Formation of zinc phosphate coatings on AA6061 aluminum alloy

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Conditions for forming zinc phosphate conversion coatings on AA6061 aluminum alloy have been investigated by characterizing coatings formed for different parameters of the coating bath. Morphological and compositional information on the coatings was assessed by SEM, EDX and XPS, and simple adhesion tests were undertaken to indicate the strengths of coating attachment. The emphasis was to identify conditions that give high coverage, uniform coatings of small, strongly adhered, zinc phosphate crystals. The use of low-zinc solutions (e.g. an atomic Zn/P ratio of 0.07) and normal-zinc solutions (Zn/P ratio 0.25) were compared; coatings formed by the two solution types appear comparable at pH 2, although at pH 4 the low-zinc solution is more effective. Fluoride in the concentration range 200–400 ppm is indicated to be a useful additive for the normal-zinc coating bath and in the 600–1000 ppm range for the low-zinc process. The use of acid etching in the pre-treatment appears to yield better coatings than when mechanical polishing alone is used. © *2001 Kluwer Academic Publishers*

1. Introduction

Chemical conversion treatments in chromate or chromate-phosphate solutions have frequently been used to improve the corrosion resistance of aluminum, as well as the adhesive application of organic coatings [1]. However, chromate solutions are now associated with concerns about their carcinogenic natures [2], and this is encouraging the development and evaluation of alternative procedures [3, 4]. Accordingly there is interest in assessing phosphate coatings, especially since they have been used extensively for iron and steels [5]. Zinc phosphate coatings on steel generally yield crystalline particles, although chromate coatings on aluminum are composed of uniform, tightly-packed, amorphous layers [1].

Phosphate coatings have not been widely considered for the corrosion protection of aluminum, although, because of recent environmental concerns associated with the use of chromate, interest in the use of zinc phosphate in this context is growing. For example, coating conditions have been reviewed for pure aluminum [5], AA5754 alloy [6] and AA7075 alloy [7, 8], although little information is available in the open literature for phosphating AA6061 alloy, which has importance in aerospace and naval platform applications.
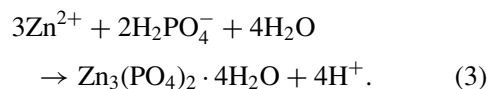
Coating solutions to form zinc phosphate conversion coatings generally contain ZnO and phosphoric acid, and two regimes have been identified, the so-called normal-zinc and low-zinc processes [9–12]. Phosphating baths in the normal-zinc regime typically have compositions in the approximate ranges 2–4 gL^{-1} of Zn and 5–10 gL^{-1} of P_2O_5, while the corresponding concentrations for low-zinc baths are in the ranges 0.4–1.7 gL^{-1} of Zn and 11–16 gL^{-1} of P_2O_5.

The phosphating of aluminum requires etching and deposition of the coating with suppression of unfavourable competing processes. The etching, or pickling, reactions

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \qquad (1)$$
$$Al + 3H^+ \rightarrow Al^{3+} + 3/2H_2(g) \qquad (2)$$
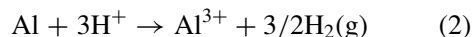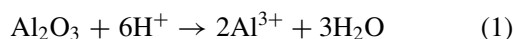
act to clean the initial surface and promote the formation of nucleation sites for the subsequent coating. In acid solution, the intended coating process is

$$3Zn^{2+} + 2H_2PO_4^- + 4H_2O$$
$$\rightarrow Zn_3(PO_4)_2 \cdot 4H_2O + 4H^+. \qquad (3)$$

The competing formation of aluminum phosphate tends to inhibit the formation of zinc phosphate coatings, but the former is restricted by adding NaF to the coating bath. Then free Al^{3+} ions in solution undergo complex

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formation

$$Al^{3+} + 6F^- \rightarrow AlF_6{}^{3-}, \qquad (4)$$

although, at high F^- concentration, Na_3AlF_6 may precipitate as a sludge which can act to deteriorate the coating adhesion [13].

The present work has examined a wide range of coating parameters, including Zn/P ratio, pH, pre-treatment and effect of fluoride in order to assess factors involved in the optimization of phosphate coatings on AA6061 alloy. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) were employed to characterize morphologies and compositions of the coatings formed. Assessments were made especially of the conditions that produce coatings composed of small particles at high coverage, since such conditions are most likely to give strong adhesive bonding and improve corrosion resistance. The approach used has two parts to it. Earlier work from this laboratory for the AA7075 alloy had emphasized phosphate coating baths in the normal-zinc range, and the present work for the AA6061 alloy started with coating solutions related to those used previously. In addition, parallel studies were made with coating solutions in the low-zinc range.

