Materials Research Bulletin 47 (2012) 3170–3176

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Effect of cerium on structure modifications of a hybrid sol–gel coating, its mechanical properties and anti-corrosion behavior

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ARTICLE INFO

Article history:
Received 16 May 2012
Received in revised form 26 June 2012
Accepted 10 August 2012
Available online 18 August 2012

Keywords:
A. Hydrides
B. Sol–gel chemistry
C. Nuclear magnetic resonance (NMR)
D. Impedance spectroscopy
E. Electrochemical properties
F. Mechanical properties

ABSTRACT

An organic–inorganic hybrid coating was developed to improve the corrosion resistance of the aluminum alloy AA 2024-T3. Organic and inorganic coatings derived from glycidoxypropyl-trimethoxysilane (GPTMS) and aluminum *tri-sec*-butoxide $Al(O^sBu)_3$, with different cerium contents, were deposited onto aluminum by dip-coating process. Corrosion resistance and mechanical properties were investigated by electrochemical impedance measurements and nano-indentation respectively. An optimal cerium concentration of 0.01 M was evidenced. To correlate and explain the hybrid coating performances in relation to the cerium content, NMR experiments were performed. It has been shown that when the cerium concentration in the hybrid is higher than 0.01 M there are important modifications in the hybrid structure that account for the mechanical properties and anti-corrosion behavior of the sol–gel coating.

1. Introduction

Aluminum alloys, especially AA 2024-T3, are characterized by high mechanical strength and relative low weight, providing suitable properties for the aircraft industry [1]. However, the presence of intermetallic compounds, which can act either as anodic or cathodic regions, makes aluminum alloys more sensitive to localized corrosion after exposure in aggressive environments [2,3]. Historically, chromate conversion coatings were used to prevent corrosion of aluminum alloys. But the presence of toxic hexavalent chromium compounds makes those coatings very hazardous to the environment. Consequently, it is necessary to develop new environmentally compliant chromate (VI)-free alternatives. A new promising approach consists to use sol–gel process to prepare hybrid protective coatings [4,5]; thus, sol–gel films were highly investigated from the last decade as possible candidates for environmentally friendly treatments on metals [5–8].

Sol–gel route consists in both hydrolysis and condensation of metal alkoxides, contained in a liquid solution, called sol, to obtain metaloxane network [8–10]. The progress of condensation reactions finally leads to the formation of a dense hybrid network. Commonly, sol–gel processes involve silane precursors as starting materials. Silane based coatings usually exhibit good barrier properties due to the development of a dense –Si–O–Si– network [11–15], which inhibits the penetration of aggressive species towards the metallic substrate. Thus, the efficiency of the metal surface pre-treatments based on silane coatings is strongly dependent on the barrier properties of the film [16,17]. However, when a defect is formed in the barrier layer, the coating is not able to stop the localized corrosion process. Thus, the presence of inhibitor species is essential to decrease or to avoid corrosion activity in these cases [18]. Recently, different inhibitors have been studied to prevent corrosion of metal surfaces. Cerium compounds appeared, through lot of works, as a promising corrosion inhibitor to replace chromate compounds for the corrosion protection of various metallic compounds, especially aluminum alloys [19–24].

The aim of this paper consists, first, in the characterization of both microstructure and barrier effect of an alumino-silane hybrid sol–gel coating. Then cerium nitrate has been introduced into the hybrid sol–gel layer in order to improve the corrosion protection. The cerium nitrate was added at different ratios in the sol to understand the possible interactions of the inhibitor with components of the sol–gel system. Anti-corrosion protection and mechanical properties of alumino-silane hybrid coating containing different cerium contents were evaluated, depending on cerium content, by electrochemical analyses (EIS) and nano-indentation. Finally, ^{29}Si, ^{13}C and ^{27}Al RMN analyzes were

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http://dx.doi.org/10.1016/j.materresbull.2012.08.034

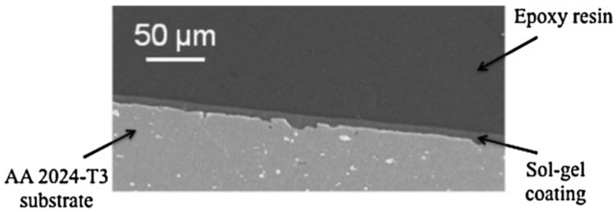

Fig. 1. Micrograph of a sol–gel film deposited on AA 2024-T3 using a cross-section view.

performed in order to understand how cerium interacts with the other components and how it integrates the hybrid network.

2. Experimental

The composition of the AA 2024-T3 aluminum alloy is described in Table 1.

