

# **Mg Magnesium Technology 2013**

## **Corrosion II**

## FORMATION OF VANADATE CONVERSION COATING ON AZ31 MAGNESIUM ALLOY

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### Abstract

Magnesium alloys have high strength-to-weight ratios, excellent castability, machinability, weldability, and thermal stability, and good damping capacity. Therefore, Magnesium alloys are recognized as alternatives to Al alloys and steel to reduce the weight of structural materials. However, a major obstacle to the widespread use of magnesium alloys is its poor corrosion resistance, particularly in wet environments. Therefore, further surface treatment of magnesium and its alloy is important in meeting several industrial specifications. In the present investigation, a chromate-free, corrosion-resistant conversion coating using vanadium based solution was applied to AZ31 magnesium alloy. Conversion coating was carried out in vanadium based solution. The effect of vanadium concentration and treatment time on the coating film was characterized by SEM, EDX and XRD. The corrosion characteristics of anodic films were evaluated using potentiodynamic polarization test in deaerated NaCl solution. Corrosion resistance property was improved with conversion coating treatment.

### Introduction

Magnesium is the lightest of all structural metal materials in practical use, with a density equivalent to two-third the density of Al, one-third that of Zn and one quarter that of steel. It also has a good electrical/heat conductivity, damping properties and machining abilities. These properties make magnesium alloys an attractive target in a number of applications, especially in fields where weight reduction is critical or there are particular technical requirements. However, a major obstacle to the widespread use of magnesium alloys is its poor corrosion resistance: magnesium alloys are highly susceptible to corrosion attack, particularly in wet environments. Therefore, further surface treatment of magnesium and its alloy is important in meeting several industrial specifications. The common coating processes are electrochemical plating, chemical conversion, anodizing, physical vapor deposition, and electroless nickel plating.

Of these, conversion coatings are economical, easy to use and offer a variety of valuable properties to extend the service life and improve the performance characteristics of the magnesium alloy parts being treated. Chromate conversion coating is widely used in industry because of its desirable properties: it provides excellent corrosion

protection through the corrosion-inhibiting properties of the hexavalent chromium present in the film and through the physical barrier of the film itself. However, changing environmental regulations and pollution prevention requirements have led to a significant push to find a new alternative to the use of poisonous Cr<sup>6+</sup>, therefore, developing an environmentally friendly surface treatment has attracted a great deal of research interest in recent years. Several non-chromate solutions are thus developed, such as rare earth salt [1, 2, 3, 4, 5], stannate [6], phosphate [7] and phosphate/permanganate solutions [8, 9]. Vanadate was also suggested as pretreatment candidates aiming to self-healing conversion coating [10] Guan et al. developed a new type of inorganic conversion coating formed on aluminum alloy substrates by dipping the substrate in aqueous vanadate-based solutions at ambient temperatures [11]. The anticorrosion properties was improved with vanadate contained coatings, which showed that in near-neutral solutions, vanadate increases the pitting potential, and decreases the oxygen reduction reaction rate on AA2024-T3 Al alloy. Sodium vanadate was added to solution contains phosphate and fluoride ions with other active corrosion inhibitor in order to form an improved chromate-free corrosion resistant conversion coating for magnesium alloy [12]. The addition of sodium vanadate is a preferred choice because it improves the humidity resistance of the conversion coating over a wide range of concentrations and enables use of a 50% shorter coating cycle. Vanadium solution is usually used as the corrosion resistant inhibitor for the paint or pigment systems. However, only few works are reported on the application of vanadium-based conversion coatings on magnesium alloys. The vanadate-based conversion coating can significantly improve the corrosion resistance of the AZ61 magnesium alloy [13]. Vanadate conversion coating was formed on the Mg-Li-Al-Ce alloy in NH<sub>4</sub>VO<sub>3</sub> + K<sub>3</sub>(Fe(CN)<sub>6</sub>) solutions. Uniform coating with regular distributed pores was formed the anticorrosion property was improved with his conversion coating [14]

In the present research, the formation of conversion coatings on AZ31 magnesium alloy in vanadium based solution was investigated. The effect of time and concentration of vanadium on the anti-corrosion property of the coating films were evaluated using the potentiodynamic polarization curves. Furthermore, the surface morphologies and phase structure were detected using SEM, EDX, XPS and XRD.

