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Observations related to the phosphating of aluminium alloy 7075-T6 using a spraying technique

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An initial review is made of the effects of changing parameters involved in forming a zinc phosphate coating layer by spraying an aluminium alloy 7075-T6. Various coatings were evaluated by X-ray photoelectron spectroscopy, scanning electron microscopy and adhesion tests. The coating solution reported represents a modification of that previously used for coating the same system by the dipping method (*J. Mater. Sci.* **31** (1996) 565), but for spraying it was necessary to add the accelerators $KClO_3$ and $NaNO_2$ in order to achieve an adequate phosphate layer. For this solution, the favoured coating conditions by spraying corresponded to 1 min at 85 °C. A significant effect on the phosphating process is also indicated for the polishing pre-treatment of the substrate; the coating formed on a surface polished by 1200 grid aluminium oxide sandpaper showed good adhesion to paint, whereas that polished with 1200 grid silicon carbide failed to form an adhesive phosphate coating. In general, conditions for spraying are less easy to control than for dipping, but directions are indicated for obtaining promising coatings by the former approach.

1. Introduction

Zinc chromate has traditionally been used in chemical conversion coatings and as a pigment in anticorrosive primers for aluminium and its alloys in the aerospace and automobile industries, although recent concern about its carcinogenic nature are encouraging searches for replacement materials [1]. In this regard, phosphate coatings have been proposed, and in part this extends from their extensive use and study for iron and steel [2–4]. However, for aluminium and its alloys, optimal conditions for phosphate application are not generally available [5]. In recent work we have investigated some of the basic variables (pH, temperature, components of the coating bath, surface conditioning and pre-treatment) that affect zinc phosphate (ZPO) coatings and their properties including corrosion stability, when formed by a dipping process [6–10]. However, for many practical applications (e.g. to repair part of a large structure without disassembly), application of the coating material by spraying can be very advantageous, although conditions for favourable application are likely to be quite different from those appropriate with dipping [11].

The present study focuses on spraying processes for forming phosphate coatings on aluminium alloy 7075-T6. The approach extends from earlier work in this laboratory [9, 10] in which trends in the natures of thin-film coatings formed by dipping processes were characterized by X-ray photoelectron spectroscopy (XPS) for surface composition, by scanning electron microscopy (SEM) and secondary-ion mass spectrometry (SIMS) in the imaging mode for coating morphology. The present research uses a similar approach and has the objective of relating trends in the behaviours and properties of spray-coated ZPO films to the details of the application. Issues emphasized here are treatment time and temperature, as well as the effects of accelerators and sample polishing; adhesion tests are also applied in order to compare the macroscopic bonding for the different coatings. A reference point for this work is provided by conditions previously investigated for dipping, and this in turn helps to provide a basis for comparison between the two approaches.

2. Experimental procedure

Square panels (dimensions, 1 cm × 1 cm × 0.12 cm) of aluminium alloy 7075-T6 (approximate minority components: 6 wt% Zn, 3 wt% Mg, 2 wt% Cu, 0.5 wt% Fe, 0.4 wt% Si, 0.3 wt% Mn and 0.2 wt% Ti) were prepared as detailed previously. Briefly, all sample panels were polished with sandpaper and water, then degreased with acetone and methanol in an ultrasonic

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TABLE I Specification of treatments applied to different samples (see Section 2)

Sample code	Treatment
A1	Aluminium alloy 7075-T6 panel wet polished with 1200 grid aluminium oxide sandpaper, folowed by degreasing with acetone and methanol
A2	Sample A1 given Ti-colloid surface conditioning for 2 min at 40 °C
B1	Sample A2 after spraying with phosphating solution 1 at 85 °C for 1 min
B2	Sample A2 after spraying with phosphating solution 1 at 85 °C for 5 min
B3	Sample A2 after dipping in phosphating solution 1 at 75 °C for 5 min
C1	Sample A2 after spraying with phosphating solution 2 at 85 °C for 1 min
C2	Sample A2 after spraying with phosphating solution 2 at 85 °C for 2 min
C3	Sample A2 after spraying with phosphating solution 2 at 85 °C for 3 min
C4	Sample A2 after spraying with phosphating solution 2 at 45 °C for 1 min
C5	Sample A2 after spraying with phosphating solution 2 at 65 °C for 1 min
D1	Aluminium alloy 7075-T6 panel wet polished with 1200 grid silicon carbide sandpaper, followed by degreasing with acetone and methanol
D2	Sample D1 given Ti-colloid surface conditioning for 2 min at 40 °C
D3	Sample D2 after spraying with phosphating solution 2 at 85 °C for 1 min

