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Study on influence of native oxide and corrosion products on atmospheric corrosion of pure Al

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ABSTRACT

Effects of native oxide and corrosion products on atmospheric corrosion of aluminium in rural and coastal sites were studied by electrochemical impedance spectroscopy (EIS), open-circuit potential (OCP) and scanning electron microscope (SEM) techniques after outdoor exposure. In the rural atmosphere, only the compact, adhesive native oxide layer exists, and the rate controlling step is diffusion process, while in the coastal atmosphere, another loose, inadhesive corrosion products layer exists, and a charge transfer process controls the corrosion process. The pitting area in the coastal atmosphere increases over time more obviously than that in the rural atmosphere.

1. Introduction

Aluminium and its alloy are widely applied in various fields, such as building, electrical engineering and transportation, due to their excellent mechanical property and corrosion resistance. But Al and its alloy are apt to atmospheric corrosion in main forms of pitting, intergranular corrosion and stress corrosion cracking. It is of great importance for industrial application to realize atmospheric corrosion behaviour and mechanisms of aluminium. Some outdoor exposure tests in different environments and laboratory accelerating experiments have been carried out to study the influence of atmospheric environment, such as corrosive ions (e.g. Cl^-, SO_2, NO_x, and CO_2), relative humidity, time of wetness, etc., on corrosion behaviour of aluminium [1–12]. The time of wetness and the contaminations of SO_2 or Cl^- are the two main external factors governing the corrosion rate of aluminium, and the latter is much more important [13]. Cl^- tends to destroy the natural oxide films and cause surface degradation significantly of aluminium [14,15]. Sulphate ions are incorporated into the corroding surface layers, but field exposures of aluminium result in good resistance in sulphur oxide polluted atmospheres [16,17]. Nevertheless, the presence of sulphate in the chloride solution enhances the rate of corrosion [18,19].

It has been shown that corrosion products play an important role in corrosion behaviour [20]. The protectiveness of corrosion products formed on exposed metal depends on its chemical composition, conductivity, adherence, compactness, solubility, thickness, hygroscopicity and morphology [6,21]. Some reports [22–26] discussed the structure and ion selective permeability of rust formed on steel, which influenced the corrosion process greatly. Ion selectivity of rust layer may contribute to the corrosion resistance of weather steel [22,23], and low ion permeability rate inside the rust layer conduces to decreasing the corrosion rate of low-alloy steel [22], while a porous and incompact structure increases the corrosion rate [23,24]. A three-layer structure about aluminium was proposed by Graedel [18]: the aluminium itself and its native oxide, the corrosion layer atop the oxidized aluminium, and a surface contamination layer. In this work, contamination layer is quite thin and cannot be distinguished from corrosion layer easily. So the two layers are put together to discuss, and called corrosion products layer, with the characteristics of looseness and cracks. The influences of native oxide layer and corrosion products layer on atmospheric corrosion are discussed in the paper. The composition of native oxide layer is alumina (Al_2O_3) and boehmite (γ-AlOOH) or bayerite [$Al(OH)_3$] [27]. Sulphur compounds and aluminium hydroxychlorides are the principal constituents of the corrosion products layer [14,18]. The structure of native oxide and corrosion products and the evolution of their composition on aluminium have been researched systematically [14,18]. The effects of native oxide and corrosion products on atmospheric corrosion of Al, however, are seldom studied.

As a powerful method to study the surface condition of metals, electrochemical impedance spectroscopy (EIS) has been increasingly used in the field of corrosion [22,28]. EIS data could provide detailed information about the corrosion process at electrolyte/electrode interface [29]. EIS is sensitive to changes in the resistive-capacitive nature of the metal/electrolyte interface, thus more effective for studying the localized corrosion via small pores [29].

The aim of this work is to illustrate the role of native oxide and corrosion products in the pitting corrosion process of industrial

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pure aluminium in coastal and rural environments using EIS, OCP and SEM techniques.

2. Experiment

2.1. Material preparation

Industrial pure Al 1060 was selected as sample material which contains (in mass%) 0.35Fe, 0.25Si, 0.05–0.06Cu, 0.03 Mg, 0.03Mn, 0.05Zn, 0.03Ti and Al. The plate samples, of dimensions 15 mm × 15 mm × 3 mm, were ground down to 2000# with grade emery paper, cleaned ultrasonically in acetone, rinsed with alcohol, and then dried with a dryer. The plates were used to observe the morphologies of corrosion products, pits and cross-section.

Samples for electrochemical experiment were cut into 10 mm × 10 mm × 3 mm, connected with copper wires, then mounted in epoxy resin with an exposure area of 1 cm^2. Electrode samples were also ground, cleaned and dried as the aforementioned methods.

