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Pyrrole-based silane primer for corrosion protection of commercial Al alloys. Part II. Corrosion performance in neutral NaCl solution

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ABSTRACT

A chromate-free, direct-to-metal treatment using pyrrole-based silane (PySi) was developed for protection against corrosion of as-received commercial Al alloys, following the typical procedure for silane deposition. The protection performance of composite PPySi films, containing polysiloxane linkages and polypyrrole units, was evaluated in near neutral NaCl solution by simple corrosion tests such as single-cycle anodic polarization, corrosion potential monitoring and long-term immersion experiments. Control coatings of polymethylsiloxane (PMeSi) and electrochemically synthesized polypyrrole (Ppy) were also studied. The superior performance of PPySi with respect to PMeSi and Ppy was attributed to highly crosslinked, well-packed and adherent composite films of thickness of the order of microns, manifesting both barrier action and active protection. The use of pyrrole-based silane for corrosion protection of Al alloys constitutes a promising approach for effective replacement of chromium-based treatments in practical applications. Further investigation from the fundamental point of view is deserved.

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1. Introduction

Organic coating technologies have evolved towards environmentally friendly systems to eliminate highly effective but toxic hexavalent chromate-based treatments. Silane-based treatments have attracted many researchers [1–9] motivated by advantages such as environmental compliance, simple application and outstanding corrosion protection of a wide range of metals and alloys in addition to improved paint (or topcoat) adhesion. The actual major limitation of silane-based coatings is that they are like “passive” coatings, acting essentially as a physical barrier for the penetration of aggressive species towards the metallic substrate. Doping with small amounts of chemicals having corrosion inhibiting properties is needed for these films to acquire active protection [7,8]. A rather new superprimer concept – a single layer, direct-to-metal primer, invariably containing silanes but obviating the need for a pretreatment layer – was first introduced by Seth and van Ooij [10]. Superprimer formulations, based on organofunctional silanes mixed with conventional primers or binders have shown excellent corrosion protection of different metals and alloys [11].

Relatively new alternative coatings are those based on electronically conducting polymers (ECPs). The first reports on corrosion protection of metals by ECPs were presented by Mengoli et al. [12] and Deberry [13], who studied the behavior of polyaniline (Pani) electrodeposited on steel. Since then, ECPs have continued to be investigated either directly as a primer coating or surface treatment [14–20], or as a component blended with more conventional coatings [21,22]. Polypyrrole (Ppy) coatings are preferable over Pani because the former is likely more effective in the suppression of pitting corrosion within defect. Further, aniline monomer is carcinogenic and Pani-based coatings protection is limited by pH (<7), making its use in marine environments difficult.

How corrosion protection by ECPs might work is actually subject of intense research [15,16,20,23,24]. The redox activity offered by ECPs together with positive equilibrium potentials relative to those of Fe and Al, as is the potential of chromate, suggest that the mechanism is likely to involve anodic protection [14]. The most popular mechanism is the so-called “ennobling” that is based on the assumption that ECPs could provide anodic galvanic protection keeping the metal passive in small defects [25,26], or may act as oxidizer, improving the oxide layer at the ECP/metal interface [27]. The possible reaction between the oxidized form of the polymer (ECP^{m+}) and the metal (Me) is:

$$\frac{1}{n}\mathrm{Me}+\frac{1}{m}\mathrm{ECP}^{m+}+\frac{y}{n}\mathrm{H_2O}\rightarrow\frac{1}{n}\mathrm{Me}_y^{(n-y)+}+\frac{1}{m}\mathrm{ECP}^0+\frac{y}{n}\mathrm{H}^+$$

being ECP re-oxidized by atmospheric or dissolved oxygen:

$$\frac{m}{4}\mathrm{O_2}+\frac{m}{2}\mathrm{H_2O}+\mathrm{ECP}^0\rightarrow\mathrm{ECP}^{m+}+m\mathrm{OH}^-$$

In addition, the electrons produced during metal oxidation at the defect can move into the polymer and thus dislocate the oxygen reduction process from the metal/ECP interface to the ECP/solution

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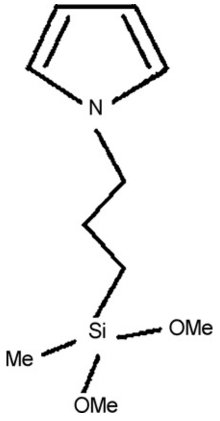

Fig. 1. N-(3-(trimethoxysilyl)propyl)pyrrole (PySi).

interface [28,29]. This alleviates the local pH increase at the former and in turn the cathodic coating disbonding. All of the above processes may simultaneously contribute to substrate protection. It was also suggested that ECPs can be used as a reservoir of corrosion inhibitors that could be released as a result of the reduction of the conducting polymer [30].