2. Experimental procedures

Samples of commercial AA6061 aluminum alloy sheet (composition 0.8–1.2% Mg, 0.25% Zn, 0.15–0.4% Cu, 0.7% Fe, 0.4–0.8% Si, 0.15% Mn, 0.15% Ti and 0.04–0.35% Cr), cut into square panels with dimensions $1 \times 1 \times 0.12$ cm^3, were employed in all experiments conducted in this study. Prior to phosphating, all samples were mechanically polished with sandpaper up to 1200 grit aluminum oxide and water, and this was followed by degreasing in acetone and methanol in an ultrasonic bath, and drying in air. Some samples were subsequently given an acid etch by immersing for 2 min in a 50/50 vol% H_2SO_4-H_2O solution at 40°C. Results given here apply to dipping pre-treated AA6061 samples into one of the specified phosphating solutions for 3 min at 60°C. Two reference coating solutions were used, namely a "normal-zinc" solution (made up from 16.0 mL H_3PO_4 (85%), 5.3 g ZnO and 0.5 g NaF per L) and a "low-zinc" solution (8 mL H_3PO_4 (85%), 6.3 g $NaH_2PO_4.H_2O$, 1.0 g ZnO and 0.5 g NaF per L). These solutions have F^- concentrations at 216 ppm (mgL^{-1}); the normal-zinc solution has a pH of 2 and a Zn/P atomic ratio equal to 0.25, while the corresponding values for the low-zinc solution are 2 and 0.07 respectively. Treatments discussed in this paper to give the coatings designated N1 to N4 and L1 to L4 are specified in Table I. The pH adjustment was made by adding NaOH to a coating solution. In this work, sample N1 is used as a common coating for comparing trends in behaviour as parameters of the coating bath and sample treatment are varied. The adhesive behaviour of a coating was assessed by the Scotch tape test made just after its formation.

Micrographs of coating morphologies were obtained with a Hitachi S4100 scanning electron microscope (SEM) operated at 14 kV. Analyses for local regions of a coating were made by energy dispersive X-ray

TABLE I Specification of pre-treatments and coating procedures for the eight samples discussed in text; all coatings are formed by dipping for 3 min in the defined coating solution at 60°C

Sample code	Treatment
N1	Mech. polished, n-Zn ref. soln.*
N2	Acid etched, n-Zn ref. soln.
N3	Mech. polished, modified n-Zn ref. soln. (pH 4)
N4	Mech. polished, modified n-Zn ref. soln. (pH 4 & 800 ppm F$^-$)
L1	Mech. polished, ℓ-Zn ref. soln.*
L2	Acid etched, ℓ-Zn ref. soln.
L3	Mech. polished, modified ℓ-Zn ref. soln. (pH 4)
L4	Mech. polished, modified ℓ-Zn ref. soln. (pH 4 & 800 ppm F$^-$)

*n-Zn ref. soln. and ℓ-Zn ref. soln. refer respectively to the normal-zinc and low-zinc reference solutions specified in Section 2. The other solutions are modified from the reference solutions only by the changes noted in parenthesis.

spectroscopy (EDX) measurements using a Hitachi S2300 SEM. Complementary characterizations of surface compositions were made with a Leybold MAX200 spectrometer using a Al Kα source (1486.6 eV) operated at 10 kV, 20 mA with a system pressure of 2×10^{-7} Pa. Survey spectra, for use in qualitative analysis, were obtained with the analyzer pass energy set at 192 eV, while the higher-resolution narrow-scan spectra were obtained with a pass energy of 96 eV. Peak areas for Zn 2p$_{3/2}$ (binding energy 1021.5 eV), P 2s (191.0 eV), O 1s (532.5 eV), C 1s (285.0 eV) and Al 2p (oxide and metallic components at 75.8 and 72.6 eV respectively), determined after background subtraction, were taken to indicate relative amounts after correction with sensitivity factors provided by the manufacturer. Binding energies were commonly referenced to the Au 4f$_{7/2}$ peak at 84.0 eV although, for coated samples that are non-conducting (e.g. metallic Al 2p peak not detected), the C 1s peak from adventitious carbon was set to 285.0 eV.

