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# Effect of surface pretreatment on corrosion resistance and bond strength of magnesium AZ31 alloy

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## ABSTRACT

A phosphate-permanganate surface treatment with additives $Na_2MoO_4$ and NaF was developed to improve the corrosion resistance and bond strength of magnesium AZ31. The phosphate coatings which have the magnesium phosphate, MgO, Mg $(OH)_2$, $MgF_2$ and a minor of $Al_2O_3$, $Al(OH)_3$ $Al_{0.35-0.55}Si_{0.10-0.48}P_{0.13-0.35}O_{2.1-2.2}$ and, $Al_{0.35}Si_{0.48}P_{0.18}O_{2.2}$, and $Al_{0.52}P_{0.48}O_{2.2}$ were formed on the surface of magnesium AZ31. A combination addition of the $Na_2MoO_4$ and NaF in the phosphate solution improves the corrosion resistance and bond strength of phosphated magnesium alloys. The optimal contents of NaF and $Na_2MoO_4$ are 0.8 g/L and 0.5 g/L, respectively.

## 1. Introduction

Magnesium and its alloys have the advantage of low density, high strength/weight ratio, being easily recycled, and used as an ideal structural material for automotive and a number of other light-weight engineering applications [1,2]. But magnesium is chemically active in nature. The magnesium alloys are easily oxidized to form a loose oxide film on the surface in a natural environment. This film provides little protection for magnesium alloys which are easily corroded in corrosive environments such as in moist air, atmosphere with sulphur and marine atmosphere [3]. The loose oxide film may result in poor mechanical performance of adhesively-bonded magnesium alloys. Therefore, it is necessary to improve the corrosion resistance and joint strength of magnesium alloys for its broad applications.

To increase the corrosion resistance of magnesium alloys, the simplest and most economic method is chemical conversion treatments on the magnesium surface. The most popular and effective conversion process to produce a protective layer on the surface of metals is based on the immersion of the alloys in a bath containing chromate ions. But the conventional chromium-based conversion coatings contain highly toxic carcinogens [4]. Increasing awareness of health and environmental problems has led to the prohibition of the use of chromate. In searching for alternatives to chromate conversion coating, more and more researchers focus on chromium-free conversion coatings, such as permanganate-phosphate conversion coatings [5–7], fluorozirconate conversion coatings [8,9], stannate treatments [10–13], rare earth conversion coatings [14,15], silane coating [16] and so on. Conversion coatings protect the substrate from corrosion by acting as an insulating barrier of low solubility between the metal surface and the environment [1].

Molybdates, tungstates, permanganates and vanadates, including similar chemical elements to chromium (groups VB, VIB and VIIB of the periodic table), were the first chemicals tried as alternatives [17,18]. Molybdenum is well known as a localized corrosion inhibitor when present in electrolyte as Mo (VIB) or as an alloying element in steel [19]. Like chromate, molybdate acts as an oxidant in the chemical conversion treatments, its adsorbent production can inhibit the penetration of the inimical ions such as $Cl^-$ to protect the substrate. Molybdate treatments have been applied on Zn, Al alloy, steel and magnesium alloy substrates to improve the corrosion resistance of those substrates [20–24]. More recently, molybdate/phosphate composite conversion coatings have been developed to obtain further improvement of corrosion protection for magnesium alloys [23,25,26].

In a previous investigation [27], we have studied the effect of $Na_2MoO_4$ on the joint performance of the magnesium alloys and found that the additive $Na_2MoO_4$ in a phosphate-permanganate solution exhibited little effect in the formation of the phosphate coating. It mainly acted as an accelerator to the coating formation by decreasing the current density and restraining the hydrogen evolution in micro-cathodes. However, when adding it into a phosphate solution with a high content of NaF, it exhibited a very apparent enhancing effect on the formation of the coating and

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the mechanical performance of adhesive-bonded magnesium alloys. But the effect of $Na_2MoO_4$ on the corrosion resistance of phosphate coating magnesium AZ31 sheets was not investigated.

In this study, the additives $Na_2MoO_4$ and NaF were added into a permanganate-phosphate pretreatment solution to investigate the effect of surface pretreatment on the corrosion of magnesium alloys. The permanganate-phosphate treatment solution with $Na_2MoO_4$ was used to parkerise 2 mm thick magnesium AZ31. There are three main parts in this report; the first presents the experimental procedure including material, surface pretreatment methods, surface characterization, sample fabrication, corrosion resistance assessment and mechanical testing. The next section shows the surface characteristic of the phosphate coating. The characteristics and chemical composition of the phosphate coating were analyzed with scanning electron microscope (SEM) and X-ray photoemission spectroscopy (XPS) technology. The corrosion resistance is evaluated by immersion test, hydrogen evolution detection and electrochemical impedance spectra test (EIS). The strength of adhesive-bonded Mg AZ31 was evaluated using lap-shear joints. Finally, an empirical model is proposed to evaluate the effects of additives $Na_2MoO_4$ and NaF on the corrosion resistance and bond strength of magnesium AZ31.

## 2. Experimental procedure

### 2.1. Material

2.0 mm thick magnesium AZ31 alloy was used in this study. The chemical composition and mechanical properties per our experimental measurements are listed in Tables 1 and 2, respectively.

