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Protection against corrosion of magnesium alloys with both conversion layer and sol–gel coating

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ABSTRACT

The anticorrosion performances of a system consisting of a phosphate based conversion layer and a hybrid sol–gel coating have been evaluated for the magnesium alloy Elektron21. The lone sol–gel coating affords a significant protection of the magnesium substrate. However, the presence of an intermediate conversion layer is presumed to improve the corrosion resistance of the system. The surface morphology of the protection coatings was characterized by optical microscopy, scanning electron microscopy (SEM) and white-light source interferometry. The corrosion behavior of the systems was analyzed by electrochemical impedance spectroscopy (EIS). The impedance measurements show that the presence of the added conversion layer increases the resistance of the whole system during immersion in a 0.05 M NaCl solution, compared to the single sol–gel coating.

1. Introduction

In the recent past decades, the interest for weight-saving materials has increased considerably in the automotive as well as in the aeronautics field. Structural components and some mechanical parts are often made with materials presenting a favorable strength-to-weight ratio, such as light metals and their alloys, which are widely used in industry. The constant challenge to improve the performances of vehicles led to search for multifunctional materials with improved properties. With a density equivalent to 2/3 of that of aluminum, magnesium is a good candidate due to the fact that it is the lightest structural metal used in industry.

However, compared to steel and aluminum alloys used as structural materials, magnesium alloys have a very low corrosion resistance [1]. In order to improve its resistance, magnesium is often alloyed with other elements such as Al, Zn, Zr, Y, and rare-earths [2–4]. Among the family of rare-earth magnesium alloys, the Elektron21 alloy (El21) has been developed to enhance the anticorrosion and mechanical properties of magnesium [5]. Nevertheless, this alloy still presents poor corrosion resistance in most of aggressive environments, especially after exposure to moisture, or saline environment.

A way to prevent corrosion is to cover the base material by a protective coating. A number of surface treatments and coating techniques have been proposed and developed for magnesium alloys, including electrochemical plating, conversion coatings, anodizing, hybrid coatings, organic coatings and vapor-phase coatings [6,7]. Industrial processes such as anodizing have already been developed in the last century, forming protective coatings with excellent protective properties for magnesium alloys. However, the production of these coatings which includes the utilization of hexavalent chromium (Cr VI) compounds which have been classified as carcinogen, mutagenic and reprotoxic, will be strictly forbidden in the next years. That is why it is urgent to find effective and ecological technological alternatives.

For all of these reasons, the development of protective coatings that replaces the chromium-based treatments is a real key issue. In the literature, new protective coatings are reported and particularly relative to the production of conversion films for magnesium alloys. These films are composed of insoluble and stable compounds that protect the metallic substrate from corrosive species. These conversion treatments generally include the use of phosphates [8–13], phosphate–permanganate [14,15], fluorides [16–23] and rare earths [24–26]. However, the protection afforded by many of these coatings is limited, and generally they are used as a support base for additional coatings, like paints or/and other organic coatings [27].

In this context, hybrid inorganic/organic films have been widely studied for corrosion protection of steels, aluminum alloys, and other metallic substrates, with excellent results [28–33]. The sol–gel route proves to be an efficient method to produce these ceramic/polymeric coatings. This chemical process consists on the hydrolysis and condensation of metallic alkoxides in aqueous solution, transformed into a solid polymerized network. The chemical reactions involved in this route are described elsewhere [34]. Polymerization and condensation reactions of the sol–gel coatings can be accelerated by applying a heat treatment, and generally this is a crucial step to obtain a fully condensed film. The temperature and time of the heat treatment depend on the kind of precursors and solvents used to produce the coating, but economically it is more interesting to work at lower temperatures and

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shorter times. Many works report the production of sol–gel coatings with low-temperature heat treatments [33,35–42].

In this work, the anticorrosion properties of a combined system, phosphate-based conversion film and a hybrid sol–gel coating, were studied in order to prevent the corrosion of a cast magnesium Elektron21 alloy. First, the general metallographic characteristics of this alloy were studied. Second, the morphology of the sol–gel coating, and the conversion layer, was separately investigated. Finally, the properties of the combined system of conversion layer and sol–gel coating were analyzed by electrochemical and physical–chemical techniques and results were discussed taking into account the requirements of such a system.

2. Experimental

2.1. Materials

The substrate used in this work was a cast Elektron21 magnesium alloy (composition on Table 1), provided by Fondérie Messier (France). After casting into ingots, the El21 alloy was machined to obtain samples with dimensions of 40 × 20 × 6 mm.

These metallic samples were initially degreased with acetone before polishing with a SiC paper up to grade #1200, and then rinsed with ethanol and dried with a stream of air. After polishing, the magnesium substrates were etched in 20 g L^{-1} of nitric acid (HNO_3), for 2 min at room temperature, rinsed with ethanol and dried with compressed air.

The conversion layer was then formed on etched substrates by immersion in phosphoric acid (H_3PO_4) at different concentrations, 0.5, 1, 3, 5 and 10 g L^{-1} for 2 min, at 25 °C, followed by rinsing with deionized water, ethanol, and finally air-drying at room temperature.