3. Results and discussion
3.1. Effect of Zn/P
Various coating baths with different Zn/P ratios were examined in order to assess recipes for zinc phosphate coatings on AA6061 aluminum alloy, but the comparisons emphasized in this section involve the specific normal-zinc and low-zinc reference solutions noted in Section 2. The coatings N1 and L1 are formed by dipping samples of the alloy in the respective solutions after a common pre-treatment, which just involved a mechanical polish. SEM images from these two samples (Fig. 1) show that the phosphating processes give relatively large clusters ($\sim$15 μm dimension), and that the nucleation occurs especially at scratches arising from the mechanical polishing. Overall the coverages appear similar for these two samples, although there are differences in morphology (e.g. the coating for L1 appears more fragmented).

The chemical compositions of the mechanically polished (blank) sample, and of the coatings formed, were assessed with XPS. The survey spectrum from the blank sample (Fig. 2a) shows the presence of Al, O, C and Mg. Oxygen is present from oxide which is incompletely
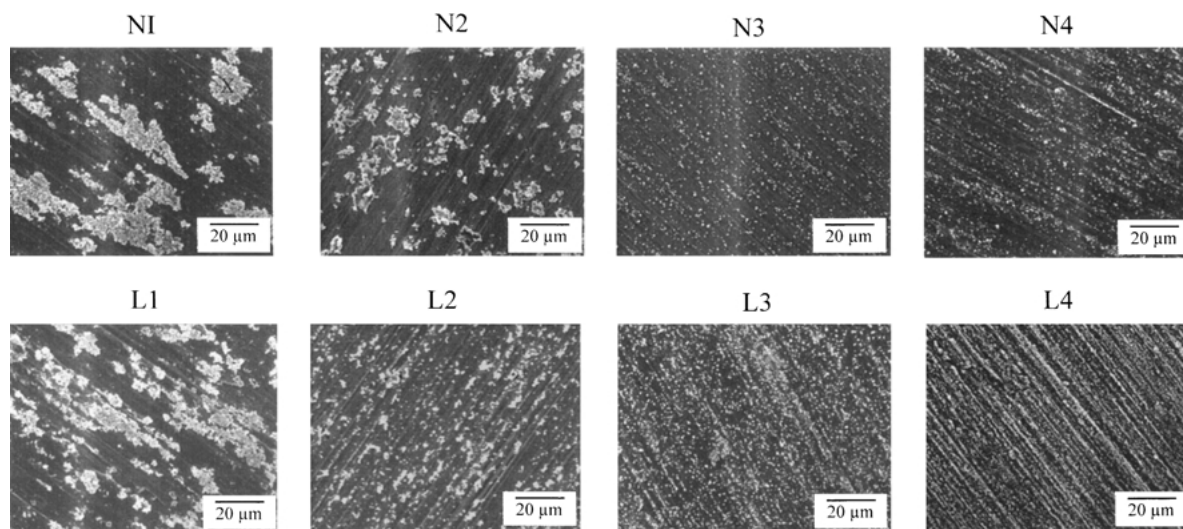
Figure 1 Scanning electron micrographs for coatings designated N1 to N4 and L1 to L4 formed according to procedures specified in Table I (all magnifications ×1000).
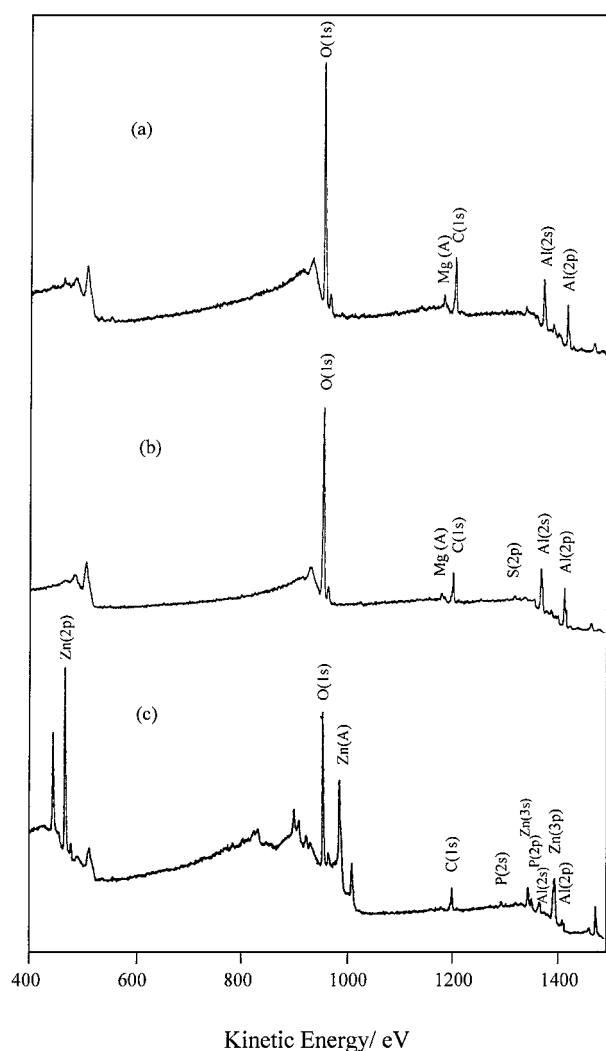

