Journal of Alloys and Compounds xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Optimal conditions for the deposition of novel anticorrosive coatings by RF magnetron sputtering for aluminum alloy AA6082

S.B. Brachetti-Sibaja [a,b], M.A. Domínguez-Crespo [c,*], S.E. Rodil [d], A.M. Torres-Huerta [c]

[a] *Instituto Politécnico Nacional, Postgraduate Student of CICATA-Unidad Altamira, Mexico*
[b] *Instituto Tecnológico de Cd. Madero, Cd. Madero, Tamaulipas, Mexico*
[c] *CICATA-Altamira, Instituto Politécnico Nacional, IPN Km 14.5 Carretera Tampico-Puerto Industrial Altamira, C.P. 89600 Altamira, Tamaulipas, Mexico*
[d] *Universidad Nacional Autónoma de México, IIM, D.F., Mexico*

A R T I C L E I N F O

Article history:
Available online xxxx

Keywords:
RF magnetron sputtering
AA6082 aluminum alloy
Rare earths
Coatings
Corrosion resistance

A B S T R A C T

Cerium and lanthanum coatings were deposited on glass, silicon (100), and aluminum alloy by RF magnetron sputtering in which several experimental conditions such as power, substrate temperature, and deposition time were varied, using pure CeO_2 and La_2O_3 targets. The effect of deposition parameters on the bonding structure, surface morphology and properties against corrosion of rare earth (RE) coatings formed on metallic substrate was reported. The microstructure and chemistry of the thin film were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and X-ray photoelectron spectroscopy (XPS); whereas their use as corrosion resistant coatings was studied in aqueous NaCl solution (3.0 wt%) by using polarization curves. Variations in these properties were observed by increasing the substrate temperature which modifies the crystallinity of the rare earth coatings. XRD and XPS findings indicate that the cerium coatings are composed by CeO_2 and a significant quantity of Ce_2O_3 due to oxygen deficiency in the sputtering chamber, whereas $La_2O_3/La(OH)_3$ and some La intermetallic compounds are detected in the lanthanum films. Variations in the E_{corr} and I_{corr} were found as a function of the thickness, texture, and morphology of the as-prepared coatings.

1. Introduction

The corrosion of metallic structures has a significant impact on the economies of countries. Hence, a big effort is made every year to overcome its effects. Most high strength aluminum alloys used in aircraft and machining industries are susceptible to pitting corrosion [1], inter-granular corrosion [2], and stress corrosion cracking [3]. For decades, the corrosion protection of aluminum alloys relied on highly effective hexavalent chromium compounds to form conversion coatings [4] or corrosion inhibitor pigments in epoxy primer coatings [5]. However, the high toxicity of these chromium compounds has limited their use [6]. Coatings containing rare earth (RE) ions, such as cerium or lanthanum [7], constitute an interesting alternative to eliminate traditional chromium compounds because of their good self-healing properties and low environmental impact [8]. However, some limitations of RE coatings obtained by conventional methods are: (i) the precipitation of an insoluble protective Ce oxide/hydroxide layer that produces coatings with irregular characteristics; (ii) the presence of cracks that can penetrate the entire cross-section of the layer. These cracks represent preferential pathways to attack the substrate by aggressive corrosive species. For this reason, the development of new environmentally friendly protective coatings to enhance the anticorrosive properties of materials is of great research interest. Using physical vapour deposition processes, simple coatings that consist of only one phase, or of multiple layers, and coatings with a gradient composition within the layer [9], can be deposited at sufficiently low substrate temperatures [10]. To our knowledge, there are few reports of the use of sputtered Ce and La oxide coatings to protect aluminum alloys against corrosion.

The results reported in this paper are a consequence of research sponsored by the National Council of Science and Technology of Mexico (CONACYT) to study the anticorrosive properties of sputtered rare earth coatings and to develop new alternatives to improve the corrosion resistance of aluminum alloys. Specifically, this study aims to investigate the effect of sputtering power, substrate temperature and deposition time on the bonding structure, surface morphology and corrosion resistance of deposited CeO_2 and La_2O_3 films formed on AA6082 aluminum alloy using a RF magnetron sputtering.

* Corresponding author.
E-mail address: mdominguezc@ipn.mx (M.A. Domínguez-Crespo).

http://dx.doi.org/10.1016/j.jallcom.2014.01.195
0925-8388/© 2014 Published by Elsevier B.V.