2.2. Outdoor exposure experiment

Two types of atmospheres were chosen to do outdoor exposure experiments: coastal (Wanning, 18°58′N, 110°05′E) and rural (Banna, 21°35′N, 100°40′E). The detailed environmental parameters are given in Table 1. The two sites are almost on the same vertical column, and both are tropical monsoon climate. However, a large number of Cl^- and SO_2 exist in the coastal environment, while rural environment is relatively clean. Plates and electrochemical samples were exposed in duplicate and triplicate respectively at an angle of 45° from the horizontal plane. Samples batches were withdrawn from each test site after 6 and 12 months of exposure.

2.3. Electrochemical measurements

Open-circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) were performed by an EG&G PARSTAT 2273 potentiostat connected to a computer equipped with Powersuite software. A classical three-electrode system was used in all electrochemical measurements: saturated calomel electrode (SCE) as reference electrode (all potentials given in this work based on the reference electrode), platinum plate as counter electrode, and un-exposed or corroded aluminium as working electrode. The electrolyte was 0.1 mol/L Na_2SO_4 (pH = 5) solution, which was stable enough and minimum changed the original property of native oxide and corrosion products when samples were immersed. EIS measurements were carried out at corrosion potential in the frequency range of 100 kHz–10 mHz, with a 10 mV amplitude signal. All the measurements were conducted at room temperature (25 °C). The EIS data were analysed with ZSimpwin software.

2.4. Analysis of corrosion products and pitting

A scanning electron microscope (Philips XL30FEG) was used to observe the morphologies of the corrosion products, pits and cross-section. One of the two plate samples withdrawn from each test site every period was mounted and polished to observe cross-section. The other one, after the analysis of corrosion products, was put into the solution (50 mL H_3PO_4 + 20 g CrO_3 + 1 L H_2O) for 5–10 min at 80 °C to remove the corrosion products chemically to reveal the morphologies of pits.

3. Results and discussion

3.1. Morphologies of corrosion products and pits

Fig. 1 shows the surface morphologies of corrosion products on aluminium exposed 6 and 12 months to rural and coastal environments. In rural atmosphere, the pitting areas are quite small, and the substrate can be seen clearly after 6 months exposure (Fig. 1a). With extension of exposure time, much more inconsecutive corrosion products are deposited (Fig. 1c). In coastal atmosphere, the corrosion products almost fully cover the entire surface after 6 months exposure (Fig. 1d). Some corrosion products fall off after the samples were exposed 12 months due to its loose, inadhesive structure and the existence of stresses (Fig. 1d). Aluminium samples suffer less corrosion in rural atmosphere than coastal atmosphere, which is also proved by the thickness of corrosion products and the density of pits shown in Figs. 2 and 3.

Fig. 2 shows the cross-section morphologies of the corrosion products formed on aluminium in rural and coastal atmosphere after 6 or 12 months exposure. In the rural atmosphere, the corrosion products layer is hardly recognized after 6 or even 12 months exposure (Fig. 2a and c). In contrast, the corrosion products layer formed in the coastal atmosphere can be seen obviously after 6 months exposure (Fig. 2b and d). The thickness of corrosion products layer increases with the prolonging of time.

Surface morphologies of the samples after corrosion products were removed are shown in Fig. 3. In the rural atmosphere, the density of the pits is low, and does not increase obviously with time (Fig. 3a and c). In the coastal atmosphere, there are much more pits on the surface, and the pitting area increases visibly (Fig. 3band d).

Aluminium is easy to be oxidized at ambient temperature. The oxide films (alumina Al_2O_3) with excellent characteristics of adhesion, continuity, compactness and passivity are formed as soon as aluminium is exposed, which may protect the substrate from corrosion. The thickness of the alumina film usually ranges from 40 to 100 Å. The surface of an alumina film will be evolved into boehmite and bayerite with the extending of time [14,27]. Once the oxide film on aluminium is sufficiently thinned by dissolution or bypass by solution into pores or by ion transport down defects, pitting corrosion occurs [18]. The corrosive ions in the atmosphere are the dominating reasons to cause the corrosion of aluminium. As shown in Table 1, the total content of Cl^- and SO_2 in the coastal atmosphere is much larger than that in rural atmosphere, which is the main reason for the more serious corrosion of aluminium in coastal atmosphere. The reaction rate between oxygenated aluminium and sulphate is similar to that for oxygenated aluminium and chloride [30]. The rate of aluminium dissolution is primarily dominated by Cl^- owing to its high content in coastal atmosphere. The corrosion products contained Cl^- is formed by a stepwise chlorination of aluminium hydroxide [31].

Table 1
Annual environmental data of coastal and rural sites.

Atmosphere	Mean temperature (°C)	Mean relative humidity (%)	Total sunshine time (h)	Total rain time (h)	Cl^- ($mg\ m^{-2}\ d^{-1}$)	SO_2 ($mg\ m^{-2}\ d^{-1}$)	pH of rain
Coastal (Wanning)	25.1	85	1832.5	391.71	50.39	5.59	5.34
Rural (Banna)	22.2	79	1909.1	111.44	0.45	2.12	6.40