Thin Solid Films 590 (2015) 33–39

Contents lists available at ScienceDirect

Thin Solid Films

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

Electrophoretic deposition of hybrid coatings on aluminum alloy by combining 3-aminopropyltrimethoxysilan to silicon–zirconium sol solutions for corrosion protection

Mei Yu, Bing Xue, Jianhua Liu [*], Songmei Li, You Zhang

School of Materials Science and Engineering, Beihang University, Beijing 100191, China

ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form 21 July 2015
Accepted 22 July 2015
Available online 26 July 2015

Keywords:
Aluminum alloy
Organic–inorganic coatings
Scanning Electron Microscopy
Electrochemical Impedance Spectroscopy
Electrophoretic deposition

ABSTRACT

Electrophoretic deposition (EPD) silicon–zirconium organic–inorganic hybrid coatings were applied on LC4 aluminum alloy for corrosion protection. 3-Glycidoxypropyl-trimethoxysilane (GTMS) and Zirconium (IV) n-propoxide (TPOZ) were used as precursors. 3-Aminopropyl-trimethoxysilane (APS) was added to enhance the corrosion protective performance of the coatings. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize morphology, microstructure and component. The results show that the addition of APS leads to the enhanced migration and deposition of positively charged colloidal particles on the surface of metal substrate, which results in the thickness increasing of coatings. However, loading an excessive amount of APS gives a heterogeneous coating surface. The corrosion protective performance of coatings were measured by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The results indicate that the addition of APS improves corrosion protective performance of coatings. The optimal addition content of APS is about 15%. The 15% APS coating is uniform and dense, as well as has good corrosion protective performance. The impedance value ($1.58 \times 10^5\ \Omega\cdot\text{cm}^2$, at the lowest frequency) of 15% APS coating is half order of magnitude higher than that of coating without APS, and 15% APS coating always keeps the best corrosion protective performance with prolonged immersion time. This kind of coating is identified with "double-structure" properties based on the analysis of EIS and potentiodynamic polarization. Furthermore, the equivalent circuit results indicate that the intermediate oxide layer plays a main role in corrosion protection.

1. Introduction

Chromate conversion coatings have been widely used for aluminum alloy protection [1,2]. However, the high hazard to human health and environment has limited the applications of chromate conversion coatings containing Cr (VI) species in industry [3–6]. Therefore, Cr(VI)-free surface treatment methods have been intensively investigated [7,8]. Silicon–zirconium (Si–Zr) organic–inorganic hybrid coatings have attracted much attention due to their remarkable properties [9]. The coatings have the advantage of both mechanical properties of inorganic networks and chemical characteristics of organic components, and have become one of the most promising environmentally friendly substitutes for chromate conversion coatings [10–13]. Inorganic networks in Si–Zr organic–inorganic hybrid coatings could enhance the thermal stability of the coatings and the adhesion to metallic matrix, as well as confer mechanical properties. Organic components in the coatings provide high flexibility and low porosity, avoiding the appearance of coating defects in the drying stage [14]. Moreover, organic and inorganic groups in the coatings are linked by stable chemical bonds, and no significant phase interfaces exist. These contribute to the stable structure of the coatings [4].

Many methods, such as dipping [11], spinning [15], spraying [16], and electrophoretic deposition (EPD) [17] were employed to prepared organic–inorganic hybrid coatings. Among these methods, EPD attracts many attentions since the coatings fabricated by EPD had the properties of uniform thickness, strong adhesion, none porous structure and good corrosion resistance, etc. [18,19]. Mandler's group [20,21] and van Ooij's group [22] found that coatings prepared at a defined cathodic potential by EPD method presented better corrosion resistance than those prepared by traditional dip-coating methods. Collinson [22] and Woo [23] et al. controlled the uniformity and orientation of coatings by cathode EPD method. The results indicated that the structure of EPD coating differed from those of coatings prepared by traditional method. The EPD coating thickness was controllable and the interfacial bonding strength was significantly improved.

The morphology, structure and corrosion protective performance of coatings can be optimized by controlling the zeta potential of colloidal particles in the EPD method [24]. High zeta potential at an appropriate pH value benefits the quality of coatings [25]. As a saline coupling agent with an amino-group, 3-aminopropyl-trimethoxysilane (APS) is a kind of non-ionic surface active agents. It can catalyze the ring-

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[*] Corresponding author.
E-mail address: yumei@buaa.edu.cn (J. Liu).

http://dx.doi.org/10.1016/j.tsf.2015.07.055
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Table 1
Evolution of coating thickness and zeta potentials of colloidal particles in sols with different APS contents.

APS (%)	0%	10%	15%	20%
Thickness of coatings (μm)	1.7	3.2	4.4	4.8
Zeta potential (mV)	+4.2	+9.9	+18.6	+34.6

opening reaction of epoxide group to form polymer networks with complex structure and high density [26]. In addition, APS, as positively charged colloidal particles in sol solution after hydrolyze reaction, can be used as additives to change the zeta potential of colloidal particles in sol solution. As a result, it is of interest to study the effect of APS on the structure, morphology and corrosion protective performance of the organic–inorganic hybrid coatings prepared by EPD method.

