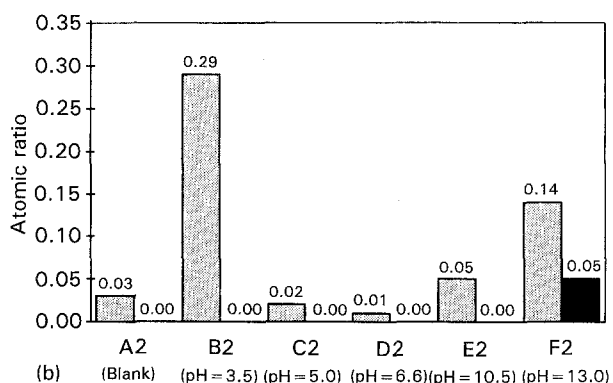
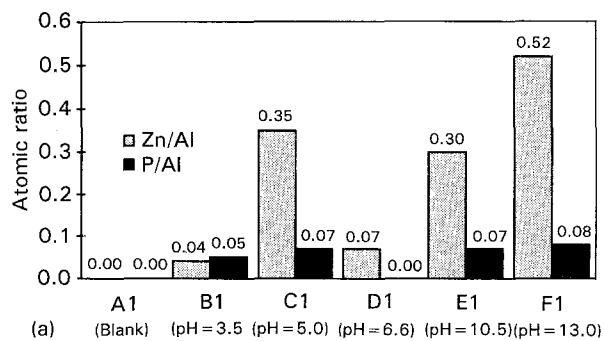


Figure 2 Relative Zn/Al and P/Al ratios for aluminium alloy samples treated with ZPO at different pHs: (a) before the corrosion test, and (b) after the corrosion test.

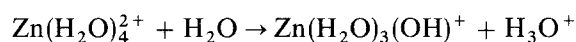
These estimates were made using atomic sensitivity factors provided by the manufacturer. Table II includes information on the coating composition as seen by XPS as a function of the take-off angle; smaller values of θ emphasize the layers nearer the surface of the sample (values for $\theta = 90^\circ$ are plotted in Fig. 2a). Values of the Zn/P ratio can be used to follow trends in the composition, although it is not generally possible to relate these trends to absolute compound composition. For example, the ratio measured for the ZPO reference compound was 0.88. Aside from any uncertainties in the atomic-sensitivity factors, differences from the value 1.5, which is predicted by the formula $Zn_3(PO_4)_2$, may be expected to arise from changes in surface composition (for example, this ratio will vary markedly with any involvement by HPO_4^{2-} and $H_2PO_4^-$ ions near the surface of the reference material).

The following subsections discuss the XPS observations arising from the different ZPO coating solutions.

3.1.1 Natural ZPO coating solution (sample D1)

XPS detected a small amount of zinc on this surface coated at pH 6.6, but no phosphorus. The latter observation may relate to the low photoionization cross-section, but it is also consistent with ZPO having a low solubility product in water at room temperature ($K_{sp} = 9.1 \times 10^{-33}$) [6]. The weakly acidic nature of the solution results from the hydrolysis

reaction [7]

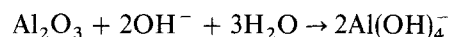


The Zn/Al ratio determined from XPS observations is essentially independent of θ , and this was previously taken to indicate [1] that the hydrated-zinc-hydroxide ions interact with the surface and are deeply incorporated to the aluminium oxide structure to give a ZnO_x and AlO_x mixture. This behaviour provides a reference point with which to compare the samples prepared in alkaline and acidic coating solutions.

3.1.2. Alkaline coating solutions (samples E1 and F1)

Table II shows that, compared with the ZPO coating solution at natural pH (sample D1), large amounts of both zinc and phosphorus occur on the alloy surfaces which have been coated at pH values of 10.5 and 13.0. These enhanced values of the Zn/P ratios (compared with ZPO) suggest that both ZnO_x and ZPO are likely to be involved in the coating. The Zn/Al ratios vary only slowly with the take-off angle, and the P/Al ratio should be taken as angle independent; these observations suggest that both zinc and phosphorus are distributed somewhat randomly in the AlO_x matrix. Accordingly, it is believed that these coating layers involve a mixed ZnO_x-AlO_x-ZPO material, formed as a result of both etching and coating processes.

It is proposed that with the alkaline coating solutions, OH^- ions etch the aluminium-oxide layer according to



In addition, the ZPO solubility is enhanced because of the formation of zinc-hydroxide complexes, including $Zn(OH)_4^{2-}$, and in this environment adsorption and incorporation of PO_4^{3-} and $Zn(OH)_4^{2-}$ (and related species) can be anticipated. Possibly, the slight enhancement of the zinc content for the coating at pH 13.0, compared with that at pH 10.5, arises because of the higher etching rate and the consequent accumulation of more zinc from the alloy bulk.

3.1.3. Weakly acidic coating solution (sample C1)

The results from Table II show that a lot more zinc and phosphorus were found on sample C1 than on sample D1. These enhanced values of the Zn/P ratio again suggest that the treated surface involves ZnO_x and ZPO, implying that both etching and coating processes occurred. The Zn/Al and P/Al ratios appeared almost unchanged at small take-off angles, but they decreased for the larger values of θ . This suggests that zinc and phosphorus are mixed in the AlO_x matrix, but with distributions that are relatively richer at the outermost surface region.