Figure 2 XPS survey scan spectra for AA6061 alloy samples: (a) after mechanical polishing, (b) after acid etching, and (c) after phosphating to form sample N1.

TABLE II Relative compositions of zinc phosphate coatings determined by XPS

Sample	Zn%	O%	P%	Al_{OX}%	Al_{MET}%	Zn/Al	P/Al
N1	12.3	66.6	7.9	6.3	6.8	0.9	0.6
N2	13.4	67.7	6.3	6.4	6.1	1.1	0.5
N3	11.5	66.0	15.2	5.9	1.4	1.6	2.1
N4	7.7	67.3	12.1	13.0	0.0	0.6	0.9
L1	9.1	67.2	4.5	9.5	9.8	0.5	0.3
L2	11.8	66.9	3.7	10.0	7.5	0.7	0.2
L3	14.9	71.0	10.3	3.1	0.8	3.8	2.6
L4	19.8	70.5	6.1	3.7	0.0	5.4	1.7

tected by XPS after the coating procedures noted above. Survey spectra for the coated samples show the presence of Zn, P, O, C and Al, and relative compositions indicated within the probe depth of the XPS technique are reported in Table II (these values represent averages over several independent measurements). All indications are that the C is concentrated at the surface, and is not an inherent component of the coating, and accordingly this element has not been included in the relative compositions reported. But for Al the allocation is made, on the basis of high-resolution Al 2p spectra, between the metallic and 3+ oxidized forms. The P 2s spectra are fully consistent with the P being present in the 5+ oxidation state [14].

The EDX spectrum shown in Fig. 3 is obtained from the particular crystallite cluster in sample N1 which is marked by the probe position x for that sample in Fig. 1. The large Al signal arises from the underlying substrate, but the presence of Zn, P and O is consistent with a thin coating of zinc phosphate, as indicated in a similar situation by Ishii *et al.* [13]. The XPS measurements provide complementary information insofar as they assess an average composition from across the surface region of a sample to the depth probed (typically ~50 Å). XPS signals from the coating produced by the normal-zinc process (sample N1) are relatively larger for Zn and P, and relatively smaller for Al, compared with the situation for the sample produced by the

removed by the polishing, or regrows after that process, but some oxygen and carbon are expected both from air-borne contamination and residue from the degreasing procedure. The Mg is an intrinsic component of the AA6061 alloy, although this element is not de-
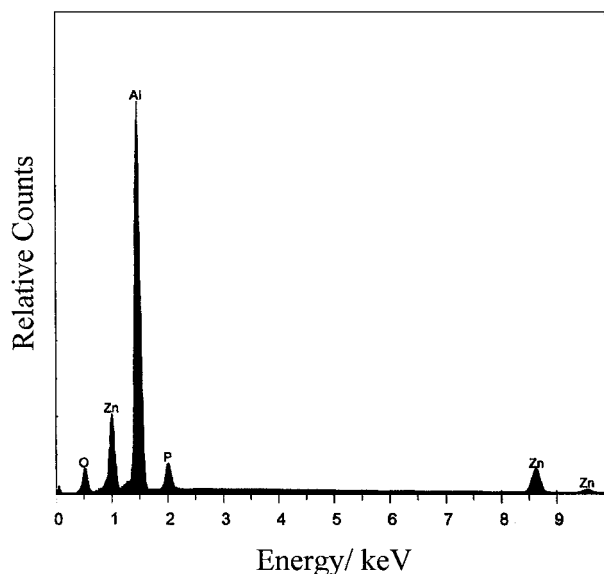
Figure 3 EDX from sample N1 at point marked by x in Fig. 1.

corresponding low-zinc process (L1). Together, these observations are consistent with sample N1 having a more extensive coating (i.e. net increase in thickness and coverage) compared with L1.