## Experimental

### Specimens

Commercially available AZ31 Mg alloys were used as the substrate. The chemical composition of the alloy is listed in Table 1. The surface of the alloy was polished up to #2000 emery paper followed by 0.05  $\mu\text{m}$  alumina powders. The specimens were carefully cleaned with water, rinsed with acetone and dried under air. All of the experiment specimens were mounted using polytetrafluoroethylene (PTFE) resin tape, leaving 1  $\text{cm}^2$  surface area.

**Table 1** Chemical composition of AZ31 Mg alloy (mass%)

Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
3.0	1.0	0.43	0.01	<0.01	0.001	<0.003	Bal.

### Conversion coating

Anodizing was performed at room temperature for 300 - 1800 s in the aqueous electrolyte of Vanadyl Sulfate at various concentration range 5 - 25 g/l. After the treatment, the specimens were carefully rinsed using distilled water and dried under air before analysis.

### Morphology and Structure of Anodic Film

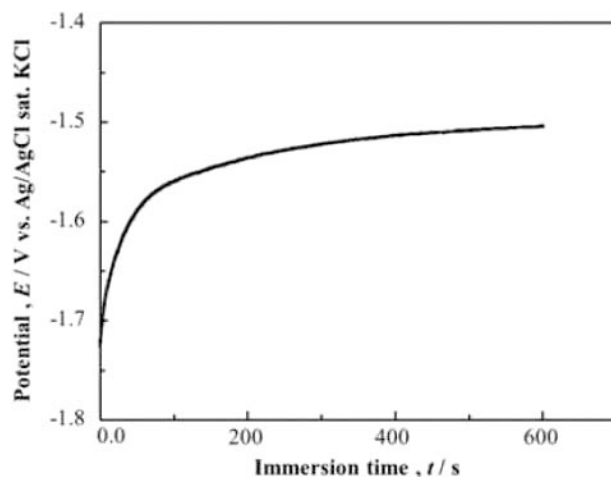
The morphology and microstructure of the anodic films were observed with a Hitachi S-800 scanning electron microscope (SEM), the phase structure and the composition of the coating films were identified with X-ray diffraction (XRD) and Energy Dispersive X-ray Spectrometry (EDS).

### Corrosion Measurements

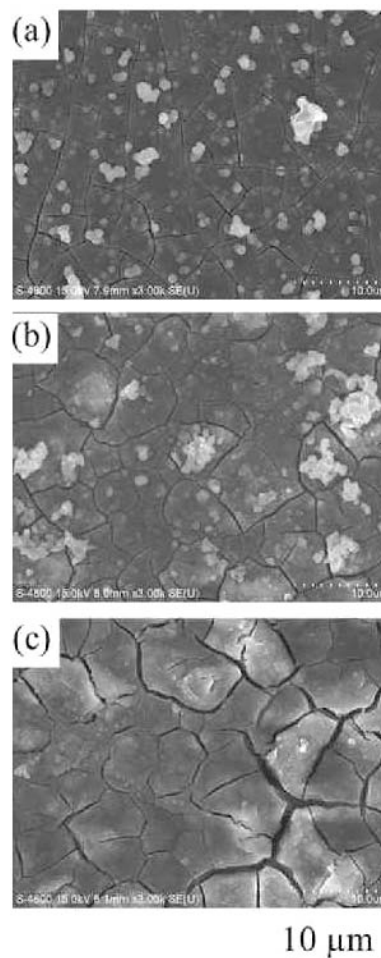
The potentiodynamic polarization test was carried out using a Solartron 1285 potentiostat from Solartron Analytical, Farnborough, United Kingdom. The measurements were controlled by Scribner Associates Corrware electrochemical experiment software. The anodic and cathodic polarization curves were measured in 0.017 M NaCl and 0.1 M  $\text{Na}_2\text{SO}_4$  solution at 298 K with a scanning rate of  $1 \text{ mVs}^{-1}$ .

## Results and Discussion

Figure 1 shows the open-circuit potential (OCP) as a function of time throughout the conversion coating treatment of AZ31 magnesium alloy in 5 g/l  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$  for 600s. The OCP increased from approximately -1.72 V upon immersion in vanadium-based solution to -1.5 V after 600 s.



**Figure 1.** The open-circuit potential-time transient curve throughout conversion coating treatment of AZ31 magnesium alloy in 5 g/l  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$  for 600s.



