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Degradation of fluorinated polyurethane coating under UVA and salt spray. Part I: Corrosion resistance and morphology

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ABSTRACT

The degradation of fluorinated polyurethane (FPU) coating on AA7075 Al-alloy was studied by electrochemical impedance spectroscopy (EIS) through accelerated ageing tests under ultraviolet A (UVA) irradiation and salt spray tests (SST), respectively. The morphological changes of the coating were observed by scanning electron microscope (SEM) and atomic force microscopy (AFM). Furthermore, the variation of thermal performance and functional groups of the FPU coating were characterized by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). EIS results showed that SST caused faster decrease of corrosion barrier than the UVA irradiation, especially in the initial stage. Nevertheless, the UVA rather than the SST increased the glass transition temperature (T_g) and the brittleness of FPU coating, indicating that the UVA could accelerate the chemical degradation of FPU coating. In addition, many blisters and wrinkles could be found on the surface of FPU coating during UVA but only micropores could be found during SST. These micro flaws provide fast channels for aggressive ions to migrate to the coating/ metal interface, accelerating the delamination of FPU coating and the Al matrix.

1. Introduction

Polyurethane coatings are widely used to protect metal in various industrial applications. After long-term service, however, they suffer a variety of weathering, such as ultraviolent irradiation, salt ions erosion, water/humidity and temperature fluctuations, which could lead to the decomposition of urethane bonds and reduce the service life [1–9]. Therefore, it is of great necessity to study the degradation mechanism of polyurethane coating under various ageing conditions, such as ultraviolet A (UVA) irradiation and/or salt spray tests (SST).

In recent years, many studies have concentrated on the natural or accelerated degradation process of coating, especially in the presence of artificial defects or different pigments [10–16]. Yang et al. [17] investigated the degradation of polyurethane coatings under UVA and prohesion alternating exposures, and reported that the pigment and bead enriched surface protected the topcoat from rapid UVA-inducing degradation. Morsch et al. [18] examined the degradation mechanism of a corrosion resistant epoxy-phenolic can coating through ion transport and water sorption during immersion in electrolyte and water. Rosu and Cascaval [19] proved that UV light modified the chemical structure of PU due to the scission of the urethane group and photo-oxidation of the central methylene group. Hu et al. [20] investigated the ageing behaviour of acrylic polyurethane varnish coating under fluorescent UV and xenon lamp exposure, and suggested that UV exposure cause greater degradation than xenon lamp exposure. Irigoyen et al. [21] studied the effect of UV on electrochemical behaviour of epoxy paints, and observed that the photochemical inducing post-drying process decreased the uptake volume water. Rashvand et al. [22–24] investigated the effect of nano-ZnO on the corrosion resistance and photo-degradation of polyurethane under UV irradiation, and found that ZnO filler reduced the photo-degradation of aromatic polyurethane binder. However, investigations about the degradation mechanism of PU coating under different ageing approaches are rare and unclear, particularly the comparative studies between UV irradiation and SST.

In this paper, we tried to explore the degradation process of fluorinated polyurethane (FPU) coating under different environmentally accelerated factors (UVA irradiation and SST). Electrochemical impedance spectroscopy (EIS) was employed to investigate the corrosion resistance change with ageing time of FPU coating on AA7075 aluminium alloy under UVA irradiation and salt spraying, respectively. Furthermore, the ageing processes were

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analyzed and compared with the fitting results of EIS by suitable equivalent electrical circuit. Moreover, the coating surface morphology was observed by atomic force microscope (AFM) and scanning electron microscopy (SEM), aiming at illustrating the relationship between the corrosion resistance and the morphologies of ageing FPU coating. In addition, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) were employed to evaluate the difference of thermal performance and molecular structure of FPU before and after degradation under UVA and SST.

2. Experimental

2.1. Samples preparation

AA7075 Al-alloy of 3 mm in thickness was prepared as matrix specimen and then cut into wafer samples with the diameter of 45 mm. Epoxy resin was used to seal the specimens with only one surface exposed to be working surface. The working surface of all samples was mechanically abraded with emery papers (400 and 600 grit in turns) to obtain similar surface roughness. After polishing, all specimens were degreased with ethanol and acetone in turn, and then dried in the air prior to coating process.

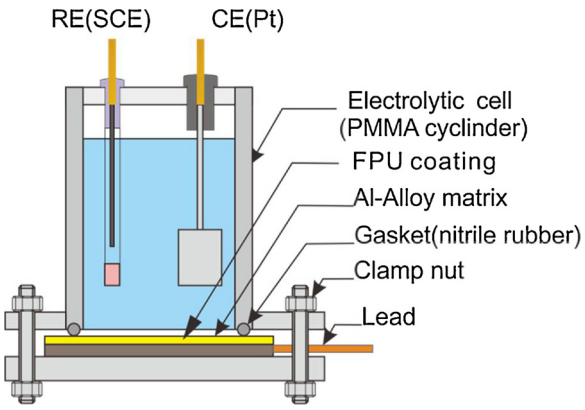
Type TS 96-11 fluorinated polyurethane (30–60 wt.% fluororesin + 20–50 wt.% butyl acetate, and a small amount of Zinc naphthenate and Calcium naphthenate. Tianjin Beacon Painting & Coating Co., Ltd. China) was applied on the Al-alloy specimens by air spray. Then the coating samples were naturally cured in air at room temperature for 5 days to ensure the uniformness and consistent surface morphology. The thickness of the dry coating was measured with a digital coating thickness gauge Elecometer 415 and was controlled to be 50 ± 5 μm (an average of five measurements on different regions of coating). The adhesion strength of the coating specimens was measured by a pull-off adhesion tester (PosiTest AT-A, Defelsko Co.), and only those samples with adhesion strength over 4 MPa were chosen. Three coating samples were prepared in each measurement for good reproducibility.