3.2. Effect of pre-treatment
The effect of different pre-treatments was assessed in this work especially by comparing the coatings formed, after dipping in a common reference solution (3 min, 60°C), on surfaces which had first been given either a mechanical polish or an acid etch (according to the procedures noted in Section 2). With the normal-zinc reference solution, these two situations define samples N1 and N2 respectively. The chemical compositions of the surfaces after the pre-treatments are generally similar, according to the XPS spectra in Fig. 2a and b, although some residual S from the acid etch is detected in the second case. The relative compositions of the coatings are given in Table II, and the differences between samples N1 and N2 appear small. The more significant difference is in the morphologies revealed by the SEM micrographs in Fig. 1. The coating formed after the acid etch clearly has the more uniform, denser structure with smaller crystals ($\sim$4 μm for sample N2 compared with $\sim$15 μm for N1).

Investigations were made for the corresponding coatings formed with the low-zinc solutions. The SEM images for the L1 and L2 samples (Fig. 1) again show that inclusion of acid etching in the pre-treatment results in smaller crystals in the coating, but XPS measurements do not indicate any appreciable change in the coating composition. In summary, it is concluded for both types of phosphating process that acid etching in the pre-treatment contributes to the formation of more uniform coatings formed from smaller particles.

In a comparison of the different pre-treatments, it is noted that mechanical polishing has the basic role of scraping off layers, whereas the acid etching process is more active at highlighting heterogeneities on the surface. For example, although the acid reactions involve a general anodic dissolution of aluminum, the

hydrogen evolution occurs at local cathodic sites, including grain boundaries and second-phase particles, leading to an increase in local pH [15]. Such processes open up more nucleation sites for the phosphate coatings and thereby influence the ultimate morphology. In addition, acid etching of an alloy surface may also lead to changes in surface composition. For example, recent work on H_2SO_4 etching of 2024-T3 alloy shows a surface enrichment of copper, which has a significant influence on the subsequent zinc phosphate coatings [16]. However, in the present work on the AA6061 alloy, no surface enrichment of Mg was detected from the acid etch. This fits the scheme proposed by Habazaki *et al.*, who compared the Gibbs free energy for oxide formation per equivalent ($\Delta G^\circ / n$) relative to that of aluminum [17]. Thus Mg, with a $\Delta G^\circ / n$ value less than that of Al, reveals no initial enrichment as a result of this pretreatment, whereas Cu or Zn, with a $\Delta G^\circ / n$ value greater than that of Al, show enrichments in the AA2024 and AA7075 alloys that are under study in our laboratory.

3.3. Effect of pH
3.3.1. Normal-zinc solution
The reactions associated with the zinc phosphate coating process (Equations 1–4) are pH sensitive, and this work for the AA6061 alloy examined a range of pH values from 2 to 13. The clear indications are that this phosphating process works best in acidic environments. Two specific pH values (2 and 4) are compared in this section in relation to coatings formed in normal-zinc solutions, and the coatings on samples Nl (pH 2) and N3 (pH 4) are compared by their SEM micrographs in Fig. 1. The first coating reveals relatively large clusters of crystallites, but that formed at pH 4 is more uniform and consists of finer crystallites (dimension $\sim$500 nm) at higher coverage. Such characteristics are expected to be beneficial for improved adhesive bonding and corrosion resistance. The XPS signal detected from metallic Al for sample N3 is considerably reduced over that for N1 (Table II), and that is consistent with a more effective coverage by the conversion layer. This depends in part on the coating being more uniform, but it also appears to be thicker. The amount of P is increased for sample N3 compared with N1, although the Zn content has reduced somewhat. That is possibly indicative of some $AlPO_4$ being incorporated into the coating.

The principal species in H_3PO_4 solution as a function of pH are: H_3PO_4 for pH < 2, $H_2PO_4^-$ pH 2–7, HPO_4^{2-} pH 7–12, and PO_4^{3-} pH > 12 [18]. Various factors will influence the comparison between coating processes at pH values of 2 and 4. One is that the Al etching rate should reduce at the higher pH value, but the associated longer pickling time may increase the number of nucleation sites for the subsequent coating. Also, the $H_2PO_4^-$ concentration is greater at pH 4 compared with 2, and that could promote faster phosphate deposition [19]. But the phosphating process is an electrochemical phenomenon where aluminum dissolution occurs at anodic sites, while the H^+-to-H_2 conversion at cathodic sites helps drive the precipitation of zinc phosphate [20]. A consequence is that the details of these processes

depend on local pH values at micro-electrodes, as well as on the general solution pH. Research on mechanistic aspects of these processes has revealed that zinc phosphate deposition is initiated at cathodic second-phase particles [21].

