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Effect of mixture ratio on water uptake and corrosion performance of silicone-epoxy hybrid coatings coated 2024 Al-alloy

X. Yuan*, Z.F. Yue*, X. Chen, S.F. Wen, L. Li

Advanced Material Test Center, School of Mechanics and Civil & Architecture, Northwestern Polytechnical University, Xi'an 710129, China

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ABSTRACT

A silicone-epoxy hybrid coating cured with amino silane was developed to provide corrosion protection on 2024 Al-alloy using air spraying. Water uptake characteristics of the silicone-epoxy hybrid coatings were investigated by electrochemical impedance spectroscopy in a 5 wt% NaCl solution. The effect of mixture ratio of silicone-epoxy and amino-silane on the water uptake (solubility, diffusion coefficient and permeation) was studied by using a single frequency (10 kHz) capacitance method. The glass transition temperature (T_g) was also investigated through differential scanning calorimeter (DSC) before and after immersion in the NaCl solution. Consequently, the excess of silicone-epoxy resin or amino silane improved the solubility of water in the coatings. A low water permeation coefficient was obtained with the mixing ratio 8/2 of silicone-epoxy and amino-silane, in which the T_g value was found to be larger than other three mixing ratios before immersion. After immersion for 750 h, the impedance modulus of EFA 2 coating (mixing ratio 8/2) in the low frequency was still close to $10^8\ \Omega\,cm^2$ that accounts for the good protective performance.

1. Introduction

The 2024 Al-alloy used in aerospace contains so many intermetallic inclusions that it easily undergoes pitting corrosion in aqueous environment. It is a smart way to protect the 2024 Al-alloy by covering the surface with silicone-epoxy hybrid coatings taking advantage of its mechanical properties [1]. It is very attractive for silicone-epoxy hybrid coatings because of their abrasion resistance, low thermal expansion, low water permeation coefficient, chemical inertness and their strong adhesion on the substrates [2–4]. With adding functionalities to improve the performance and duability, Fabiola Brusciotti et al. [2] designed new silane-epoxy hybrid coatings to increase the corrosion protection of magnesium alloys. With improved adhesion and corrosion resistance, Khramov et al. [3] developed organic-inorganic hybrid coatings by sol-gel process to generate protective layers for magnesium materials. Qian Mian et al. [4] developed 2-part silicone-epoxy coating cured with amino silane to provide corrosion protection on carbon steel (CRSS) using dip-coating to deposit a two-layer structure. Therefore, silicone-epoxy hybrid coatings can provide barrier functions between the substrate and the corrosive environment in order to resist the transportation of water, oxygen, ions and other aggressive species to the coating/metal interface. The continuous migration of aggressive ions will lead to the delamination of coatings and under-film corrosion, and eventually give rise to the loss of corrosion protective function of silicone-epoxy hybrid coatings [5,6]. Along with the degradation of coatings, the process of water permeation is important because water is the medium for the diffusion of oxygen and aggressive ions.

However, the degree of permeability of silicone-epoxy hybrid coatings depends on the formulation, application and curing procedures [1,7,8]. For instance, if one of the components (silicone-epoxy hybrid resin or amino silane) is in excess, a full crosslinked network will not be accomplished so that this will influence the properties of the coatings. Thus, the quantity of water permeation in the coatings is often estimated with coated substrates to optimize the coating formulation. The performance of silicone-epoxy hybrid coatings which can reduce the water invasion will greatly influence their protection efficiency to the metallic substrates.

Conventionally, water diffusion coefficient (D) and solubility (S) for water permeation (P) into a coating may be obtained from gravimetric method [9]. Certainly, water diffusion coefficient may also be determined by monitoring the effective change in the coating capacitance on a conductive substrate from electrochemical impedance spectroscopy (EIS) [2,10–15]. Due to the high dielectric constant of water ($\varepsilon_w = 80$ at $T = 20\,°C$) which is compared

* Corresponding author. Tel.: +86 29 88431002; fax: +86 29 88431002.
E-mail addresses: yuancn21@foxmail.com (X. Yuan), zfyue@nwpu.edu.cn (Z.F. Yue).