**Figure 2.** SEM images of conversion coating films formed on AZ31 Mg alloy in vanadium-based solution with various  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$  concentration (a) 10g/l, (b) 15 g/l, and (c) 25 g/l for 15 min.

Figure 2 shows the SEM images of conversion coating films formed on AZ31 Mg alloy in vanadium-based solution with various concentrations. The coating film has a brown color to the naked eye. The coating revealed the presence of several micro-cracks, the wide of these micro-cracks increases with vanadium concentration increasing in the treatment solution. The maximum size of these micro-cracks was 0.35, 0.64, and 1.0  $\mu\text{m}$  for the film formed in the solution with concentration of 10g/l, 15 g/l, and 25 g/l respectively.

Potentiodynamic polarization curves of AZ31 Mg alloys before and after treatments in vanadium-based solution were measured in 0.017 M NaCl and 0.1 M  $\text{Na}_2\text{SO}_4$  solution at 298 K with a scanning rate of  $1 \text{ mVs}^{-1}$ . It was noted that the corrosion potentials ( $E_{\text{CORR}}$ ) were significantly increased with treatment in vanadium solution. Figure 3 shows that the film formed in the solution containing 25 g/l and 15g/l  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$  has nearly the same corrosion potential of -1.5 V. The film formed in the solution containing 10 g/l has the largest corrosion potential. The pitting potential ( $E_p$ ) of the coating film formed at 10g/l has the largest potential of -1.21 V compared to non-treated specimen -1.35 V and those treated in 15 and 25g/l  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$  -1.30 and -1.34 respectively. This indicate that the film formed in 10g/l has better anticorrosion property and these results agree with the SEM image results as this film has a very narrow micro-cracks compared with those formed in the solution with concentration of, 15 g/l and 25 g/l  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ . So, the concentration of 10 g/l was used to determine the effect of treatment time.

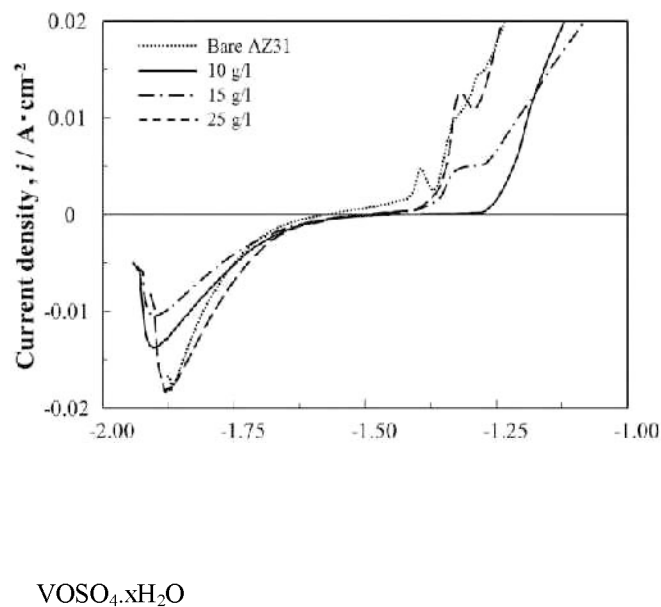
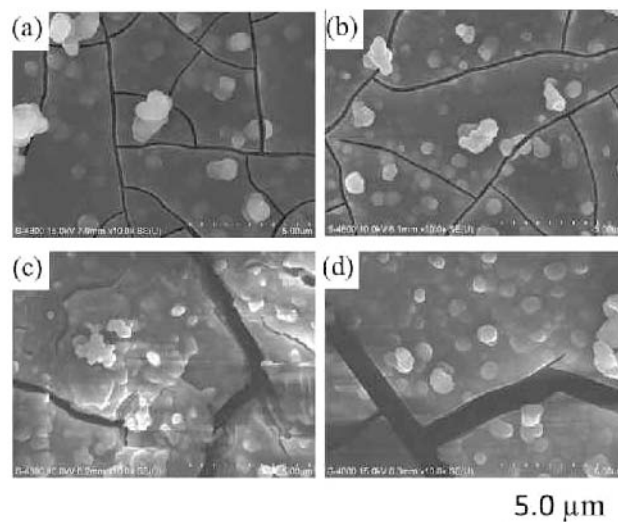