### 2.2. Surface pretreatment

The magnesium AZ31 sheets were pretreated using a phosphate-permanganate treatment solution with molybdate additive $Na_2MoO_4$ (MPPT). The phosphate solutions were prepared from anhydrous $K_2HPO_4$, $KMnO_4$, $Na_2SiO_3$, NaF, $Na_2MoO_4$ and deionized water. All chemicals used were of analytical grade. The constituent contents of various MPPT solutions are listed in Table 3. The concentration of phosphate solution is presented as the mass of constitute in one liter solution As shown in Table 3, the $K_2HPO_4$, $KMnO_4$, NaF, and $Na_2SiO_3$ are the base constituents of the solution used for forming the phosphate coating while $Na_2MoO_4$ is the additive used for modifying the quality of the phosphate coating. For the purpose of comparison, a reference pretreatment process (RPT) was used. The reference phosphate treatment process was a phosphate solution without the additive $Na_2MoO_4$, as developed in our previous investigation [23]. The details of each process are shown in Table 4.

### 2.3. Surface characterization

SEM and XPS were used to examine the morphology, thickness and structure of the conversion coatings. The appearance and component of the coatings were observed with scanning electron microscopy (SEM), and a combination of Energy Dispersive X-ray Spectroscopy (EDS) and X-ray photoemission spectroscopy (XPS), respectively. XPS spectra of the coatings were acquired with an ESCALABMk 250 spectrometer using Monochromated Al K alpha X-ray (200 W). Cycles of XPS measurements were done in a high vacuum chamber with a base pressure of $1.33 \times 10^{-6}$ Pa.

**Table 1**
Chemical composition of magnesium AZ31 (mass%).

| Al | Zn | Mn | Si | Fe | Cu | Ni | Ca |
|---|---|---|---|---|---|---|---|
| 3.14 | 0.82 | 0.45 | 0.058 | <0.002 | <0.01 | <0.01 | <0.04 |

### 2.4. Adhesive-bonding of magnesium AZ31

After pretreating the surface, the adherents were joined with one-part Henkel toughened epoxy. The lap-shear specimen was fabricated from 38 × 127 × 4 mm magnesium AZ31. To simulate the bonding along a vehicle body flange, a bond area of 38 × 15 mm was selected. Shims are bonded on the adherents to keep the load plane of the specimen coincident with the central plane of the tensile tester. The adhesive-bonded specimens were prepared as follows: (1) applying the adhesive through a hand-held injection gun on one of the two adherents which were stored in an ambient laboratory environment (20 °C and 50% R.H.); (2) positioning the adherents with and without dispensed adhesive using a fixture; (3) bringing the adherents together by a fixture under ambient laboratory conditions; (4) pressure was applied via the fixture so that a bondline thickness (set up by a 0.2 mm thick metal shim) of 0.2 mm can be maintained; (5) curing the specimens in the oven per supplier's recommended curing procedure (25 min at 165 °C). All finished specimens are examined and the spew fillets around the edge of the overlap were retained to simulate real production conditions.

### 2.5. Immersion test

To screen the corrosion resistance of the phosphate coatings, the immersion tests were first conducted at ambient temperature. All tests were conducted referring to ASTM D870–02 [28]. According to this standard, the corrosive medium in immersion test is distilled or de-mineralized water. Considering its corrosive ability to magnesium is too weak to quickly evaluate the corrosion resistance of coated Mg alloys, a 3.5% NaCl solution was selected to replace distilled or de-mineralized water as a corrosive medium in immersion test in the study. Since the corrosion of the magnesium occurs at the nature conditions, the NaCl solution was made with tap-water to correspond with the real service conditions of magnesium alloys. The phosphate pretreated Mg AZ31 substrates were soaked in 3.5 wt.% NaCl solution for 45, 150, 300 and 400 min, respectively, and then the corrosion area were examined to assess the corrosion resistance of the coatings.

### 2.6. Hydrogen evolution detection

To measure the corrosion rate of the phosphated Mg AZ31 in 3.5 wt.% NaCl solution, hydrogen evolution detection tests were conducted at ambient temperature. Fig. 1 shows the hydrogen evolution detection instrument. The specimens were first immersed in a 3.5 % NaCl solution where the hydrogen is released due to the corrosion of magnesium AZ31 in the NaCl solution. The volume of $H_2$ was collected every hour in the gas collecting tube. The hydrogen release rate of the samples represents the corrosion rate and is used to evaluate the corrosion resistance of the phosphated samples. Three replicates were performed for every coating.

### 2.7. Electrochemical impedance spectra test (EIS)

To evaluate the effects of $Na_2MoO_4$ and NaF on the electrochemical corrosion and the corrosion kinetics of phosphate magnesium AZ31 in 3.5 wt.% NaCl solution, the EIS spectra were measured. The electrochemical cell consisted of saturated calomel reference electrode, large-area platinum counter electrode, and the working electrode. A sample area of 0.5 $cm^2$ was exposed in the solution. All EIS spectra were measured at the spontaneously established open circuit potential. Prior to starting measurements, the specimens were