Each sample surface (80 mm × 42 mm × 1 mm) was first cleaned and degreased in acetone. Then, a chemical pretreatment is needed before sol deposition in order to improve hybrid coating adhesion. It was performed as follows: an immersion in a NaOH bath maintained at 60 °C, followed by rinsing with deionized water; a neutralization in an acidified solution of $NaNO_3$, at room temperature. The samples were finally washed in ethanol and dried in air.Sols were prepared by mixing glycidoxypropyl-trimethoxysilane (GPTMS) (Fig. 1) and aluminum *tri-sec*-butoxide $Al(O^sBu)_3$ (Fig. 2) with distilled water and propanol in molar ratio 5:1:10:12. Then $Ce(NO_3)_3{\cdot}6H_2O$ was added to investigate the cerium range: 0–0.1 M. Then, the obtained sol was stirred during 2 hours at room temperature and aged for 24 hours before deposition on the substrate.Sol–gel films were obtained by dip-coating process, using an immersion step followed by a withdrawal at a controlled rate of 20 cm min^{-1}. After deposition, coated samples were dried at 110 °C during 24 hours.

The microstructures of the coatings were observed by scanning electron microscopy (SEM) on a JEOL JSM-6060 device.

The electrochemical behavior of the systems was evaluated by electrochemical impedance spectroscopy (EIS) in a 0.05 M NaCl static solution (pH = 6.0). For the electrochemical measurements, a three-electrode electrochemical cell was used, consisting of a platinum counter electrode, a saturated calomel reference electrode and the sample was used as a working electrode, with an exposed area equal to 15 cm^2. The experimental apparatus used for the electrochemical investigation was a potentiostat (AUTOLAB PGSTAT 30) and a frequency response analyzer (FRA). EIS measurements were performed in potentiostatic mode at the OCP, obtained after a 1 hour stabilization of the potential in the electrolyte. The amplitude of the EIS perturbation signal was 10 mV, and the frequency studied ranged from 100 kHz to 10 mHz.

The mechanical properties of the films were conducted using a UltraNanoHardness Tester machine from CSMb Instruments (Switzerland). Young's modulus E and nano-hardness H of each film were measured with a Berkovich three-sided pyramid diamond indenter. The Poisson ratio of the hybrid coatings was taken at a value of $\upsilon = 0.3$. Experiments were performed in a laboratory air environment at ambient temperature. In all CSM nano-indentation tests, a total of five indents were averaged to determine the mean Young's modulus and nano-hardness, E and H values for statistical purposes. The calibration and analysis procedure suggested by Oliver and Pharr [25] was used to correct for the load-frame compliance of the apparatus and the imperfect shape of the indenter tip and to determine hardness and elastic modulus. The area function $A(hc)$ was calibrated on fused silica and relates the contact area to the contact depth hc. Data of hardness and elastic modulus of various films [26] and coating deposited using the sol–gel route [27] from experimental data using this technique can be found in the literature. The maximal normal force was 100 μN, the loading rate is 1 μN s^{-1} and the penetration depth was kept under 100 nm in order to avoid substrate influence.

Table 1
Chemical composition of the AA 2024-T3 aluminum alloy.

	Element							
	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
wt%	0.06–0.09	0.14–0.16	4.1–4.6	0.49–0.57	1.37–1.40	0.15	0.02	Balance

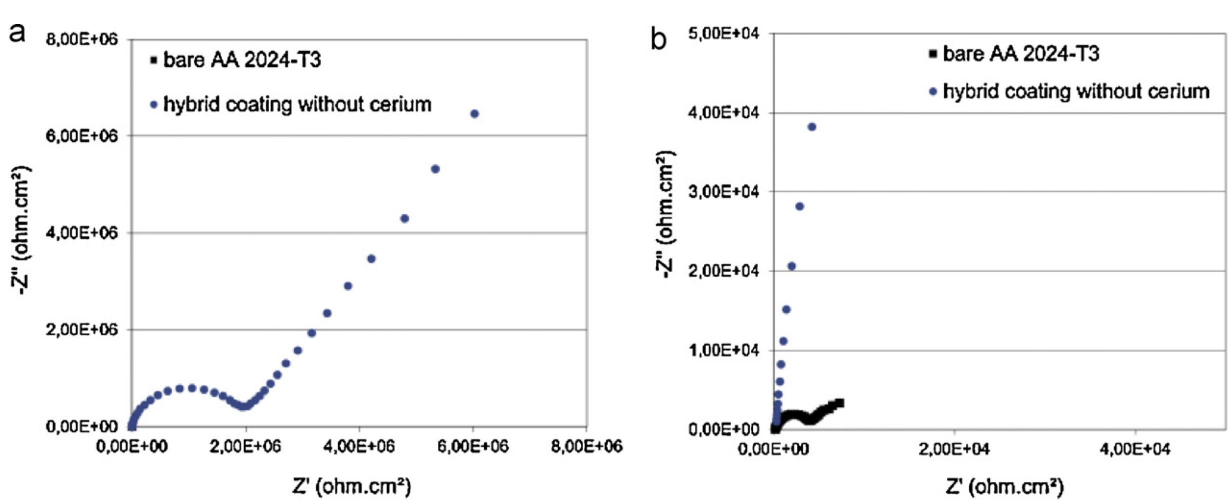

Fig. 2. Nyquist diagrams obtained after 1 hour in a 0.05 M NaCl solution, for uncoated and coated 2024-T3 aluminum alloy.