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The effect of pH and role of Ni^{2+} in zinc phosphating of 2024-Al alloy
Part II: Microscopic studies with SEM and SAM

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Abstract

Coatings formed on 2024-T3 aluminum alloy were studied by scanning electron microscopy (SEM) and scanning Auger microscopy (SAM) after dipping in zinc phosphating (ZPO) baths at different acidities, with or without the Ni^{2+} additive. The objective was to learn more about the ZPO coating mechanism on the different microstructural regions of 2024-T3. When the initial coating solution pH is 4 (optimal acidity), a slower etching rate at the Al–Cu–Fe–Mn intermetallic particle causes significant precipitation of ZnO, which differs from the coating on other regions of the surface where phosphate predominates. The larger crystals (~μm dimension) on the matrix and the Al–Cu–Mg particle contain more phosphate compared to other areas on the surface. When Ni^{2+} is added to the coating solution, the Al–Cu–Mg particle is more thickly coated compared to when the Ni^{2+} is not present. The slower rate of precipitation when Ni^{2+} is present in the coating solution increases the exposure of the alloy substrate to the acidic environment, so allowing more dissolution of Mg and Al from the Al–Cu–Mg particle. This results in the particle becoming more cathodic in nature, and therefore more coating deposits at this location. Evidence from SAM supports the presence of $NiAl_2O_4$, hypothesized in Part I, forming at coating pores later in the process.

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Keywords: Aluminum alloy; Conversion coatings; Zinc phosphate; Ni^{2+} additive; Auger electron spectroscopy; Scanning electron microscopy

1. Introduction

The background for this work, on the zinc phosphating (ZPO) of 2024-T3 aluminum alloy, was given in Part I [1], and so just a brief overview is given here. The electrochemical process that leads to phosphating starts by the acidic solution etching the initially covering oxide layer to allow electronic access with the underlying metal. The conventional view of the ZPO process is that the following reactions occur:

$$Al \rightarrow Al^{3+} + 3e^- \quad \text{(anodic)} \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2\uparrow \quad \text{(cathodic)} \tag{2}$$

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4{}^- \leftrightarrow 2H^+ + HPO_4{}^{2-} \leftrightarrow 3H^+ + PO_4{}^{3-} \tag{3}$$

$$3M^{2+} + 2PO_4{}^{3-} \rightarrow M_3(PO_4)_2\downarrow \tag{4}$$

where M^{2+} represents a species like Zn^{2+} or Ni^{2+} in the coating solution.

In the previous study, X-ray photoelectron spectroscopy (XPS) was used to study coatings formed on 2024-Al alloy after dipping in ZPO baths at different acidities, for different lengths of time, and with or without Ni^{2+} additive. The results show that the Ni^{2+} additive has several roles in this process. First, evidence was presented that the rate of increase in local solution pH, from step (2), is retarded by the slower kinetics of reactions involving Ni^{2+} compared to Zn^{2+}, leading to thinner ZPO coatings when Ni^{2+} is present in the coating solution. Second, Ni^{2+} deposition occurs especially during the later stages of the coating process. At the starting pH of 4, this probably involves the formation of a Ni-rich oxide and/or nickel phosphate (possibly mixed Zn–Ni phosphate, e.g. $Zn_xNi_{3-x}(PO_4)_2$) deposition. However, it was also found that secondary phosphate dominates the Ni-containing coating when the

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coating solution starts with the pH values 3 or 5. This contrasts with the predominance of tertiary phosphate when starting at the optimal pH of 4, although XPS indicates that the coating process initiates with deposition of ZnO (and/or $Zn(OH)_2$).

The 2024-Al alloy sample contains precipitated intermetallic compounds (also known as second-phase particles) of the Al–Cu–Mg (i.e. Al_2CuMg) and Al–Cu–Fe–Mn (i.e. $Al_6(CuFeMn)$) types, where the concentration of alloying elements can be an order of magnitude greater than in the alloy matrix. When exposed to the coating solution, they may exhibit microanodic or microcathodic behavior compared with the matrix [2]. The XPS study in Part I gave an overall view of the processes occurring, but without considering changes at the local level. In Part II scanning Auger microscopy (SAM) and scanning electron microscopy (SEM) are now used to investigate the local variations, including for the use of coating solutions with and without Ni^{2+}, and at different pH values. This extends a previous study that used SAM to observe ZPO coatings at different regions of a 2024-Al surface, but which focused primarily on the Al–Cu–Mg particles and the matrix [3]. The prime objective of the present work is to assess how the conclusions reached with XPS in Part I [1] need extension given that the coating occurs on an intrinsically heterogeneous surface.