The sol–gel coating was produced by mixing starting precursors consisting of 3-glycidyloxypropyl-trimethoxysilane (GPTMS) and aluminum-tri-sec-butoxide (ASB), deionized water and propanol in a molar ratio of 2:1:1:10. The resulting mixture was stirred for 2 h and matured for 24 h at room temperature before application on the magnesium substrates. The pH of the sol was 4.1. The sol–gel films were obtained by dip-coating procedure, with controlled withdrawal speed of 200 $mm \cdot min^{-1}$, followed by drying at 50 °C for 2 h and curing at 110 °C for 3 h.

2.2. Characterization techniques

The morphology of the El21 substrate and coatings was analyzed by scanning electron microscopy (SEM) with a JEOL JSM-6510LV microscope, using an operating voltage of 20 kV. Optical microscopy images where obtained using a Keyence VHX-1000E microscope. The surface of the sol–gel coatings was sputter-coated with gold in order to allow their observation with the optical microscope, since these coatings are naturally transparent. The light-source of the microscope was switched to a "light-shift mode" to perform observations at different incidence angles. Electrochemical impedance spectroscopy and open circuit potential (OCP) were performed in 0.05 M NaCl at room temperature, using a Bio-Logic SP-150 potentiostat. The measurements were performed using a one-chamber three-electrode cell. The working electrode consisted of an exposed area of 2 cm^2. The reference and auxiliary electrode consisted on a saturated calomel electrode (SCE) and a platinum foil electrode, respectively. The EIS spectra were drawn using a potentiostatic mode in the frequency range from 65 kHz to 10 mHz, with an applied voltage of 10 mV vs. OCP. The surface roughness was evaluated by white-light source interferometry, using a Zygo-Instruments New View 100 apparatus. Three samples were analyzed on each characterization technique in order to check the reproducibility of the tests.

Table 1
Chemical composition of the cast Elektron21 magnesium alloy used in this work.

Elektron21						
Element	Nd	Gd	Zr	Zn	Other rare earths	Mg
Wt.%	3.1	1.7	1	0.5	<0.4	Balance

3. Results and discussion

3.1. Pretreatment of the magnesium El21 substrate

Polishing was applied in order to obtain a similar surface for all the samples, because after machining (as-received), their surfaces were completely different from one to each other. After polishing, the obtained average roughness (R_a) evaluated for all the samples was 0.13 μm.

In order to clean the surface, the substrate was etched with HNO_3 (Fig. 1a). After that, the microstructure of the alloy is revealed, which presents an average grain size of 80 ± 20 μm. However, the surface roughness (R_a) considerably increases (0.55 μm). Also, the presence of agglomerates (white) in relief at the surface may be seen.

The EDX analysis of this surface shows three main regions with different compositions, one corresponding to the grains of magnesium, the second to the grain boundaries of neodymium, and the third one to the agglomerates (or compounds) of zirconium. The alloying elements gadolinium and zinc are distributed homogeneously on the magnesium alloy. The cross-section image (Fig. 2) of the surface of El21 alloy after mechanical polishing and chemical etching shows the morphology of agglomerates rich on neodymium and zirconium.

3.2. Sol–gel coating without conversion film

First of all, during the preparation of sol–gel films by dip-coating, an active production of gas at the surface of the El21 alloy samples was observed, when they were immersed in the sol. This indicates that a chemical reaction took place between the magnesium alloy and the sol, reflecting the high degree of reactivity of this alloy.

The hybrid coatings are naturally transparent, and to perform the observation of the coating surface by optical microscopy, the coated samples were gold-coated. It is possible to observe that the coating presents a heterogeneous morphology, with several defects, with a size in the range of 30–100 μm (Fig. 3a). The light-source of the optical microscope consists on a ring that provides illumination of the sample. By switching between full-ring illumination and half-ring illumination, it is possible to observe the objective at different angles of reflection, since there is a change on the incidence angle of light. The images shown in Fig. 3a and b were taken at the same spot of the sample, and they correspond to the surface of the hybrid sol–gel coating and the El21 alloy surface, respectively. Fig. 3b clearly shows the magnesium grains, and the neodymium and zirconium compounds (black points, with light-gray surrounding area). Compared to Fig. 3a, it may be seen that the defects on the hybrid sol–gel coating are located at the same position of the neodymium and zirconium compounds of the El21 alloy. The white arrow on the image marks the location of a defect on the hybrid sol–gel film, which coincides with the location of the Nd grain boundary on the substrate. Other defects can be also identified on the sol–gel hybrid film, and their location coincides with the typical position of Zr or Nd compounds.

A SEM image of the sample shows the morphology of the surface of the hybrid sol–gel coating, where the presence of many nodules and pits at the surface can be identified (Fig. 4). The cross-section of the sample (Fig. 5) shows that the thickness of the coating is around 5 μm. A difference of thickness on the coating between the intragranular zone of magnesium and the compounds of the alloy may be seen. It may be seen that the neodymium compounds remain at the same level of the magnesium grains. However, the yellow square on the left image indicates the position of a protuberance that emerges