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Microstructure and electrochemical behavior of cerium conversion coating modified with silane agent on magnesium substrates

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ABSTRACT

The cerium conversion coating with and without different concentrations of silane agent bis-(γ-triethoxysilylpropyl)-tetrasulfide (BTESPT) modification is obtained on magnesium alloys. Detailed properties of the coatings and the role of BTESPT as an additive are studied and followed with careful discussion. The coating morphology, wettability, chemical composition and corrosion resistance are characterized by scanning electronic microscope (SEM), water contact-angle, X-ray photoelectron spectroscopy (XPS), potentiodynamic measurements and electrochemical impedance spectroscopy (EIS). The electrochemical behavior of the coatings is investigated using EIS. The results indicate that the coating morphology and composition can be controlled by changing silane concentration. The combination of cerium ions and silane molecules could promote the formation of more homogenous and higher hydrophobic coating. The coating turns to be more compact and the adhesive strength between the coating and the magnesium substrate are strongly improved with the formation of Si—O—Si and Si—O—M chemical bonds. The optimum corrosion resistance of the coating in the corrosive media is obtained by 25 ml L^{-1} BTESPT modification. This whole study implies that the cerium conversion coating modified with certain silane agent deserves cautiousness before its application for corrosion resistance.

1. Introduction

Magnesium alloys are commercially available for various industrial fields and biomedical applications. They have been attracting much attention worldwide for their excellent physical and mechanical properties, such as low specific density, stiffness, mechanical stability, high thermal and electrical conductivities [1–6]. However, the limited corrosion resistance is still a serious drawback for magnesium alloys and restricts their industrial applications under certain conditions. Recent studies showed that desired corrosion resistance of magnesium alloys will necessitate application of suitable surface barrier, such as anodized films, polymer films and chemical conversion treatments [7–14].

Rare earth conversion coatings are some of the most promising substitutes for chromate conversion coatings, since they are nontoxic and can provide a physical barrier to enhance the anti-corrosion protection [15]. The formation of the cerium conversion coating is simply achieved by dipping the substrate metal in baths containing cerium salts/hydrogen peroxide aqueous solution for a short period. The addition of H_2O_2 is favorable for accelerating the formation of the conversion film. In the past few decades many studies were devoted to cerium based conversion coatings and its anti-corrosion properties on different metallic substrates. Such conversion coatings improved the corrosion resistance to some degree. Nevertheless, the loose structure and weak adhesion properties are still the main defects for these coatings [16], which are prior to be attacked and accelerate the coating degradation. It is necessary to improve the morphology and microstructure of traditional cerium conversion coatings to obtain better corrosion resistance under various conditions. Despite many research works have been devoted to the optimization of the cerium conversion coatings, including phosphate post-treatment [16], alkaline cleaning and activation before conversion treatment [17], water solution gelatin added [18] and so on, the problem of porous and low adhesion has not been effectively resolved yet.

Our interest is focused on using silane agent to modify the traditional cerium conversion coatings. Silane is emerging as an environmentally friendly alternative for improving the corrosion resistance of the magnesium substrates [7,19,20]. Due to their unique chemical structure, the hydrolysable groups can connect with the hydroxyl groups of metallic substrates to form covalent bonds and make the silane used for modification of a substrate/coating interface [21]. On the other hand, the silanol groups can react with each other to form siloxane bonds, thus self assem-

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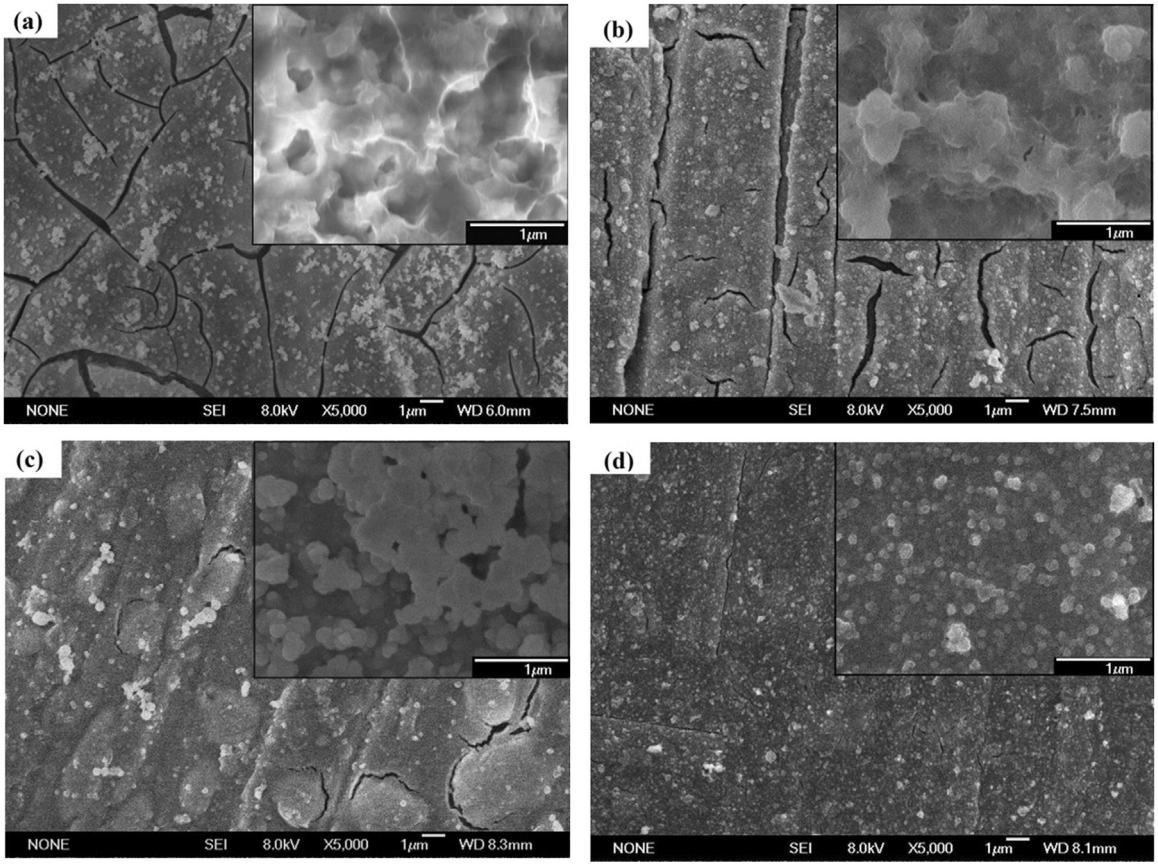

