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Journal of Magnesium and Alloys 000 (2018) 1–10
www.elsevier.com/locate/jma

Full Length Article

Evaluation of self-healing properties of inhibitor loaded nanoclay-based anticorrosive coatings on magnesium alloy AZ91D

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Received 14 February 2018; accepted 9 May 2018
Available online xxx

Abstract

This study emphasizes on the evaluation and comparison of the anticorrosive properties of sol–gel coatings with and without inhibitor loaded nanocontainers. In this case, naturally available clay nanotubes (halloysite) were loaded with cationic corrosion inhibitors Ce^{3+}/Zr^{4+}. These nanocontainers were dispersed in hybrid organic–inorganic sol–gel matrix sol. Coating was applied on magnesium alloy AZ91D using the sols containing modified and unmodified nanocontainers employing the dip coating method and cured at 130 °C for 1 h in air. Corrosion resistance of coated/uncoated substrates were analyzed using electrochemical impedance spectroscopy, potentiodynamic polarization and weight loss measurements after exposure to 3.5 wt% NaCl solution for varying time durations between 24 h to 120 h. Self-healing ability of coatings was evaluated by micro-Raman spectroscopy after 120 h exposure to 3.5 wt% NaCl solution. Coatings generated after dispersion of corrosion inhibitor loaded clay in hybrid sol–gel matrix have shown more promising corrosion resistance when compared to just the sol–gel matrix coatings, after prolonged exposure to corrosive environment.

Keywords: Self-healing coating; Halloysite nanoclay; Cationic corrosion inhibitors; Magnesium alloy AZ91D; Micro-Raman spectroscopy; Corrosion protection.

1. Introduction

Magnesium alloys are characterized by their low density (65% that of aluminum and 25% that of iron) and high specific strength which make them valuable materials for components in automobile and aerospace applications [1,2]. However, when compared to other metals and alloys, corrosion resistance of magnesium alloys is inadequate due to their high-chemical reactivities (standard electrode potential: −2.37 V) and this limits the range of applications for magnesium and its alloys. The galvanic couples formed between secondary phases and the matrix, as well as the damage of the passive thin film of oxide are the main sources of localized corrosion in magnesium alloys [3,4]. Hence, it is necessary to develop appropriate coating compositions/configurations for the corrosion protection of magnesium alloys. The conventional coating techniques such as electrochemical plating, conversion coatings, anodizing, chemical vapor deposition, laser cladding, gas phase deposition and flame/plasma spraying, etc. have their own limitations such as poor adhesion, less wear resistance, difficult to obtain uniform and pore-free layer and environmental concerns [2].

Thin (0.1–10 µm) sol–gel coatings is an alternative, eco-friendly, attractive approach that has the potential to overcome the aforementioned limitations of other techniques. The thickness of coatings varies depend on the coating compositions. Sol–gel coatings exhibit a great potential to provide bar-

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https://doi.org/10.1016/j.jma.2018.05.003

Please cite this article as: S.H. Adsul et al., Evaluation of self-healing properties of inhibitor loaded nanoclay-based anticorrosive coatings on magnesium alloy AZ91D, Journal of Magnesium and Alloys (2018), https://doi.org/10.1016/j.jma.2018.05.003

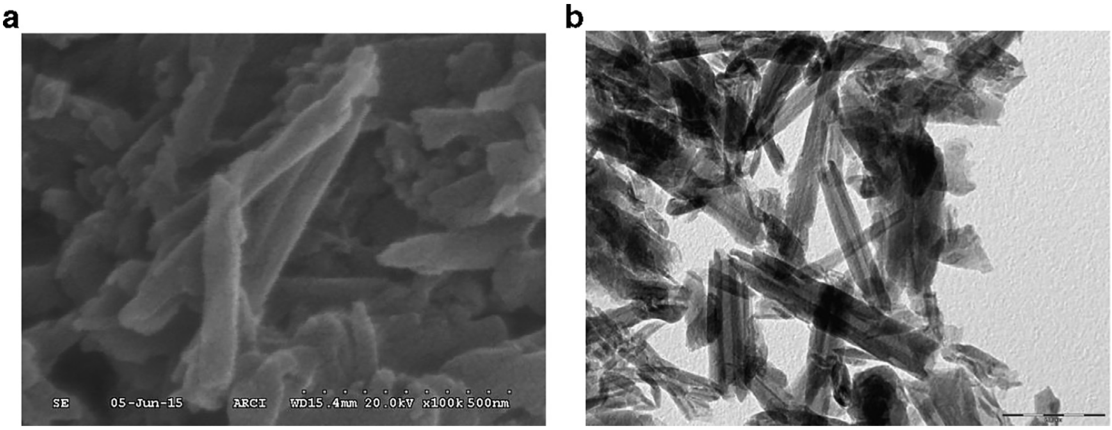

Fig. 1. (a) FESEM image and (b) TEM image, of as-received HNTs.