The formation of phosphoric acid in this acidic medium can etch the alloy surface and thereby expose zinc from the substrate. Also the enhanced solubility of ZPO in this medium ensures that the surface is exposed to Zn^{2+} and phosphate ions (for example,

H_2PO_4^-), which can be adsorbed and incorporated into the AlO_x matrix. This is consistent with the formation of a $\text{ZnO}_x\text{-AlO}_x\text{-ZPO}$ coating on the alloy. Insofar as the zinc and phosphorus compositions are greater at the outer surface region, relative to the inner coating region, the precipitation of zinc appears to occur relatively faster than the zinc build up from the etching process.

3.1.4 Strongly acidic coating solution (sample B1)

Table II shows that sample B1 has relatively low values for the Zn/Al and P/Al ratios, compared with the other treated alloy surfaces, but the Zn/P ratio for this sample is closest to that of the ZPO reference compound. The Zn/Al ratios appeared to be independent of the take-off angle; likewise the P/Al ratio is almost unchanged from 90° to 45° , although it increased at $\theta = 30^\circ$. The latter suggests that there may be more phosphorus at the outermost surface region. In any event, the amounts of zinc and phosphorus on this treated surface are small. These observations are consistent with any zinc on the surface passing rapidly into solution, and this applies to both zinc uncovered by etching and the instability of any precipitated ZPO [8].

3.2. Corrosion studies

Atomic ratios measured at normal take-off angles for the surfaces treated in a 3.5% NaCl solution (samples A2 to F2) are plotted in Fig. 2b (note that the scale is expanded in comparison with Fig. 2a). XPS detects the presence of zinc in the surface regions of all six samples. Comparisons of the measurements before and after corrosion showed that the relative amounts of zinc in the surface regions of samples A2 and B2 increased while the amounts of zinc reduced for the other four samples. Phosphorus was identified only on sample F2. Fig. 2b summarizes these results. Metallic aluminium was still detected on samples B2, C2, E2 and F2, although the intensities were substantially reduced in comparison with those from the corresponding samples prior to the corrosion treatment. Interestingly, the oxide layer was sufficiently thick that metallic aluminium was not detected on either sample A2, the polished (but not coated) alloy surface, or sample D2, the surface initially treated with the ZPO suspension at pH = 6.6.

Previous studies of the corrosive effect of NaCl solutions on aluminium alloy surfaces have shown that Cl^- attack induces oxidation and dissolution of aluminium [1, 9–12]. It can also cause the exposure of zinc, one of the bulk alloy components, to the surface region [1, 13]. Part I [1] reported that the panel, which was ZPO coated at the natural pH (sample D1), was able to suppress the dissolution of aluminium in the presence of a 3.5% NaCl solution for 2 h.

In this work, it was found that under the longer corrosion period (5 h) the amount of zinc on the surface (sample D2) reduced indicating that the $\text{ZnO}_x\text{-AlO}_x$ structure was weakened and that zinc was lost from the surface region. Similar phenomena were observed on samples C2, E2 and F2, where the

amounts of zinc left were reduced in comparison with the amounts on the original surfaces. The reduction of the phosphorus contents to undetectable levels (samples C1 and E1) suggests that the Cl^- attack starts from the outermost surface with dissolution of both zinc and phosphorus. The fact that significant phosphorus remains on sample F2 supports the view that this sample initially had a sufficient ZPO coating to defend against the corrosion attack.

The detection of metallic Al by XPS from samples B2, C2, E2 and F2 indicates that the coating either: (i) acts as a protection layer; or (ii) is so ineffective, and the dissolution so rapid, that the oxide film attains only limited thickness. With (i) a physical barrier [14] is formed which (at worst) is sacrificed under the corrosion attack and thereby slows the aluminium oxidation and dissolution. This appears to be the situation for the samples C1, D1, E1 and F1. Possibility (ii) apparently operates for the sample B1, where its surface zinc content increases strongly after corrosion. In this case, it is believed that the zinc from the coating process is removed rapidly, and that the zinc detected on sample B2 comes from the bulk alloy as a result of the Cl^- attack.

4. Conclusion

The exploratory study reported in this paper indicates that the nature and the chemical properties of the coating formed by treating a 7075-T6 aluminium alloy surface with a ZPO suspension depends markedly on the coating pH. The overall situation is complex, because different processes occur concurrently, but for coating solutions at pH values of 5.0, 10.5 and 13.0 the outer layers were all indicated to have a mixed $\text{ZnO}_x\text{-AlO}_x\text{-ZPO}$ structure. However, details of the atomic compositions and distributions were different, and they depended in turn on the detailed rates of the etching and precipitation processes. By contrast, the coating formed at the natural pH (6.6) corresponded to a $\text{ZnO}_x\text{-AlO}_x$ material, while that formed at pH = 3.5 existed as a thin ZPO-like compound. Of the coating pH values tested, the optimum conditions for corrosion protection appears likely to be provided by the coating at strongly alkaline conditions (pH = 13.0), while coating at strongly acidic conditions apparently gives even less protection than the original native-oxide layer. More detailed probes of the comparative structures of these coating materials would be useful for further assessing their possibilities for corrosion protection in this context.

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