Fig. 1. SEM images of the cerium conversion coatings modified with various BTESPT concentrations (a) 0 ml L^{-1}; (b) 15 ml L^{-1}; (c) 20 ml L^{-1}; (d) 25 ml L^{-1}.

bled robust Si-O-Si network linkages, which provides high stability and effective barrier against electrolyte uptake [22]. Electrochemical measurements and accelerated corrosion tests showed that silane molecules provided enhanced corrosion protection of different metallic substrates [23]. Recently many studies based on the formation of silane film were modified with cerium ions or ceria nanoparticles [24]. However, there is little literature researched on the silane as an addictive to the cerium conversion solution on magnesium alloys, and the action mechanism of silane needs to be further explored.

The present work aims at morphology, chemical composition, electrochemical properties and behaviors of a novel cerium conversion coating modified with different BTESPT concentrations on magnesium alloys. BTESPT is a non-functional silane that can form six hydrolysable silanol groups, which would facilitate the reaction with the metallic substrates. Further research is carried out on characterization of the influence of BTESPT concentration on coatings. In order to give a comprehensive evaluation of the potential application of this new coating, electrochemical properties of the coatings during the corrosion process are investigated and correlated with the coating microstructure, which can be controlled by BTESPT concentration. On the basis of the experiment results, the role of BTESPT as an additive in the silane modified cerium conversion coating is discussed.

2. Experimental

2.1. Preparation and surface treatment

The AZ31 magnesium alloy was used in this work. Each coupon was cut into 10 mm × 10 mm × 3 mm panels. The samples were degreased in ethanol and mechanically polished with abrasive papers from 400 to 1200 grit. In preparation for coatings the coupons were immersed in 4 g L^{-1} NaOH solution for 5 min at room temperature and then thoroughly washed with deionised water.

BTESPT was supplied by Sinopharm Chemical Reagent Co., Ltd. Prior to coating preparation, BTESPT solution was prepared for hydrolysis and condition for BTESPT hydrolysis was well established [25]. In this paper, the hydrolysis condition was employed by dissolving 5% (v/v) of BTESPT in 90% (v/v) ethanol and 5% (v/v) H_2O and kept under constant stirring for 24 h before use. Afterwards the BTESPT solution was added to the cerium conversion solution composed of 0.1 M cerium chloride and 5 ml L^{-1} 30 wt.% H_2O_2 with different concentrations of 15 ml L^{-1}, 20 ml L^{-1} and 25 ml L^{-1}. The cleaned samples were immersed in the above solutions for 5 min and then oven-dried at 110 °C for 20 min to enhance the cross-linking of silane. For investigation of the silane action mechanism, the cerium conversion coating without silane modification was also prepared and discussed.

2.2. Characterization

The morphology and corrosion surface after immersion for 72 h in 0.05 M sodium chloride solution of the unmodified and modified with different silane concentration coatings were observed using a Japanese Electronics Co., Ltd. JEOL JSM-6700F SEM (Akishima, Tokyo Japan). The contact angle of the coatings was examined using a Shanghai Zhongchen Digital Technical Apparatus Co., Ltd. JC 2000C1 contact angle meter (Shanghai China). The measurement was conducted in air with the accuracy of ±0.5° and each result presented here was an average of five tests. The XPS analysis was performed using a Thermo Fisher Scientific Inc. ESCALAB 250 (Waltham, Massachusetts USA) X-ray photoelectron spectroscopy