In this work, the effect of APS on corrosion protective performance of EPD coatings on LC4 aluminum alloy was studied based on our previous work, which optimizes the operation parameter of the EPD process [10]. Zirconium (IV) n-propoxide (TPOZ, metal alkoxides containing Zr) and 3-glycidoxypropyl-trimethoxysilane (GTMS, silane containing Si) with epoxide group were selected as precursor of the coatings, and APS was chosen as additive to change the charged colloidal particles in the sol solution. Zeta potential of colloidal particles is changed with APS addition. The morphology, microstructure and component of the coatings with different content of APS were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR). In particular, the corrosion protective performance of coatings with different immersion time was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. And equivalent circuit was applied for numerical fitting of the experimental results. The results show that the optimized APS content is 15%, at which the coating exhibits the best corrosion protective performance.

2. Experimental details

LC4 aluminum alloy samples (chemical composition: 0.50 wt.% Si, 0.50 wt.% Fe, 1.4–2.0 wt.% Cu, 0.20–0.60 wt.% Mn, 1.8–2.8 wt.% Mg, 0.10–0.25 wt.% Cr, 5.0–7.0 wt.% Zn, 0.10 wt.% Ti, balance Al) (40 × 30 × 3 mm) were grinded using SiC waterproof sandpaper to 600 grit, cleaned with deionized water, and then dried with clean air. These samples were immersed in an alkaline aqueous solution for 1 min at 50 °C to remove oil, and then immersed in the acid aqueous (CrO_3, 50 g/l; HNO_3, $\rho = 1.42$ g/ml, 100 g/l; HF, 40 wt.%, 10 g/l) to remove oxide at room temperature. After that, these samples were rinsed

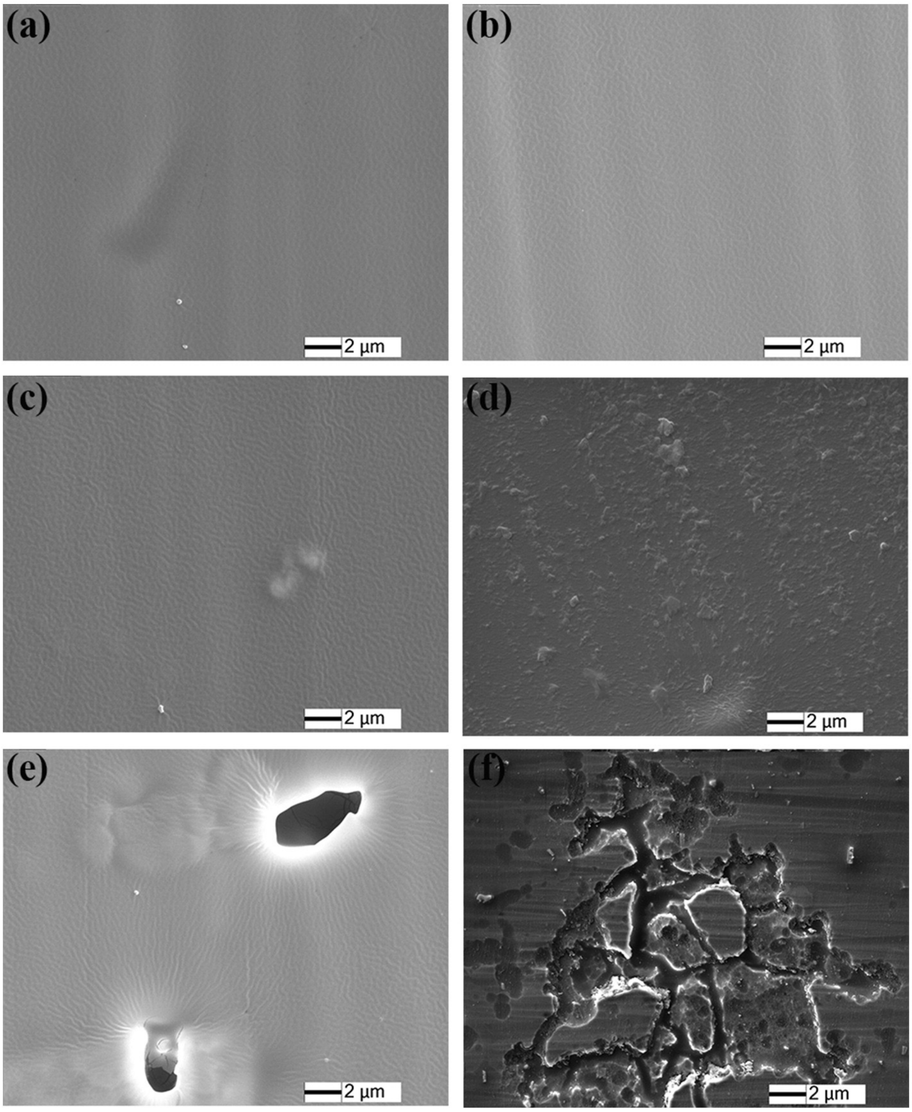

Fig. 1. Morphologies of coatings prepared by EPD method with different APS contents. a) 0%; b) 10%; c) 15%; d) 20%; e) 20%; f) 30%.