2. Experimental procedure

Aluminum alloy 6082 plates with a thickness of 10 mm, were cut into 2×2 and $1 \times 1\ cm^2$ pieces and used as substrates. Prior to deposition, the substrates were finely abraded using 1000, 1500, and 2000 grade SiC paper, cleaned by rinsing with deionized water, and finally, by sonication in isopropyl alcohol and deionized water for 20 min, respectively.

The rare earth oxides films were deposited using an RF magnetron sputtering system built in our laboratory. CeO_2 and La_2O_3 targets (99.99% purity, 2″ in diameter with copper bonding, Plasmaterials) were used in an Ar atmosphere of ultra-high purity with a gas flow of 30 sccm. The equipment has an automated gas flow system that keeps the deposition pressure constant. The chamber pressure was 20 m Torr (266.45 m Pa) and the substrate to target distance was 6 cm. Two RF sputtering power were used, 60 and 90 W (P). The rare earth coatings were deposited at each power using two different substrate temperatures (*T*, 80 and 200 °C) and three different deposition times (*t*, 25, 40, and 60 min). The coatings were simultaneously deposited onto glass and silicon (1 0 0) substrates, which were chosen for analytical purposes.

The phase composition and crystal structure of as-synthesized films were determined by powder X-ray diffraction using an Advanced Bruker D8 diffractometer, with Cu Kα radiation at 35 kV, 25 mA, and a scan rate of 0.021 min^{-1}. Film morphology was examined by scanning electron microscopy using a JEOL JSM 7600F. Thickness of films deposited on silicon (1 0 0) substrates were examined by Spectroscopic Ellipsometry (SE, at a 70° angle of incidence) using a HORIBA JOBIN–YVON UVISEL ellipsometer. The chemical compositions of the films were characterized by X-ray Photoelectron Spectroscopy (XPS) using a commercial XPS VG Microtech Multilab ESCA 2000 with a CLAM MCD detector, Al Kα radiation ($h\upsilon$ = 1453.6 eV), operating at 8E−7 Pa, using a 500 μm spatial resolution and 50 and 20 eV pass energy for the acquisition of the survey and high resolution spectra, respectively. Curve fitting of high resolution XPS spectra acquired in the regions of the C 1s and O 1s and the La 3d and Ce 3d photoelectron peaks, respectively, for the different metal oxide films, was performed with the SDPv4.1 software® to obtain the elemental composition. The topography and roughness were analyzed and measured by an AFM, Veeco, Model diMultiMode V, controller diNanoScope V, with cantilever RTESP tips.

The corrosion behaviour of coated and uncoated aluminum alloy was determined by polarization resistance (Rp) and potentiodynamic polarization measurements. A potentiostat/galvanostat (Gamry 600 series) was used with a conventional experimental set-up of a three-electrode cell. A graphite bar (counter electrode) and a saturated calomel electrode (SCE, reference electrode) were employed to perform the corrosion experiments. The working electrode had an exposed area of 0.126 cm^2 and 3.0 wt% NaCl solutions was chosen as the corrosive medium, because the chloride ion is present in many corrosive environments. At least three replications were used for every corrosion-rate measurement. Polarization resistance (Rp) plots were conducted from 20 mV cathodic to 20 mV anodic of corrosion potential at a 0.5 mV s^{-1} sweep rate. Rp is defined as the slope at zero current on the potential versus current graph obtained from the experiment. To evaluate the susceptibility of the surface of the samples to pitting corrosion and to obtain information about the corrosion rate and corrosion potential, potentiodynamic polarization curves were scanned. These curves were measured from cathodic to anodic areas from −500 mV vs. SCE (E_{ocp}) to 1000 mV at a sweep rate of 0.5 mV s^{-1}.

3. Results and discussion

3.1. Influence of process parameters on coatings (sputtering power, substrate temperature, and deposition time)

Coating technology has evolved and developed in the last decades in different industries, using a wide range of preparation methods. Techniques such as evaporation, plating, dipping, chemical vapour deposition and spraying have been commonly used to growth thin films on different substrates however, they are somewhat limited to the melting temperature materials, and some of them are restricted only to metallic coatings. By contrast, the sputtering process has different advantages such as: deposition ranges from 1 nm s^{-1} to 10 nm s^{-1}, coating uniformity in the range of few percentage even for several meters long cathodes, deposition of large variety of film materials (nearly all metals and compounds) and easy to scale up, among others. In summary, the industrial use of this technique has let the economic manufacturing of innovative products [11]. In this manner, the major steps of the coating process can be divided in pre-treatment of the alloy surfaces prior to coating, establishing of coating deposition parameters and treatment of the coated surfaces after deposition [12].