2. Experimental

All sample preparations and coating treatments followed the descriptions given in Part I [1], where the coating solutions with Ni contained 2000 ppm of Ni^{2+}. The SAM analyses reported here were performed with a Microlab 350 spectrometer (Thermo Electron Corp.), which used a field emission source and hemispherical energy analyzer; point analyses were carried out using the primary electron beam set at 10 keV and 3 nA. The quantitative analysis used the Avantage software for non-linear background subtraction, peak area measurement and calculation of relative amounts using sensitivity factors provided by the manufacturer for the Auger structure: Zn LMM (kinetic energy 990.0 eV), Ni LMM (845.8 eV), O KLL (508.8 eV), P KLL (1856.0 eV), Al KLL (oxide 1388.1 eV, metallic component 4.5 eV greater), Cu LMM (917.0 eV) and Ca LMM (291.7 eV). The EDX characterizations, made for compositional identification of the second-phase particles, used a Hitachi 3000 N/X instrument with the incident beam accelerated through 20 kV; the associated probe depth (several μm) is much greater than that for the SAM measurements (5–10 nm). In general, determined values of elemental composition, within the probe depths of the various analytical techniques, are believed to be reliable to within 10% of the values quoted (with lower errors for the majority components).

3. Results and discussion

3.1. Ni^{2+}-containing coatings

The coatings described below were formed by dipping 2024-Al samples in the Ni^{2+}-containing ZPO bath for 2 min (optimal coating time).

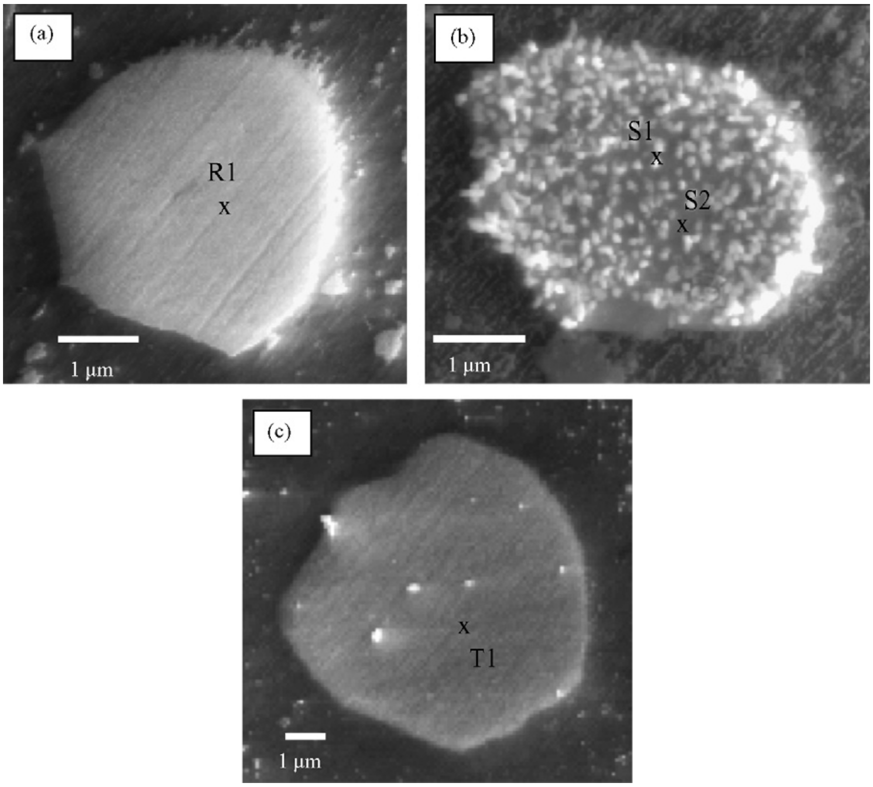

Fig. 1. SEM micrographs for Al–Cu–Mg second-phase particles on the 2024-Al surface after dipping for 2 min in Ni^{2+}-containing coating solutions at different pH values: (a) 3, (b) 4 and (c) 5.