bath, dried in air and finally given the Ti-colloid surface conditioning treatment described previously [10]. Two water-based solutions were used for the phosphating processes either by dipping or spraying: solution 1 (each litre contained 16.0 ml of 85% H_3PO_4, 5.36 g of ZnO and 0.5 g of NaF) and solution 2 (based on the composition of solution 1 but additionally each litre contained accelerators in the amounts 1.1 g of $KClO_3$ and 0.2 g of $NaNO_2$). A specification of the preparation procedure used for each main sample (and its code) studied in this work is included in Table I; before further study each sample was rinsed with distilled water and air dried.

Scanning electron micrographs were taken on a Hitachi S4100 SEM scanning electron microscope using an accelerating voltage of 30 kV. X-ray photoelectron spectra were measured in a Leybold MAX200 spectrometer [12] using a Mg Kα source (1253.6 eV), operated at 10 kV and 20 mA, for a system pressure of 6×10^{-7} Pa. Survey spectra were recorded with the analyser pass energy set at 192 eV, but the higher-resolution spectra were obtained for a pass energy of 48 eV. Peak areas for Zn $2p_{3/2}$, P 2p and Al 2p components, determined after background subtraction, were taken to indicate relative amounts after correcting with the appropriate sensitivity factors provided by the manufacturer. Binding energies were commonly referenced to the Au $4f_{7/2}$ peak at 84.0 eV but, for coated samples that were non-conducting (e.g. metallic Al 2p peak not detected), the C 1s peak from adventitious carbon was set to 285.0 eV. Spectra recorded with the bias potential technique were obtained by applying an external potential (−94.0 V) to the sample and then, after measurement, mathematically shifting the energy scale back by 94.0 eV as described previously [13]. Some measurements were made with variation in the take-off angle, θ, which is defined as the angle between the plane of the sample and the axis of the detector.

Adhesion tests were applied to various samples listed in Table I using the arrangement indicated schematically in Fig. 1. In each case the sample was painted with acrylic primer (Devoe Coatings Co., Amerguard 148 w/b) and dried in air, and glue (Lepage Ltd; 5 min epoxy) was applied to stick the painted side of the sample to a metal holder. After drying in air (about 2 days), forces perpendicular to the sample were applied in opposite directions to the two metal sides until the assembly broke apart. Analysis of the fracture surfaces then identified the region of weakest adhesion for each sample.

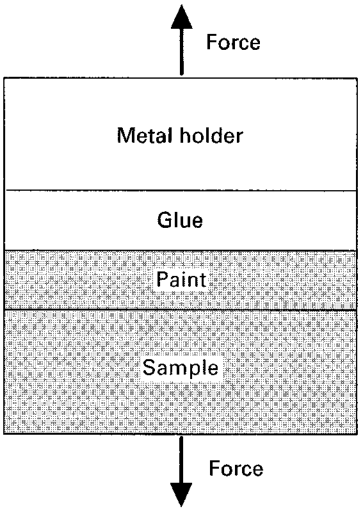

Figure 1 Schematic diagram to illustrate the adhesion test in this work.

3. Results and discussion

3.1. General comments

The main blank sample used in this work is designated A1 (Table I), and the XPS survey spectrum from it indicates the presence of Al, Zn, O and C in the near-surface region (i.e. within the probe depth of the XPS technique). For later reference it is important to note that this Zn is present as an intrinsic component of the aluminium alloy 7075-T6 being studied. Some carbon is inevitably present from air-borne contamination and possibly from residual acetone and/or methanol used in the degreasing procedure; similarly the oxygen arises from various sources including metal oxide, residual O-containing organic compounds and air-borne contamination. The Al 2p spectrum contains signals from both aluminium oxide (binding energy, 75.8 eV) and metallic aluminium (72.6 eV), thereby confirming that the thickness of the oxide film is less than the probe depth.