Figure 4 shows the SEM images of the conversion coating films formed on AZ31 Mg alloy throughout the immersion



in 10g/l  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$  solution for (a) 15 min, (b) 30 min, (c) 60 min, and (d) 120 min. The figure shows that the micro-cracks have propagated throughout the coating surface. The films formed mainly from a compact white precipitates from magnesium and vanadium oxides. Only a few unattached white precipitates were located on the surface of the coatings. The maximum size of these micro-cracks was 0.09, 0.09, 0.71 and 1.19  $\mu\text{m}$  for the film formed in the solution with concentration of 10g/l for 15 min, 30 min, 60 min, and 120 min respectively. The results clearly show that the film formed at 30 min. has smooth surface with minor micro-cracks.

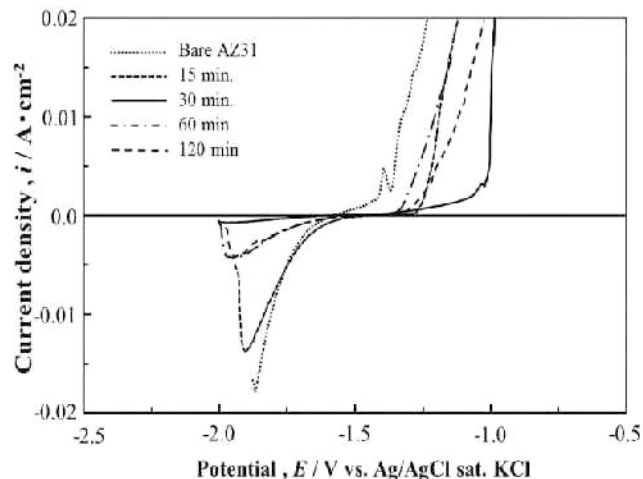
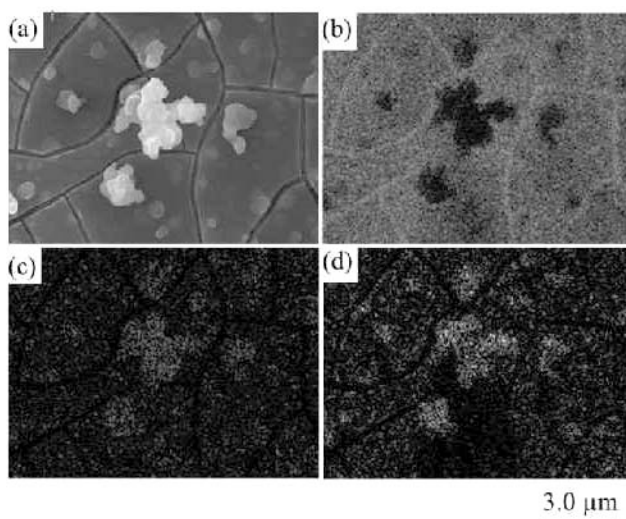


Figure 5 shows the potentiodynamic polarization curves of AZ31 Mg alloy after treatment in various times in vanadate solution. The pitting potential of the films formed in the solution containing 10 g/l  $\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  for various treatment times were better than bare AZ31. However, the film formed at 30 min. has the noblest pitting potential of 1.03 V. Therefore, the EDS analysis was carried out on the coating film formed in 10g/l  $\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  for 30 min to reveal the elemental presence and distribution on the surface. Figure 6(a) show the SEM image of the conversion coating film. The EDS elemental mapping Fig 6(b, c, d) clearly shows the distribution of Mg, O, and V respectively in the coatings. The Vanadium elemental mapping confirms their presence in the coating film as shown in Fig. 6(c). Magnesium and oxygen elemental mapping reveal that the film contains MgO and/or  $\text{Mg}(\text{OH})_2$ . Furthermore, results shows that the white color precipitates which observed on the surface are mainly compose of Vanadium and Oxygen which reveal to formation of Vanadium oxide and/or hydroxides. Further investigation is needed to determine the exact mechanism of the conversion coating.



### Conclusions

Conversion coating was performed on AZ31 Mg alloy in various concentration of  $\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ . The effect of treatment time on the microstructure and anticorrosion property of the films were examined and. The best anticorrosion property was obtained with treatment in 10g/l  $\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  for 30 min. this film has a smooth surface with minor micro-cracks compared to other films. The

results show that vanadium oxides and/or hydroxides were included in the coating films.

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