Corrosion Science 111 (2016) 753–769

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Self-healing plasma electrolytic oxidation coatings doped with benzotriazole loaded halloysite nanotubes on AM50 magnesium alloy

M. Sun [a], A. Yerokhin [b,c,*], M.Ya. Bychkova [c], D.V. Shtansky [c], E.A. Levashov [c], A. Matthews [b]

[a] University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, UK
[b] University of Manchester, Oxford Rd., Manchester, M13 9PL, UK
[c] National University of Science and Technology 'MISiS', Leninsky prospect 4, Moscow 119049, Russia

ARTICLE INFO

Article history:
Received 18 September 2015
Received in revised form 13 June 2016
Accepted 14 June 2016
Available online 15 June 2016

Keywords:
A. Magnesium
B. EIS
B. Polarisation
C. Oxide coatings
C. Atmospheric corrosion
C. Pitting corrosion

ABSTRACT

Halloysite nanotubes (HNT) and benzotriazole (BTA) loaded HNT were added to a silicate-based electrolyte to produce PEO coatings on AM50 alloy. The coatings were characterised by SEM, EDX and XRD methods. Corrosion behaviour in 3.5 wt.% NaCl was studied by EIS and PDP scans. The HNT increased coating scratch resistance greater than BTA-HNT, although the latter enhanced corrosion resistance due to a self-healing effect. This was triggered by a dense $Mg(OH)_2$ film being formed on corrosion sites following partial coating degradation, preventing pitting corrosion. The single-step process for producing self-healing PEO coatings has good potential in corrosion protection of Mg.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Owing to advantages, such as low density, high strength-to-weight ratio, good electric shielding, excellent damping capacity, good thermophysical properties and recyclability, magnesium and its alloys have long been regarded as materials of choice for many industrial applications [1–3]. The usage of Mg, as the lightest structural metal on earth, has significantly increased during the last decade because of increasing importance of weight saving in many products, especially related to aerospace, transportation and electronics [4]. However, the low corrosion resistance has significantly restricted further applications of magnesium alloys and effective methods are currently being sought to deal with those issues. To date, a great deal of research focusing on understanding corrosion behaviour and enhancement of corrosion protection of magnesium alloys has been carried out [5–19]. Among these studies, plasma electrolytic oxidation (PEO) coatings have attracted significant attention, because this environmental friendly surface treatment can provide relatively good protection for lightweight metals, such as aluminium, magnesium and titanium [17,18,20–24]. Recently, extensive studies have been carried out aimed at obtaining high-quality wear- and corrosion-resistant PEO coatings on components manufactured at a large scale [25,26]. Duplex and hybrid treatments have received significant attention to produce composite PEO coatings [6,27] that can provide synergistic effects leading to significant improvements in corrosion and wear resistance as well as the provision of additional functionalities to the surface. Despite these developments, PEO coatings still offer only passive corrosion protection, which relies mainly on their barrier properties. However, research on attaining these coatings with the function of active corrosion protection, *e.g.* by loading them with inhibitors, is in its infancy.

Inspired mainly by biological systems, in recent years, attempts have been made to develop smart self-healing materials that are able to repair themselves when damage occurs. Due to this special capability, self-healing materials can have a longer service life and a greater potential of overall life-cycle cost reduction, compared with conventional materials. There are various types of self-healing materials and some of them have already been practically applied [27–31]. Recently, several studies have been published on using halloysite nanotubes (HNT) as perspective nanocontainers for corrosion inhibitors to produce anticorrosive coatings with self-healing functionality [32–36]. HNT consist of a two-layered aluminosilicate structure and they can provide suitable containers for corrosion inhibitors and other active agents. Usually, the size of individual nanotube varies from 1 to 15 μm in length and about 10–100 nm inner diameter. A combination of the small particle size with thermal stability of aluminosilicate (which can poten-

* Corresponding author at: School of Materials, University of Manchester, Oxford Rd., Manchester, M13 9PL, UK.
E-mail address: Aleksey.Yerokhin@manchester.ac.uk (A. Yerokhin).

http://dx.doi.org/10.1016/j.corsci.2016.06.016
0010-938X/© 2016 Elsevier Ltd. All rights reserved.

tially withstand high instantaneous local temperatures developed at the sites of plasma discharges during the PEO process) makes it an attractive candidate to develop hybrid self-healing PEO coatings by incorporating in-situ inhibitor-loaded HNT in the surface layer, during a simple single-step treatment.

In this work, the application of the corrosion inhibitor benzotriazole (BTA) loaded into HNT containers is considered in order to obtain the self-healing functionality in PEO coatings thus improving the corrosion protection of AM50 Mg alloy. Fabrication, characterisation and comparative evaluation of the three groups of PEO coatings—pristine (PEO), HNT-doped (HNT-PEO) and BTA-loaded-HNT-doped (BTA-HNT-PEO), are studied and discussed.

2. Experimental procedures

2.1. Preparation of inhibitor loaded halloysite nanotubes

The HNT and BTA precursors (Fig. 1a) were acquired from Sigma-Aldrich, UK. Before the PEO treatment, the BTA loaded HNT were prepared using a procedure similar to that described elsewhere [37]. To perform the loading, 20 g HNT powder was mixed with 250 mL BTA aqueous solution (10 g/L). The mixed suspension containing BTA and HNT was evacuated in a vacuum jar to remove air from the hollow core of the HNT. After that, the HTN were extracted from the BTA solution by centrifuging, washed in distilled water and dried in air for 48 h. This procedure was deemed to allow efficient BTA loading and subsequent energy dispersive X-ray (EDX) analysis (Fig. 1b) revealed increased peaks of carbon and oxygen, indicating BTA presence in the nanotubes. However, nitrogen was below the sensitivity limit, possibly due to a combination of several factors, including low BTA solubility in water and shielding by higher-Z elements, such as Al and Si, contained in the HNT. Additional verification was therefore performed using HNT loaded with 80 g/L acetone solution of BTA, which confirmed the presence of an N peak in the EDX spectrum (Fig. 1c).