In all subsequent phosphating treatments the resulting P 2p spectra have peaks with binding energies close to 133.0 eV. This can be taken to indicate that the P is present as phosphate in the 5+ oxidation state; this is fully consistent with the PO_4^{3-} ion, although in general there may also be some involvement by the $H_2PO_4^-$ and HPO_4^{2-} ions in the surface region. Such participation would act to reduce the Zn-to-P ratio below the value 1.5 expected for pure $Zn_3(PO_4)_2$ (which is generally seen as the favoured product). A phosphated film may contain $AlPO_4$, from the competing etching and coating reactions, which would also act to decrease the Zn-to-P ratio. Additionally the incorporation of some ZnO into a film would necessarily act to increase the Zn-to-P ratio. These effects and the possible film heterogeneity emphasize that Zn-to-P ratios from XPS should especially be used to identify trends in behaviour for the different treatments. Values of the Zn-to-P and P-to-Al ratios observed by XPS for the main samples studied here are collected in Table II. The second ratio increases with increasing amount of P present in the surface region, although the amount of Al observed can be small for a ZPO coating that is both thick and pure.

A guiding principle for this work is that an effective phosphating treatment requires a P-to-Al ratio as high as possible, a Zn-to-P ratio which approaches 1.5, and a ZPO film made up of small crystallites (e.g. a dimension of 1 μm) that are distributed uniformly and at a high coverage. Throughout this study, exploratory tests were made for a wide range of phosphating conditions and treatments. The report here emphasizes particular sets of tests where comparisons can be made for reasonably systematic changes in variables.

3.2. Effect of accelerators

The evolution of hydrogen gas acts to slow phosphating reactions [2], and this may have a larger effect using the spraying process, compared with dipping, since the coatings should be formed relatively quickly. Accordingly, although accelerators were not included in our previous work [9, 10], they do need to be considered now. In this section, these specific samples are compared, namely B1, B2 and C1; the first two involve spraying with the phosphating solution 1 (contains no accelerators) but for different treatment times, while the third is for solution 2 (with the $KClO_3$ and $NaNO_2$ accelerators). The Zn-to-P ratio indicated by XPS for sample B1 (25.8) is much higher than that of sample B2 (9.07), and no Al is detected from the first. Indeed direct observation indicates that sample B1 is coated with a white layer, which is easily removed by Scotch tape; XPS analysis of the exposed side of the Scotch tape (i.e. the under side of the film) shows only the presence of Zn and O. These observations appear consistent with a large amount of weakly attached zinc oxide being formed on B1. The coverage of ZnO is markedly less on B2 (spray treatment for 5 min instead of 1 min), and it is considered likely that the ZnO is formed directly from the zinc in the alloy. In any event, sample C1, formed by spraying with solution 2 for 1 min, shows a much reduced Zn-to-P ratio (3.82), and generally more favourable characteristics as judged both by SEM images and by adhesion tests.

Fig. 2 compares SEM images observed from the blank sample A1, and from the coated samples B2 and C1. The first shows a rough appearance with a leaf-like structure, the features having a dimension of around 8 μm. For sample B2, formed by spraying solution 1 (without accelerators) for 5 min, the coating surface is amorphous with some crystalline grains (dimension around 2–3 μm) on top. By contrast, the coating on sample C1, formed by spraying solution 2 (with accelerators) for 1 min, has a crystalline appearance (average dimension 1–2 μm) with the crystal size and distribution quite uniform; further the crystal coverage is much higher than for B2. These samples also showed contrasting adhesive properties. The adhesion test applied to the blank sample A1 demonstrates that the weakest bonding is between the paint and the alloy surface. There is an improvement with sample B2, insofar as the coated film remains adhered to the metal when the paint-to-coating bond breaks, but this coating is still not able to join the alloy tightly to the paint. However, with sample C1, even though XPS indicates that it has less phosphate than B2 (the P-to-Al ratios are 0.06 and 0.11, respectively), the adhesion breakdown occurs within the glue. Therefore the coating in sample C1 has succeeded in improving the adhesion of the aluminium alloy to the paint, and this represents a first requisite for practical applications.

