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Analytical characterisation and corrosion behaviour of bis-aminosilane coatings modified with carbon nanotubes activated with rare-earth salts applied on AZ31 Magnesium alloy

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ABSTRACT

The present work investigates the corrosion behaviour of AZ31 Magnesium alloy (Mg AZ31) substrates pre-treated with a water soluble bis-aminosilane modified with multiwall carbon nanotubes (CNTs). Prior addition to the silane solution, the CNTs were submitted to a treatment in an aqueous solution containing cerium nitrate or lanthanum nitrate. The chemical composition of the treated CNTs and of the modified silane coatings was assessed by X-ray Photoelectron spectroscopy (XPS). The thickness and the morphology of the silane coatings were investigated by scanning electron microscopy (FEG/SEM).

The pre-treatment of the Mg AZ31 was performed by dipping the metallic coupons in the silane solution modified with the CNTs. The electrochemical behaviour of the silane coated coupons was studied during immersion in 0.05 M NaCl solutions, using the scanning vibrating electrode technique.

The electrochemical investigation showed that the activation of the CNTs with the rare-earth salt delays the corrosion activity of the Mg AZ31 substrates. The analytical and microscopic study suggested that the CNTs are homogeneously dispersed in the silane coating and that the CNTs act as support for inhibitor storage.

1. Introduction

Carbon nanotubes (CNTs) are a very challenging material due to their fascinating mechanical and electrical properties. Their versatility makes them a material used in a wide array of applications. CNTs find applications in many different fields like electronics [1], gas sensors or biosensors [2], modification of biomaterials and fillers for polymers, ceramics or metal composites [3] among many others. Their unique properties, including the very high Young's modulus and tensile strength, make carbon nanotubes a suitable choice for the modification of ceramic and polymeric coatings as well as hybrid self-assembled films. The introduction of CNTs in these matrixes improves the mechanical performance, especially in applications submitted to high mechanical strength demand or exposed to aggressive environments [4].

Applications of CNTs in the field of corrosion protection are very scarce. The existing applications are very recent and most of them published in the last five years. CNTs can be used, for example, to prepare sensors for corrosion monitoring [5] or for modification of films or coatings. The modification of Ni–P matrix composite coatings with CNTs seems to result in superior corrosion resistance when the coatings are applied on iron substrates [6]. Zn–CNTs composite coatings revealed higher resistance to corrosion due to better barrier properties [7]. CNTs were successfully used to modify polypirrol coatings that can be used to protect metals against corrosion [8]. Nickel composite coatings containing carbon nanotubes showed increased corrosion resistance due to better barrier properties. Additionally, it seems that CNTs ennobled the corrosion potential, restricting localized corrosion [9]. At the present date no references could be found concerning the use of CNTs to improve the corrosion resistance of magnesium alloys, especially when combined with silane pre-treatments.

Literature reports that a stable chemical bond can be established between CNTs and silanes like amino silanes [10], 3-methacryloxypropyltrimethoxysilane [11] and 7-octenyltrichlorosilane [12]. Therefore, modification of silane coatings by addition of CNTs can be a suitable way to further improve the barrier properties of these coatings. Furthermore, CNTs can be used as support to fix metal oxides, like CeO_2 [13] or other molecules on their surface [14]. This means that they can be used as vehicles to store species with corrosion inhibition ability in the bulk of the silane coatings. This procedure combines several advantages since it improves the barrier properties of the silane coating, enhances their mechanical properties, making them able to support higher mechanical demands and, simultaneously, introduces corrosion inhibition ability. Such combination presents new potentialities and can be an innovative route to develop

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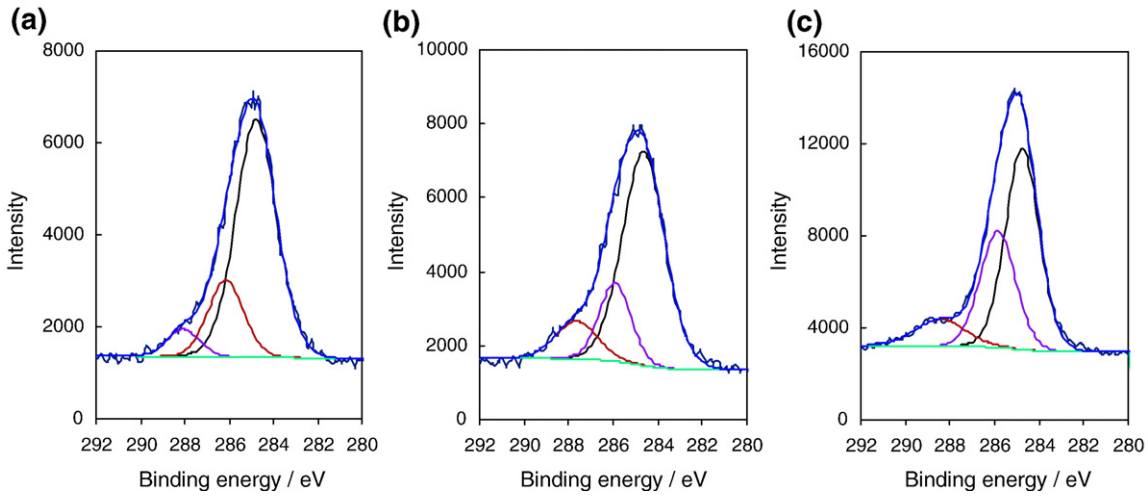