2.2. PEO coating preparation

AM50 magnesium alloy samples of dimensions 25 mm × 35 mm × 2.5 mm were cut off from bulk material and ground with up to 1200 grit SiC paper, ultrasonically degreased in acetone for 5 min and then cleaned using distilled water. The treatments were carried out for 10 min in a 2-L stainless steel container equipped with stirring and cooling systems, which also served as the counter-electrode. Electrolytes used were aqueous alkaline silicate-fluoride solutions composed of (g/L): 12 – Na_2SiO_3, 2 – KOH, and 4 – NaF, with 10 g/L additions of either HNT or BTA-loaded HNT prepared as described in Section 2.1. The electrolyte temperature was kept below 30 °C in order to avoid possible adverse effects on the PEO process and resulting coatings. Polarisation was provided by a 30-kW MDX II DC power supply (Advanced Energy Industries, Inc.) together with a SPIK2000A pulse unit (Melek GmbH). A pulsed unipolar current mode (Fig. 2) with frequency (f) of 100 Hz, duty cycle (δ) of 10% and the mean average current density of 40 mA/cm^2 was applied. The frequency f and duty cycle δ can be described as follows:

$$f = \frac{1}{(t_{on} + t_{off})} \quad (1)$$

$$\delta = \frac{t_{on}}{t_{on} + t_{off}} \times 100\% \quad (2)$$

After the PEO treatment, the samples were ultrasonically cleaned in acetone and rinsed using distilled water, then dried in air.

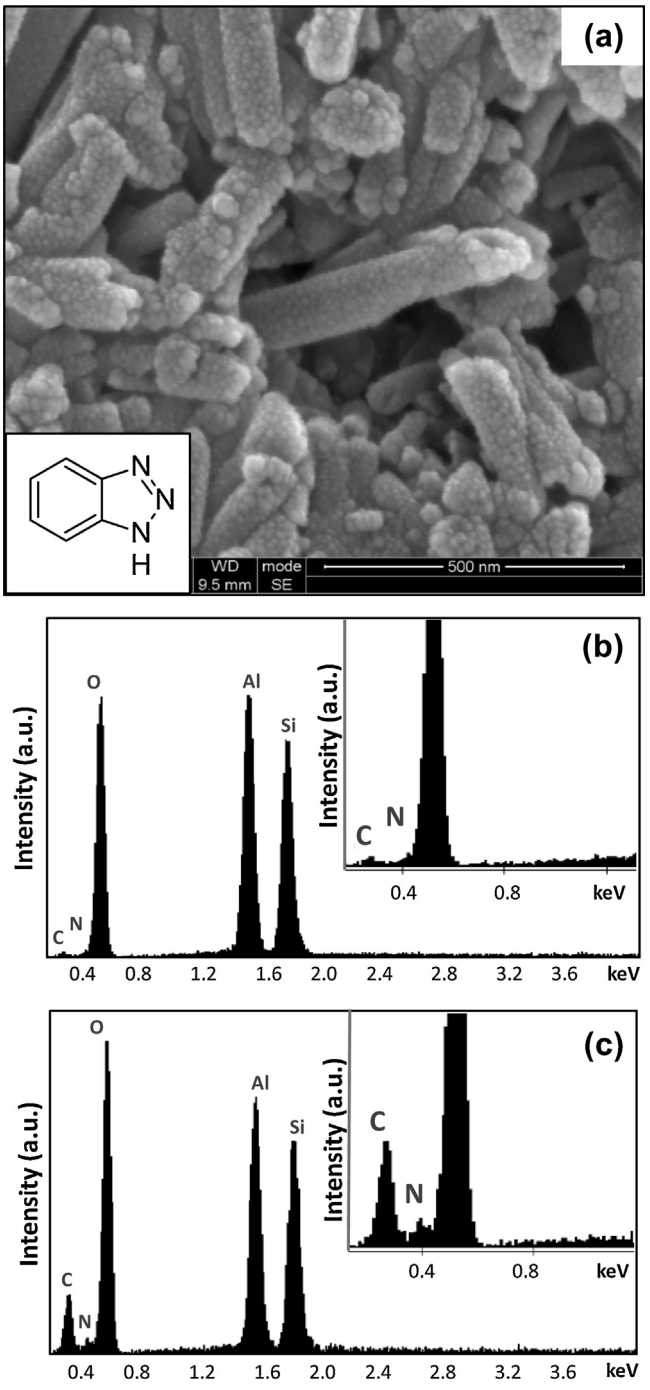

Fig. 1. Typical appearance of halloysite nanotubes used in this study (a); the inset shows chemical structure of 1,2,3-Benzotriazole loaded in the nanotubes. EDX spectra of BTA-HNT prepared in solutions: (b) 10 g/L BTA in water and (c) 80 g/L BTA in acetone.

2.3. Characterisation of PEO coatings

The coating thickness was measured using an Elcometer 355 eddy current thickness gauge equipped with a standard No. 4 anodisers probe. Ten measurements were made on each side of the sample to obtain statistically significant data sets, from which the mean average thickness values and the measurement errors were determined, the latter taking into account both the standard deviation between the readings in the set and the instrumental error.

Download English Version:

https://daneshyari.com/en/article/1468342

Download Persian Version:

https://daneshyari.com/article/1468342

Daneshyari.com