3.3.2. Low-zinc solution

Low-zinc processes have a similar effect at pH 4 as normal-zinc processes, and uniform small particles are formed over the whole surface. SEM shows that the low-zinc process at pH 4 provides a higher coating coverage, and in addition XPS indicates higher Zn/Al and P/Al ratios than is the case with the normal-zinc solution. The denser phosphate coatings with the low-zinc process appears associated with a slower deposition reaction (Equation 3) in conjunction with longer pickling reactions (Equations 1 and 2). The latter may give better chemical cleaning of the surface and in turn produce more nucleation sites for the coating deposition. Further investigations are underway for modifying low-zinc phosphate processes by the addition of other metallic components (e.g. Mn, Ca and Fe) to the coating bath.

3.4. Effect of fluoride

3.4.1. Normal-zinc solution

It is known that the presence of Al^{3+} in a zinc phosphate coating solution can strongly influence the subsequent coating both on steel and aluminum [1, 13, 22, 23]. The possibilities for reducing the involvement by $AlPO_4$ appear increased by adding F^- to the coating bath, since this minimizes the presence of free Al^{3+} in solution according to Equation 3. In principle, this addition may also help speed up the whole coating reaction, although information available to date for aluminum alloys is very limited [8, 13, 23]. Accordingly this part of the study aimed to gain some quantitative information for the effect of F^- ions on zinc phosphate coatings for AA6061 alloy.

Various F^- concentrations were investigated in conjunction with the normal-zinc solution, and the subsequent characterizations of the coatings indicate three main ranges of behaviour. SEM indicates very little coating when the solutions have F^- in the range 0–150 ppm. The coating coverages appear to be similar for the 200–400 ppm and 600–1000 ppm ranges (N3 and N4 in Fig. 1). However, XPS reveals a significant presence of Na and F in the coatings for the higher F^- range; correspondingly the amount of Zn is low, and the signal observed from Al is high. Such observations for the high F^- range suggest the presence of cryolite (Na_3AlF_6), which acts to deteriorate the coating adhesion [13].

3.4.2. Low-zinc solution

As for the normal-zinc solution, very little coating is observed with the low-zinc solution when the F^- concentration is in the 0–150 ppm range. Reasonably good coverages are observed with the low-zinc solution when F^- is present in the 200–400 ppm range (L3 in Fig. 1), but the coating appears complete for the 600–1000 ppm range (L4) (this appears consistent with the range given

by Rossio [9, 10]). XPS shows that the increase in F^- yields more Zn, but less P, in the coating, and this is consistent with the ability of F^- to inhibit the formation of $AlPO_4$ and hence enhance the conversion coating process. Overall, it is apparent that the optimal amount of F^- for this coating process is dependent on other parameters of the coating bath, including Zn/P ratio and pH.

4. Conclusion

A study was made of the coatings formed by dipping samples of AA6061 aluminum alloy into zinc phosphate coating solutions for 3 min at 60°C. A wide variation of coating conditions was considered, but this paper emphasized comparisons between eight specific coating recipes in order to highlight trends associated with particular key parameters. Throughout, the objective was to identify conditions that gave uniform coatings of relatively small zinc phosphate crystals at high coverage, and with good adhesive bonding. Comparison of low-zinc and normal-zinc processes confirms that the Zn/P ratio has a significant influence on the coating formed, and that the low-zinc regime is most favourable for the criteria used here. Acidic coating baths are required for zinc phosphate deposition, but appreciable variations occur with changing pH. For example, a coating bath at pH 4 generated a higher coverage of fine-grained crystallites than a comparable solution at pH 2. Evidence was also presented that an acid etch provides a more effective pre-treatment than mechanical polishing, with the former being a better generator of nucleation sites for the subsequent coating. The addition of fluoride to the coating bath can have a large effect, although the details vary with whether the low-zinc or normal-zinc process is being used. With no F^- added, little coating is formed for either type of process. This study indicates that the optimal range of F^- is 200–400 ppm for the normal-zinc process and 600–1000 ppm for the low-zinc case.

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