2.2. UVA irradiation and salt spray test

Ultraviolet A (UVA) irradiation and salt spray test (SST) were employed to accelerate the degradation of FPU coating. UVA test was performed in a UVA chamber with distilled water heated at the bottom to maintain the chamber temperature at 50 °C. The fluorescent lamps with irradiance of 0.77 W/m^2 (at 340 nm) were used according to ASTM G154 [25]. Neutral salt spray test was conducted to simulate marine climate according to ISO 7253 [26] standard in a salt spray chamber. All the samples were exposed to 5 wt.% NaCl solution with pH = 7 and the chamber temperature was kept 35 ± 2 °C. Three parallel samples were employed in following spectral and thermal analyses for reproducibility, thus, together fifteen coating samples were put in each weathering chamber. Afterwards, all samples were put back to the ageing chambers for further ageing.

2.3. Characterization

EIS measurement was applied to assess the corrosion resistance of FPU coating under SST and UVA irradiation, which was conducted in conventional three-electrode system by a CS350 electrochemical workstation (Corrtest, China). All coated specimens were clamped to the bottom of a coating electrochemical cell for fast installation and uninstallation, in which the coated Al-alloy specimen was used as working electrode (exposed area: 9.6 cm^2), saturated calomel electrode (SCE) as reference electrode, platinum sheet as counter electrode, and 3.5 wt.% NaCl solution as electrolyte. The electrochemical cell was made by a plastic tube of 3.5 cm inner diameter, clamped to the testing samples with a rubber ring, and the schematic diagram of EIS measurement is displayed in Scheme 1. The coated working electrode was put in the middle of the electrochemical cell at the time of testing. Three parallel coating specimens were used in the EIS measurement to improve the reliability of EIS results. The samples were taken from the weathering chamber for EIS measurement with different extended periods of time: 0.5 h, 60 h, 200 h, 395 h, 560 h, 732 h, 900 h, 1068 h, 1236 h, 1404 h, 1500 h, 1595 h, 1692 h and 1885 h, respectively. After the measurements, the samples were put in the weathering chamber again for further ageing test. The total testing time of samples was 1885 h. The applied frequency was 10^5–10^{-2} Hz at open circuit potential with AC signal amplitude to be 20 mV. All EIS plots were analysed by the Zview2 software.



Scheme 1. Electrochemical cell for EIS measurement of coated metals, where, CE: Counter Electrode, RE: Reference Electrode, WE: Working Electrode, Lead: Copper lead connecting to the Al-alloy matrix.

Differential scanning calorimeter (DSC) and thermogravimetric (TG) analysis were employed to determine the glass transition temperature (Tg) and thermal oxidation stability of FPU coatings before and after UVA/SST. DSC was carried out by a Diamond DSC (PerkinElmer Instruments) thermal analysis system with temperature ranging from −30 °C to 150 °C at the scanning rate of 10 °C/min in nitrogen atmosphere. TGA was conducted by a Pyris1 TGA (PerkinElmer Instruments) with temperature ranging from 40 °C to 600 °C under nitrogen atmosphere at the heating rate of 10 °C/min. Three coating specimens were tested and the average Tg value was reported.

The surface morphologies and compositions of FPU coatings were investigated by scanning electron microscopy (SEM) with an energy-dispersive spectroscopy (EDS) system (FEI, Sirion 200, Netherlands). Moreover, the topography of the coatings with different ageing time was characterized by a SPM 9700 (Shimadzu, Japan) atomic force microscope (AFM) in phase mode. FTIR spectroscopy to identify the chemical changes of coatings was recorded using an attenuated total reflectance (ATR) accessory of VERTEX 70 FT-IR spectrometer (Bruker, Germany) with wavenumber range of 600 cm^{-1}–4000 cm^{-1}.

3. Results and discussion

3.1. EIS measurements

3.1.1. EIS changes with ageing time

The impedance spectra presented as Nyquist and Bode plot of the Al-alloy substrate with FPU coating under UVA and SST are shown in Figs. 1 and 2, respectively. All EIS measurements were conducted after 0.5 h immersion of coated specimens in 3.5% NaCl solution. Nyquist plot shown in Fig. 1a exhibits only one large semicircle (single time constant) at the beginning of UVA irradiation, indicating a pure capacitive behaviour of the FPU coating with the low-frequency limit of the impedance modulus more than 10^9 Ω cm^2. Interestingly, the diameter

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