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The improved performance of a Mg-rich epoxy coating on AZ91D magnesium alloy by silane pretreatment

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ABSTRACT

A silane film is prepared on AZ91D magnesium alloy and the effect of the silane pretreatment on the performance of a Mg-rich primer on AZ91D alloy are studied. After the silane treatment, Si–O–Mg covalent bonds form between the silane film and magnesium substrate and Si–O–Si structure forms in the silane film. As the result, the adhesion of the Mg-rich primer to AZ91D substrate increases obviously. Machu test and electrochemical measurements indicate that the silane pre-treatment significantly improves the performance of the Mg-rich primer on AZ91D alloy, which is attributed to strengthened barrier effect of the coating system.

1. Introduction

Magnesium alloys are good materials for automotive, aerospace and other industries due to their very high specific strength and good formability. However, the engineering applications of magnesium alloys are limited mainly by their low corrosion resistance [1,2]. Magnesium is electrochemically the most active metal among structural materials. Al, Zn and other alloy elements are usually added in engineering magnesium alloys. For example, AZ91D magnesium alloy contains about 9 wt.% Al and its potential is more positive than pure magnesium [3]. Yu and Uan [4] made a magnesium (99.9%) film on AZ91D substrate by physical vapor deposition and reported that the magnesium film may work as a distributed sacrificial anode and protect the substrate. Mg-rich coatings for the protection of aluminum alloys have been developed by Nanna and Bierwagen et al. and good performance for the aluminum/Mg-rich primer system was reported [5–8]. In our previous work pure magnesium particles were added in an epoxy coating and the coating was applied on AZ91D magnesium alloy [9]. The coating shows good corrosion resistance which may be attributed to the cathodic protection and the barrier effect by the pure magnesium particles. However, the adhesion of the coating to the magnesium alloy substrate is to be further improved, since the surface of magnesium alloys in air forms oxide films which reduce the adhesion of organic coatings to the substrate [10–12].

Previous studies have shown that silane films can be used as adhesion promoters between organic coatings and aluminum alloys [13–15] or copper [16] substrates to improve corrosion resistance of the coatings. Organo-functional silanes can form chemical bonds with active sites on the substrate and with the reactive groups of polymer molecules [13,14], hence a stable and high-energy bond between the substrate and the coating may be formed. While most studies [17–19] on silane treatments on magnesium alloys have focused on improving anti-corrosion ability of the alloys, only a few studies [20,21] reported that the silane pretreatments enhance corrosion protection of organic coatings on magnesium alloy substrates. Barranco et al. [20] found that tetramethoxysilane (TMOS) and diethoxydimethylsilane (DEDMS) are especially effective precursors for pre-treatment of acrylic coatings. Zhang and Wu [21] reported that the silane film increases the corrosion resistance of E-coating on Mg substrates. In this paper, the influence of a γ-glycidoxy propyl trimethoxy silane (γ-GPS) treatment on the adhesion and the corrosion resistance of a Mg-rich epoxy primer on AZ91D magnesium alloy is investigated.

2. Experimental methods

2.1. Materials

AZ91D magnesium alloy panels were obtained from Yingkou Galaxy Magnesium Aluminum Co., LTD, China. The chemical composition is shown in Table 1 which was measured with a direct reading spectrometer. The γ-glycidoxy propyl trimethoxy silane (γ-GPS) was purchased from Beijing Antepuna Trade Co., Ltd. The epoxy resin, WSR 6101 with the epoxy equivalent of 212–243 g/equiv., was purchased from Wuxi Resin Factory, Wuxi, China. The polyamide, Type 651 with the amine value of 380–420 mg of

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Table 1
Nominal composition (wt.%) of AZ91D magnesium alloy.

Al	Mn	Zn	Fe	Si	Ni	Cu	Mg
9.4	0.23	0.82	0.005	0.01	0.002	0.02	Remainder

KOH/g, was obtained from Yan'an Chemical Plant, Tianjin, China. The solvents including xylene, n-butanol, acetone, methanol and glycerol were purchased from Beijing Chemical Works, Beijing, China. Titanate coupling agent was obtained from BYK Chemical Company, Germany. The pure Mg particles (99.9%), with the average size of 10–20 μm, were prepared by Beijing Nachen Science and Technology development Co., Ltd.

2.2. Samples preparation

AZ91D magnesium alloy was cut into the size of 50 × 50 × 3 mm, then the samples were ground using SiC abrasive papers up to 240 grit. The AZ91D substrate was washed in distilled water and acetone in turn, then dried in air. Before the silane treatment, the samples were degreased in an alkaline solution (Na_2CO_3 50 g/L + Na_2SiO_3 25 g/L + Na_3PO_4 50 g/L, 80 °C, 5 min), washed in distilled water, and dried in air.