The above observations show that the accelerators (i.e. $KClO_3$ and $NaNO_2$) have a significant role within the spraying process insofar as they affect the chemical composition, structure and performance of the ZPO coating. Basically these oxidizing agents react with the H_2 produced from the metal etching, and this speeds up both the etching and the precipitation of phosphate [2]. The more rapid neutralization may result in more active spots for crystallization, thus

TABLE II Composition ratios from samples in Table I studied by XPS where the Al in these ratios refers to the total of the oxide and metallic components

Sample	P-to-Al ratio	Zn-to-P ratio
B1	No Al	25.8
B2	0.11	9.07
B3	0.18	2.50
C1	0.06	3.82
C2	0.03	13.3
C3	0.01	17.7
C4	No P	No P
C5	0.06	6.25
D3	No P	No P

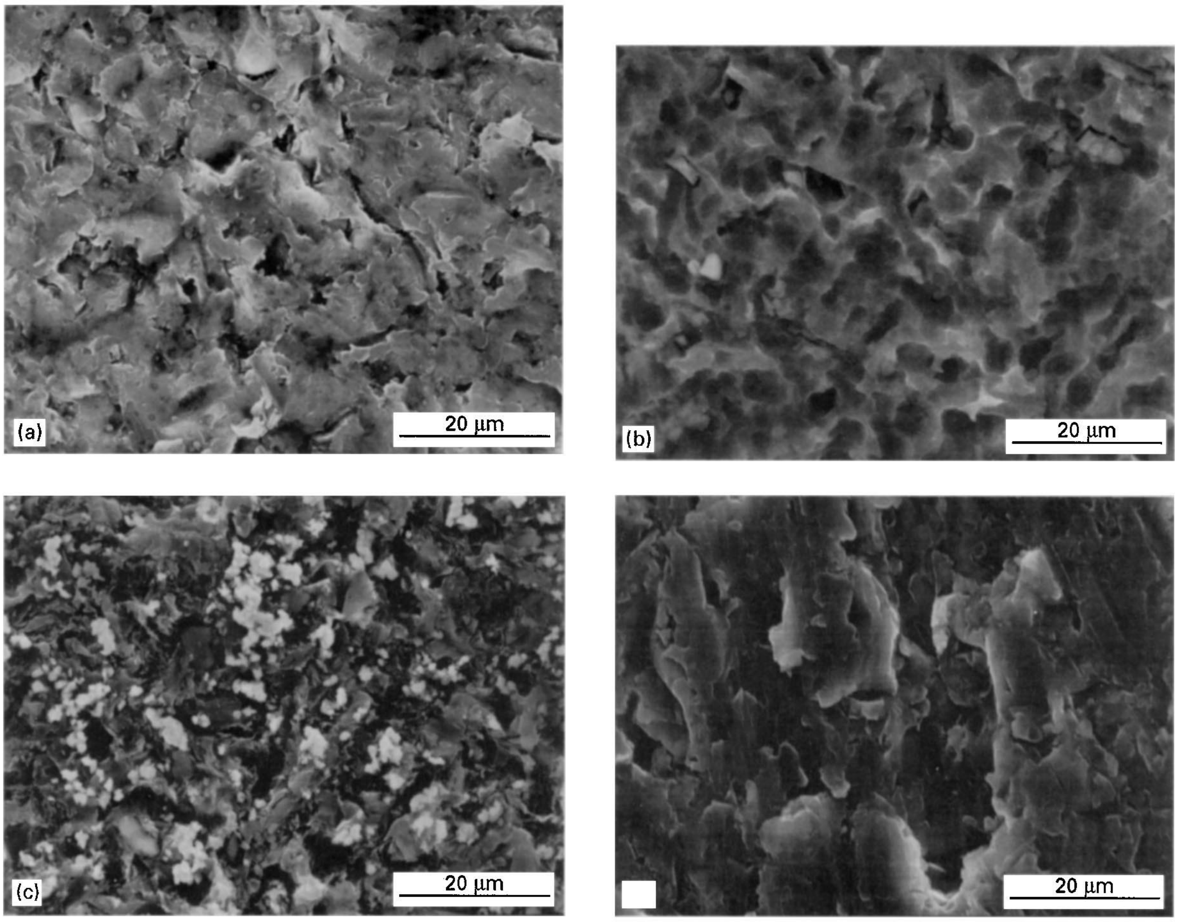

Figure 2 Scanning electron micrographs of samples: (a) A1, aluminium alloy wet polished with 1200 grid Al_2O_3 sandpaper; (b) B2, alloy surface after polishing, conditioning and spraying with solution 1 (no accelerators) at 85 °C for 5 min; (c) C1, alloy surface after polishing, conditioning and spraying with solution 2 (with accelerators) at 85 °C for 1 min; (d) D1, aluminium alloy wet polished with 1200 grid SiC sandpaper. (Magnifications 1500 ×).

possibly leading to a finer coating. In turn the larger surface area is likely to aid the paint-to-coating adhesion, even though the total amount of phosphate can be reduced by the presence of the accelerators.

3.3. Treatment time and temperature

Samples C1, C2 and C3 compare the effect of increasing spraying time (1, 2 and 3 min, respectively) while all other parameters are kept constant (Table I). Trends in both the P-to-Al ratios (0.06, 0.03 and 0.01) and Zn-to-P ratios (3.82, 13.3 and 17.7) are consistent with a decreasing amount of phosphate for increasing time of application. According to Lakeman *et al.* [14], dissolution and reprecipitation occur at the film–solution interface during the coating process, and therefore it appears that the dissolution of phosphate exceeds the reprecipitation at the longer spraying times. Basically our conclusion is that the shorter spraying times are more likely to yield appropriate coatings, and in this there is a direct contrast with the situation for the dipping process [9].