rier for corrosive environment and a good adhesion between metal substrate and organic top coat [5–7]. Hybrid organic–inorganic sol–gel coatings come with two advantages; firstly their ability to form crack-free thick coatings with low-curing temperature and secondly their flexibility to include additives for improving coating properties [8]. However, only hybrid coatings cannot give prolonged corrosion protection in case of any mechanical damage to the coated surface. Some researchers have used sol–gel method along with other conventional methods such as anodizing, conversion coatings, etc. and sol–gel coatings modified with doping agents, have achieved better corrosion protection for magnesium alloys [9–11]. Hu et al. [12] observed that molybdate conversion coating followed by multilayered silica sol–gel coating on AZ91D substrate gave better protection as compared to single layered porous molybdate conversion coating. Ecofriendly coatings of Mg(8-hydroxyquinoline)$_2$ synthesized by chemical conversion treatment in 8-hydroxyquinoline sodium solution at room temperature have shown prolonged corrosion protection to AZ91D substrates [13]. Composite coatings comprising of micro-arc oxidation (MAO) with titanium organic polymer as sealing agent were generated on AZ91D alloy. It showed that composite coating gave more effective corrosion resistance than only MAO coating, because of the latter having a porous structure [14].

Number of approaches have been implemented to attain effective corrosion protection on magnesium alloys [15,16]. However, prolonged corrosion protection requires sustained release of corrosion inhibiting additive materials, which can be achieved either by introducing corrosion inhibiting materials directly into the coating matrix or by encapsulating them into suitable micro/nanocontainers [17–20]. Previous studies [21,22] have shown that the use of rare earth elements like cerium as cationic corrosion inhibitors has been effective in improving the corrosion resistance. Use of micro/nanocontainers for encapsulating corrosion inhibiting materials is considered to be an effective way to provide sustained release of inhibitor to obtain self-healing ability in the coating. Naturally occurring halloysite nanoclay (HNT) has been considered as most promising way of encapsulating corrosion inhibiting materials. It comes with the advantages such as non-toxic, cheap, easily available and can accommodate large amount of inhibitors [23–26]. Previous studies [27] reveal that only benzotriazole was used as corrosion inhibitor loaded into halloysite nanotubes for corrosion protection of magnesium alloys. Joshi et al. [28] confirmed that corrosion inhibitor has got loaded inside the lumen of HNTs by applying vacuum evacuation. However, there are no reports on magnesium alloys with cationic corrosion inhibitors such as Ce^{3+} and Zr^{4+} loaded into nanocontainers other than our earlier work [29].

Hence, the main objective of present work was to study the effect of addition of halloysite clay nanotubes loaded with cationic corrosion inhibitors Ce^{3+} and Zr^{4+} into hybrid organic–inorganic matrix sol upon exposure to 3.5 wt% NaCl solution.

2. Materials and methods

2.1. Substrate

Magnesium alloy, AZ91D coupons of dimensions 2.5 cm × 2 cm and with chemical composition in wt% Al-9.14; Zn-0.86; Mn-0.30; Cu-0.09; Si-0.08; Fe-0.01; Ni-0.01 and rest Mg, were used as the substrates. All substrates were mechanically ground successively to 1000 grit with silicon carbide (SiC) papers followed by repeated degreasing with acetone for 30 min and were finally dried in air.

2.2. Sol synthesis and coating deposition

Halloysite nanotubes (HNTs) with lumen diameter of ∼10 nm were etched in 1 M H_2SO_4 (SD Fine Chemicals, India, 98%) for 3 days at 60 °C, followed by washing with deionized water and drying, in order to get enlarged lumen diameter [24]. Corrosion inhibitors, cerium nitrate hexahydrate (Loba Chemie, India, 99.9%) and zirconium n-propoxide (Gelest Inc., USA, 70% in propanol) were taken in molar ratio of 1:23, and added to the etched HNTs. The mixture was then dried in vacuum desiccator. The organic–inorganic

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