Fig. 1. XPS for the C1s ionisation. (a) Spectra obtained on the untreated CNT; (b) spectra obtained on the CNTs treated in cerium nitrate and (c) spectra obtained on the CNTs treated in lanthanum nitrate.

more effective pre-treatments for the corrosion protection of metallic substrates, like the Mg alloys. It's known that these alloys are highly susceptible to corrosion attack even in the presence of small concentrations of aggressive ions, but they can be effectively protected, for example, by pre-treatments based on rare-earth or silane formulations [15–17]. Silanes pre-treatments are very attractive because they lead to the formation of a functional barrier layer that protects the metallic substrate from corrosion and provides good adhesion properties for paint application [18–21]. Following our previous works [15–17], the present study reports a new approach and an innovative idea, in which the CNTs are treated in rare-earth solutions and then embedded in a silane film for improved corrosion resistance of the Mg AZ31. For such purpose CNTs were treated in solutions of $Ce(NO_3)_3$ or $La(NO_3)_3$ and then added to a water based bis-aminosilane (BAS) solution. The treated CNTs and the modified silane coatings were characterised by XPS and FEG/SEM. The analytical results revealed the presence of cerium and lanthanum species deposited on the surface of the CNTs. The SEM study revealed that the silane films formed on Mg AZ31 are relatively uniform and that the CNTs seem well embedded in the silane film. The electrochemical measurements showed that the corrosion processes were strongly inhibited for the substrates coated with the silane films modified with the rare-earth treated CNTs.

2. Experimental procedure

2.1. Metallic substrates

AZ31 Magnesium alloy with the nominal mass composition of 96% Mg, 3% Al and 1% Zn was obtained from *Goodfellow Metals* (UK). The coupons were polished with SiC paper up to grit 2400, ultrasonically degreased using acetone, washed with deionised water (Millipore) and dried in air.

The carbon nanotubes were obtained from *Sigma/Aldrich* and were activated in a mixture of concentrated HNO_3 and H_2SO_4 for 24 h to oxidise the surface. After this, the CNTs were submitted to a few cycles of filtering and washing for removal of acid as described elsewhere [22].

Two aqueous solutions of 10^{-3} M $Ce(NO_3)_3$ or 10^{-3} M $La(NO_3)_3$ were prepared. The CNTs were ultrasonically dispersed for 2 h in these solutions. After this the CNTs were filtered and dried at room temperature. These modified CNTs were then added to the silane solution.

The Bis-[triethoxy amino] silane (BAS) was obtained from *Sigma/Aldrich*. The silane solution was prepared by dissolving 5% (vol/vol) of silane in a mixture of methanol (10% vol/vol) and 85% (vol/vol) of distilled water. Silane solutions, with and without CNTs were stirred for 2 h. The pH of the silane solutions was adjusted to values around 7 using acetic acid.

For comparative purposes silane solutions, without CNTs but with addition of rare-earth in order to obtain a final concentration of 10^{-3} M $Ce(NO_3)_3$ or 10^{-3} M $La(NO_3)_3$ in the pre-treatment solution were also prepared.

The pre-treatment consisted in the immersion of the metallic coupons in the silane solution for 1 min. The excess of solution was removed by using air stream and the silane treated coupons were cured in a Memmert oven at 120 °C for 40 min.

2.2. Electrochemical measurements

The scanning vibrating electrode technique (SVET) measurements were performed using the *Applicable Electronics* equipment, con-

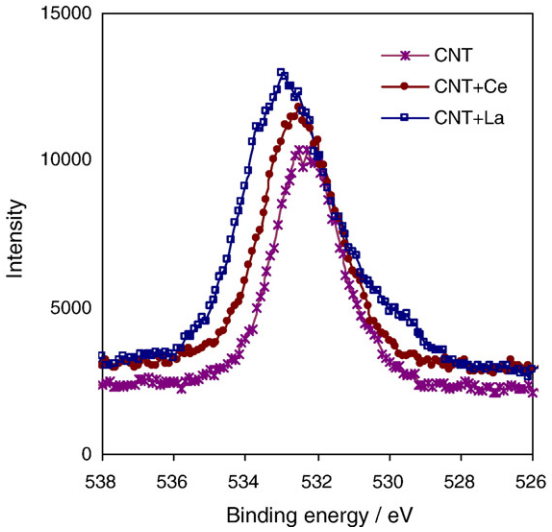

Fig. 2. XPS for the O1s ionisation. Spectra were obtained on the untreated CNT; on the CNTs treated in cerium nitrate and on the CNTs treated in lanthanum nitrate.