Previous work from this laboratory indicated that phosphating by dipping worked best around 65–75 °C. Accordingly, this range, including temperatures slightly above and below, was emphasized in the investigation for the spraying process. For the latter, the phosphating solution was held at the designated temperature before spraying, but some small temperature drop may occur during the application. The comparison here emphasizes the samples C4, C5 and C1 for which the treatment temperatures are 45 °C, 65 °C and 85 °C, respectively, while all other parameters are held fixed (Table I). No P was detected at the first temperature but, at 65 and 85 °C, values from XPS for the P-to-Al ratio (both 0.06) and Zn-to-P ratio (6.25 and 3.82, respectively) are fully consistent with the phosphating process occurring. Among the conditions studied so far for spray coating a polished aluminium alloy 7075-T6 surface, application of the phosphating solution at 85 °C appears most favourable.

3.4. Effect of polishing

There have been persistent indications that the details of the substrate polishing can significantly affect subsequent coating performance [15], and our earlier tests on the coatings pointed to the advantages of using 1200 grid sandpaper in the polishing. However, the emphasis now is to compare the use of two different 1200 grid sandpapers: one composed of aluminium oxide (initial sample A1) and the other of silicon carbide (initial sample D1). The comparison for the phosphated films involves samples C1 and D3, for which identical conditions for spraying conditions applied

(Table I). The first indication of significant differences at the macroscopic level comes from the adhesion test applied to samples C1 and D3. It has already been noted for the first that the break occurs within the glue layer; however, for D3 the de-adhesion occurs at the paint–substrate interface, so confirming in this case that the coating has not provided the overall adhesion required to the metal sample. Indeed for D3, XPS does not detect P in the coated sample, and this emphasizes that C1 and D3 differ chemically as well as in their mechanical performance. Since the only difference between the treatments that gave samples C1 and D3 involves the polishing by different sandpapers, it must be suspected that either the composition or the hardness of the sandpaper material has significantly influenced the final coating.