The silane solution was prepared by adding 10 wt.% γ-GPS to a 1:8 mixture of methanol and distilled water. Finally, glycerol (0.15 vol.% of the total silane solution) was added. The silane solution was stirred for 1 h, then was kept at room temperature for 2 days before use to insure complete hydrolysis of the silane. The cleaned Mg alloy samples were dipped in the silane solution for 2 min and cured in an oven at 150 °C for 1 h to form siloxanes.

The preparation of the Mg-rich epoxy primer was described in Ref. [9]. The primer was applied on the panels by manual brushing. After coating, the samples were cured for a week at room temperature. The thickness of the dry primer was about 130 μm which was measured with a digital thickness gauge TT230.

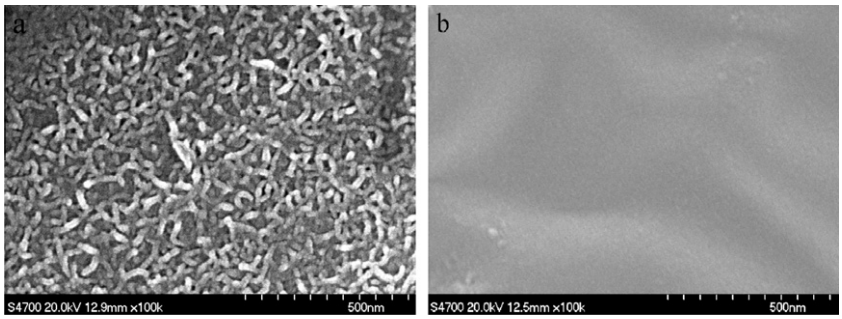

Fig. 1. Surface morphology of AZ91D magnesium alloy before and after silane treatment: (a) AZ91D magnesium alloy, (b) γ-GPS treated AZ91D magnesium alloy.

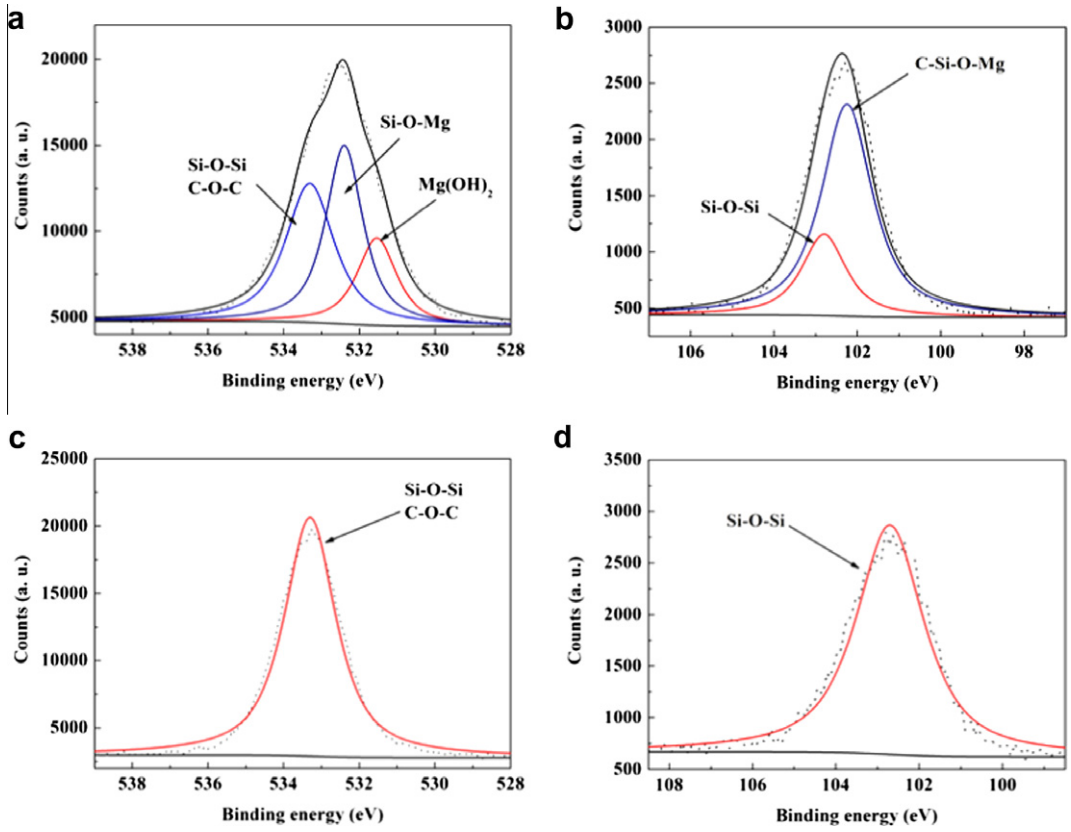

Fig. 2. The fitted O 1s and Si 2p XPS spectra of silane films: (a) O 1s spectra of the thin silane film, (b) Si 2p spectra of the thin silane film, (c) O 1s spectra of the thick silane film, (d) Si 2p spectra of the thick silane film.