Thus, to evaluate the protection against corrosion provided by the sputtered CeO_2 and La_2O_3 thin films, different experiments were carried out varying power, substrate temperature, and deposition time. Consequently, the diverse experiments are discussed in terms of the effect that the operating conditions have on the morphology, thickness, and/or electrochemical behaviour of the CeO_2 and La_2O_3 coatings deposited by RF magnetron sputtering on the AA6082 aluminum alloy.

The deposition parameters used to obtain the CeO_2 and La_2O_3 layers producing different roughness and thicknesses are listed in Table 1. As expected, it was observed an increase in the deposition rate, as the power increased from 60 W to 90 W, although a slight drop in the deposition rate can be seen with the substrate temperature. In addition, for fixed power and substrate temperature, the deposition time had an adverse effect on the thickness of both rare earth coatings.

AFM observations of the different samples were carried out, with the aim of comparing their surface roughness. From Table 1 and considering the mean roughness value of bare substrate (~81 nm), it can be observed that the mean roughness also decreased with the substrate temperature, fixed power and deposition time. An explanation for the variation in both the deposition rate and mean film roughness is not clear. Perhaps, this effect could be due to re-sputtering of the films, either by a physical process or a chemical reaction. Target poisoning is another alternative, although the atmosphere was not reactive and the targets were oxides. Moreover, no drastic variations in the voltage–current characteristics were observed. Gas rarefication due to a higher amount of reactive Ce and La atoms in the gas may be another contributor. This issue requires further experiments, which are beyond the objective of this paper.

3.2. Microstructural analysis

X-ray diffraction analysis was used to identify the phases of the rare earth coatings that were formed under the different experimental conditions described in this work. Figs. 1 and 2 show the XRD patterns for the uncoated and the CeO_2- and La_2O_3-coated

Table 1
Deposition parameters and correlation between the thickness and mean roughness.

Experiment	Thickness (nm)	Deposition rate (nm s^{-1})	Mean roughness (nm)
CeO_2			
$P_{60}T_{80}t_{25}$	19.29	0.012	103.51
$P_{60}T_{200}t_{25}$	12.73	8.4E−3	66.73
$P_{60}T_{80}t_{40}$	30.84	0.012	69.35
$P_{60}T_{200}t_{40}$	22.95	9.5E−3	50.52
$P_{60}T_{80}t_{60}$	32.38	8.9E−3	62.48
$P_{60}T_{200}t_{60}$	40.08	0.011	44.82
$P_{90}T_{80}t_{25}$	44.61	0.029	218.18
$P_{90}T_{200}t_{25}$	42.22	0.028	91.74
$P_{90}T_{80}t_{40}$	52.86	0.022	84.48
$P_{90}T_{200}t_{40}$	46.06	0.019	76.33
$P_{90}T_{80}t_{60}$	149.10	0.041	132.98
$P_{90}T_{200}t_{60}$	157.91	0.043	120.25
La_2O_3			
$P_{60}T_{80}t_{25}$	269.45	0.180	114.61
$P_{60}T_{200}t_{25}$	354.26	0.236	96.54
$P_{60}T_{80}t_{40}$	337.55	0.140	161.26
$P_{60}T_{200}t_{40}$	310.14	0.129	130.43
$P_{60}T_{80}t_{60}$	390.22	0.108	158.10
$P_{60}T_{200}t_{60}$	349.12	0.097	123.47
$P_{90}T_{80}t_{25}$	528.47	0.352	153.38
$P_{90}T_{200}t_{25}$	498.94	0.332	172.80
$P_{90}T_{80}t_{40}$	545.20	0.227	195.08
$P_{90}T_{200}t_{40}$	670.75	0.279	157.63
$P_{90}T_{80}t_{60}$	750.57	0.208	150.47
$P_{90}T_{200}t_{60}$	835.54	0.232	280.32