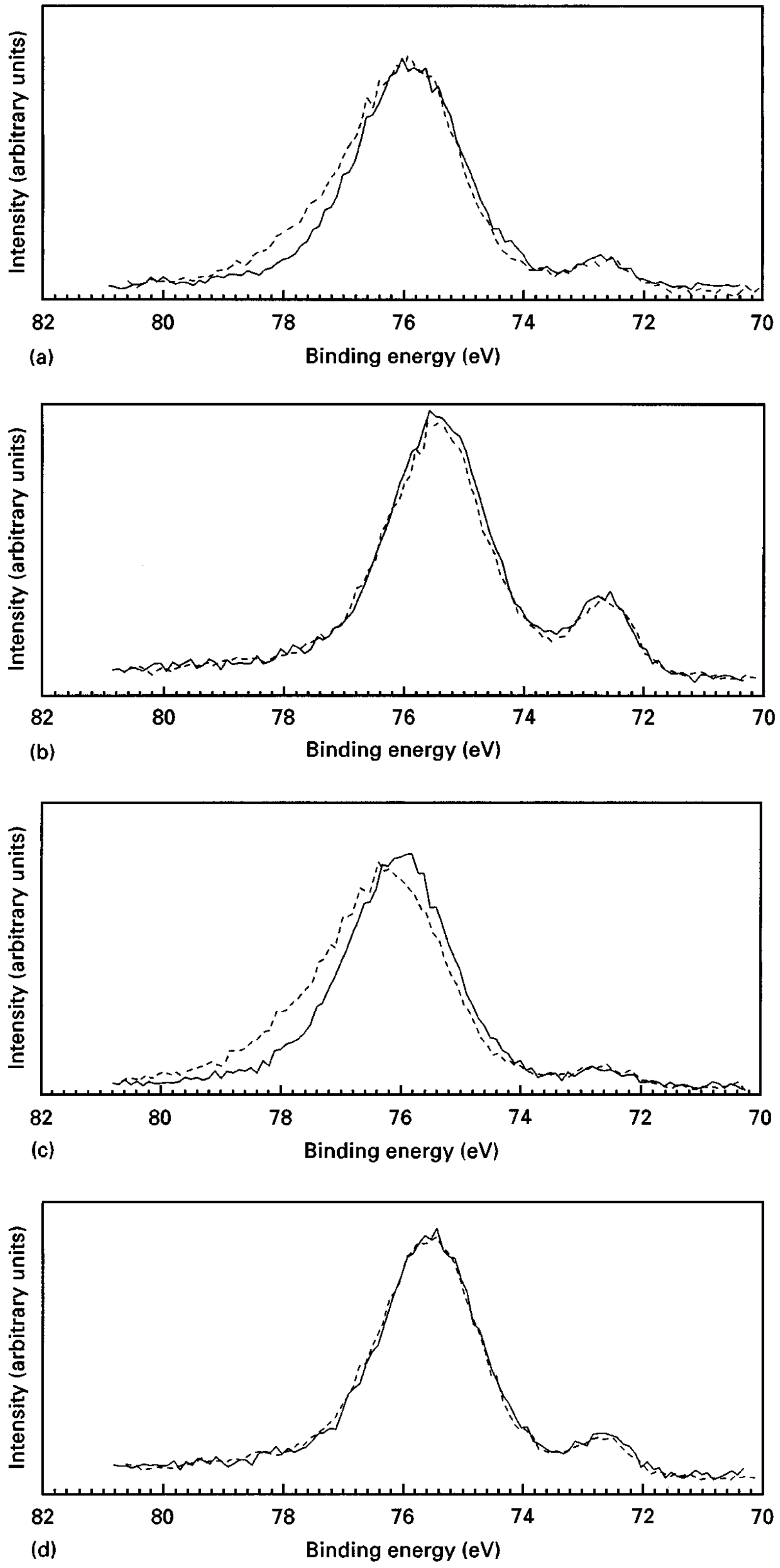

Figure 3 Comparison of Al 2p spectra measured with bias potential technique (see text) (– – –) and with the sample grounded (——): (a) sample A1, polished with Al_2O_3 sandpaper, for take-off angle $\theta = 90°$; (b) sample D1, polished with SiC sandpaper, for $\theta = 90°$; (c) sample A1 for $\theta = 30°$; (d) sample D1 for $\theta = 30°$.