One of the challenges in developing Ppy coatings for corrosion protection is overcoming of processability difficulties of this polymer, as well as improving the adhesion onto active metals. A new promising approach that has allowed to obtain a composite film containing Ppy units in a simple way was proposed by present authors [31] using a pyrrole-based silane (Fig. 1) as a primer on as-received wrought Al alloys. The synthesis and the structural characterization of composite PPySi films have been presented in the first part of this contribution [32]. Control coatings of polymethylsiloxane (PMeSi) and polypyrrole (PPy), electrochemically synthesized according to the reported procedure [33] were also investigated. Well-packed composite PPySi films with thicknesses of the order of microns were produced due to primer molecules co-polymerization via silanol groups condensation and α–α' linking of pyrrole rings, resulting in a highly crosslinked, free from gross defects, ordered network. These features, much superior to those reflected by PMeSi and Ppy films, should provide improved protection performance to the composite PPySi that could be enhanced as well by combining in a single film both polysiloxane and polypyrrole units with barrier and inhibition actions, respectively. This paper discusses the behavior of PPySi films against Al substrates corrosion in neutral 0.6 mol L^{-1} NaCl, evaluated via simple corrosion tests like single-cycle anodic polarization, open circuit potential monitoring and long-term immersion experiments. The control coatings of PMeSi and Ppy are tested as well.

2. Experimental

As-received commercial wrought Al alloys of series 1xxx, 2xxx, 5xxx and 6xxx (Table 1) were modified with methyltrimethoxysilane (MeSi), pyrrole-based silane (PySi), and polypyrrole (Ppy) as reported elsewhere [32].

Table 1
Chemical composition (wt%) of commercial wrought Al alloys (AA).

Al alloys	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr
1050 O	0.25	0.40	0.05	0.05	0.05	0.07	0.05	<0.03
6082 T6	0.90	0.36	0.04	0.56	1.00	0.02	0.02	0.04
5754 H111	0.08	0.26	0.03	0.18	2.73	0.01	<0.01	0.05
5083 H111	0.17	0.32	0.04	0.62	4.32	0.03	0.02	0.07
2024 T3	0.15	0.25	4.67	0.63	1.34	0.02	0.06	0.01

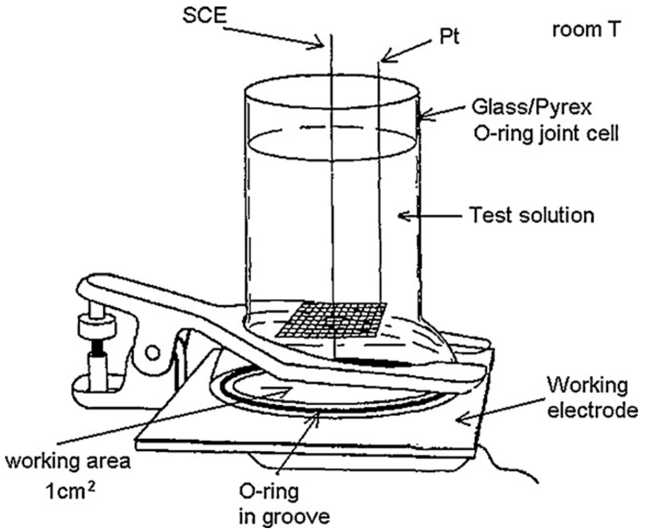

Fig. 2. Single-compartment O-ring cell test.

The corrosion behavior of the coated specimens was evaluated at room temperature in quiescent, naturally aerated near neutral (pH 6.5 ± 0.2) 0.6 mol L^{-1} NaCl solution prepared with reagent grade NaCl (98%, Aldrich). Bare substrates (as-received) were also tested after careful ultrasonic solvent cleaning with n-hexane, acetone and methanol, 15 min each.

Electrochemical corrosion testing consisted in single-cycle anodic polarization and open circuit potential (E_{oc}) monitoring up to at least 18 h. All measurements were performed using a single-compartment O-ring cell (Fig. 2) with a working (active) surface of 1 cm^2. A Pt sheet was used as a counterelectrode, and an external SCE as a reference electrode, connected to the working compartment via a salt bridge containing the test solution and a Luggin capillary. Data were recorded by means of a PC driven Solartron 1286 potentiostat.

Single-cycle anodic polarization was recorded at a rate of 10 mV min^{-1} after equilibration at open circuit potential (E_{oc}) for 10 min. When in the forward scan the anodic current attained the pre-selected limiting value of 5×10^{-3} A cm^{-2}, the sweep was reversed until the current became cathodic. In the case of silane-based coatings, the effect of different experimental conditions on the polarization response was studied. The main parameters explored for the surface treatment and the corresponding films designation are summarized in Table 2.

Long-term immersion tests were carried out in open air test solution for 7 days, according to the ASTM procedure G31 [34].

Coated and bare surfaces were examined after corrosion potential monitoring (E–t experiments) and at the end of the immersion tests, were examined by scanning electron microscope (SEM), using a LEO 1430 instrument at a chamber pressure of 8×10^{-6} Torr and

Table 2
Experimental conditions for surface treatment with silane-based hydrolyzed solutions (at 4%v/v in methanol/water 95:5, pH 4).

Substrate pre-heating (20 min)	Immersion	Curing	Film designation
120 °C	3 min	130–150 °C, 2 h	PMeSi-3
120 °C	3 min × 3	130–150 °C, 2 h	PMeSi-3 × 3[a]
60 °C	1 min	Room T, 24 h	PPySi-1*
120 °C	1 min	130–150 °C, 1 h	PPySi-1
120 °C	3 min	130–150 °C, 2 h	PPySi-3
120 °C	1 min × 3	130–150 °C, 1 h	PPySi-1 × 3[a]
120 °C	3 min × 3	130–150 °C, 2 h	PPySi-3 × 3[a]

[a] Multiple immersions in silanes hydrolyzed solutions.

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