A XPS study on both sample A1 (after polishing by Al_2O_3 sandpaper) and sample D1 (after polishing by SiC sandpaper) showed essentially identical surface compositions with the elements Al, Zn, O and C being present in both cases. No Si was detected on D1, and this supports the view that the differences in behaviour were not due to transfer of sandpaper particles directly to this surface. However, the narrow-scan Al 2p spectra shown in Fig. 3 do indicate differences. For both samples, the binding energy of the metal peak is at 72.6 eV, but this component intensity is less for A1 than D1, thereby suggesting that the former sample has the thicker oxide film. The oxide peak in the Al 2p spectrum for A1 is broader (comparative full width at half-maximum values are 2.2 eV and 1.9 eV for A1 and D1, respectively) and is observed at a higher binding energy (75.8 eV for A1; 75.4 eV for D1). Further insight is obtained by applying the bias potential technique to these samples. Sample D1 shows a good superposition of spectra measured for 30° take-off angle (as at 90°) when the sample is grounded, and when a negative bias potential is applied with the spectrum being shifted back after the measurement. However, these two measurements show differences for A1 (Fig. 3) which are most marked at 30°, although they are detectable for normal emission. It is concluded that there are differences in the surface charging experienced by these two samples.

For sample D1, the oxide layer is considered to maintain good electrical contact with the metal, whereas this is not the case for A1. It appears for the latter that the polishing treatment has produced a more loosely bonded oxide layer, and this is further suggested by the comparative scanning electron micrographs shown in Fig. 2. The surface of A1 is clearly much rougher with layers of leaf-like structure. These "leaves" appear loosely bound to each other, but the structure seems to be part of the original oxide rather than having been introduced from the sandpaper. It is hypothesized that this structure gives the poorer electrical contact with the metal, but that it also provides a favourable base for the subsequent phosphating. By contrast, the surface of D1 is smoother and lacks wrinkles and, while this bonds more tightly to the layer below, it apparently does not provide enough phosphating sites to form a well-adhered coating.

3.5. Comparison of dipping and spraying

Dipping involves immersing the metal sample to be coated into the coating solution, while with spraying the solution is pressure forced, as evenly as possible, onto the sample surface. In general the two methods of application result in significant differences between the coatings. Since effective ZPO coatings on aluminium alloy 7075-T6 could be obtained from the dipping process using solution 1 which had no accelerators (Section 2), an exploratory test of the spraying process was first made with this solution. A specific comparison is referred to here between sample B2 (coating applied by spraying) and sample B3 (coating applied by dipping). Both applications were for 5 min, although their temperatures of application (85 °C for spraying and 75 °C for dipping) were close to optimal for each method of application. The P-to-Al and Zn-to-P ratios from XPS for B2 (0.11 and 9.07, respectively) and B3 (0.18 and 2.50, respectively) indicate more phosphate in the coating from the dipping application, as well as a closer approach to the "ideal" Zn-to-P ratio of 1.5. The coatings from these two methods of application are also contrasted by SEM observations of their morphologies. Both samples show an amorphous coating phase and a crystalline coating phase. For B3, the sizes of the individual crystal grains are in the range 0.1–0.5 μm, but, as noted in Section 3.2, the average size of the crystals in B2 is much larger (2–3 μm); also the coating is less dense and the coverage lower.

The main differences observed can be broadly interpreted as follows. In dipping, as the pH of the interfacial region increases following the dissolution of metal by acid, Zn^{2+} and PO_4^{3-} ions precipitate on to the metal surface. The concentration of the Zn^{2+} and PO_4^{3-} ions in the interfacial region reduces, but replenishment occurs by diffusion from the bulk solution. As this process is gradual, it appears to facilitate the growth of the ZPO layer. By contrast, spraying is a more disturbing process with fresh solution continually impacting on the substrate surface. The etching rate can then be greater than the precipitation rate and, for otherwise comparable conditions, coatings obtained from spraying are often thinner than those prepared by dipping. Accordingly long spraying times do not generally give favourable coatings.

4. Concluding remarks

This paper has reviewed factors involved in producing effective coating layers on aluminium alloy 7075-T6 by spraying a $ZnO–H_3PO_4$–NaF solution. In general, coatings formed can be seen to involve mixtures of zinc phosphate with zinc and aluminium oxides. Comparison with a coating procedure by dipping indicates that added accelerators ($KClO_3$ and $NaNO_2$) are essential, in the spraying approach, in order to form an adequate phosphate layer. In general, coatings obtained by spraying are of lower quality than those from the more controlled dipping process, but with careful choice over the whole range of application parameters it is believed that useful coatings can still be obtained by the spraying method.

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