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to most epoxy coatings (typically $\varepsilon_c = 3–8$), the coating capacitance technique is very sensitive. The water volume fraction can be deduced from the data of the coating capacitance using the Brasher–Kingsbury equation [1,2] which is, by far, the most frequently used equation to estimate the water content in coating matrix:

$$\phi(\%) = \frac{\log(C_t/C_0)}{\log(\varepsilon_W)} \times 100 \tag{1}$$

where C_t is the coating capacitance at time t, C_0 is the initial coating capacitance and ϕ is the water volume fraction in the coating. The coating capacitance (C_H) is firstly determined using the imaginary part of the impedance Z'' at the high frequency ($f = 10$ kHz):

$$C_H = -\frac{1}{2\pi f Z''} \tag{2}$$

EIS data is also analyzed by classical electrical equivalent circuits (EECs) contained constant phase elements (CPE). Then, considering only the solution resistance R_s which is much lower than other resistances and by using the Brug' s approach, the "true capacitance" C_B is calculated by:

$$C_B = {Y_0}^{1/n}\left(\frac{1}{R_s}\right)^{(n-1)/n} \tag{3}$$

where Y_0 and n are the CPE parameters. Nguyen Dang [16] used these three parameters (C_H, CPE, C_B) followed during immersion time to calculate the water uptake from BK equation, and indicated water uptake obtained from C_H, CPE and C_B, was respectively linked to water uptake obtained from gravimetry by the following relation $\phi_H = 1.68\phi$, $\phi_{CPE} = 2.38\phi$ and $\phi_B = 0.98\phi$. These results showed that the analysis of EIS data has to be chosen with great care in order to avoid the wrong estimation of water uptake.

For the plot of a coating capacitance versus time, it is possible to determine the diffusion coefficient D, solubility S and the permeation coefficient P:

$$P = D \times S \tag{4}$$

At sufficiently short time, the water uptake is proportional to the square root of time for a supported coating as follow:

$$\frac{M_t}{M_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2 D\pi^2}{l^2}t\right) = \frac{2\sqrt{D}}{l\sqrt{\pi}}\sqrt{t} \tag{5}$$

$$M_t = \frac{lQ\rho_W}{\log \varepsilon_W}\log\frac{C_t}{C_0} \tag{6}$$

where M_t is the amount of absorbed water at time t, M_s is the amount of absorbed water at saturation, l is the coating thickness, Q is the surface area of the coating and ρ_W is the density of the water absorbed into the coating. By combining Eqs. (5) and (6), one obtains:

$$\frac{\log C_t - \log C_0}{\log C_s - \log C_0} = \frac{2\sqrt{D}}{l\sqrt{\pi}}\sqrt{t} \tag{7}$$

The solubility S of the water in the coating can be obtained from the water volume fraction at saturation point ϕ_s according to the following equation [1,9]:

$$S = \phi_s \times \rho_W \tag{8}$$

in which ρ_W is the density of the water absorbed into the coating.

Our previous work has shown that the evolution of impedance models with immersion time and the water transport behaviors in silicone-epoxy hybrid coatings on 2024 Al-alloy. However, little or no dependence of the diffusion coefficient on the mixture ratio have been obverted. In the present work, the influence of mixture ratio of silicone-epoxy resin and amino silane on the water uptake (solubility and sorption kinetics) was studied by electrochemical impedance spectroscopy (EIS) in 5 wt% NaCl solution using a single frequency. The aim of the work is not only to provide the rapid assessment with water uptake to be determined for such material, but also to optimize the coating formulation by varying the weight ratio (8/1, 8/2, 8/3, and 8/4) of silicone-epoxy and amino silane. The corrosion performance of silicone-epoxy hybrid coatings coated 2024 Al-alloy was also investigated by a classical EIS technique.

2. Experimental details

2.1. Sample preparation

The tests were carried out on 2024 Al-alloy samples. The samples (150 mm × 70 mm × 1 mm) were polished with 1 μm sang paper followed by scotch-brite and degreased in acetone, then washed with deionized water before painted. No other pretreatment was applied on the 2024 Al-alloy.

The silicone-epoxy hybrid coatings were prepared from silicone-epoxy hybrid resin and amino-silane, commercially known as SILIKOPON EF and Dynasylan AMEO from EVONIK industries. The weight ratios of silicone-epoxy resin and amino silane were 8/1, 8/2, 8/3 and 8/4, named EFA 1, EFA 2, EFA 3 and EFA 4, respectively. The coatings were applied by air spray to spread on the 2024 Al-alloy, cured at 26 °C and 60% humidity during 6 h and then dried at room temperature environment for 7 days. The thickness of the coatings evaluated by thickness gauge QNix 4500 is about 25 ± 5 μm, where ± indicates the standard deviation.

2.2. EIS measurements and data analysis

EIS measurements for four silicone-epoxy hybrid coating/Al-alloy systems (being named EFA 1 coating, EFA 2 coating, EFA 3 coating and EFA 4 coating, the corresponding weight ratio of 8/1, 8/2, 8/3 and 8/4) were performed in the 5 wt% NaCl solution by using three-electrode system. The schematic diagram of immersion tests and EIS measurements are displayed in Fig. 1, in which the coated Al-alloy in the middle layer acts as the working electrode, a saturated calomel electrode acts as the reference and a platinum electrode acts as the counter. The inner diameter of the tube was

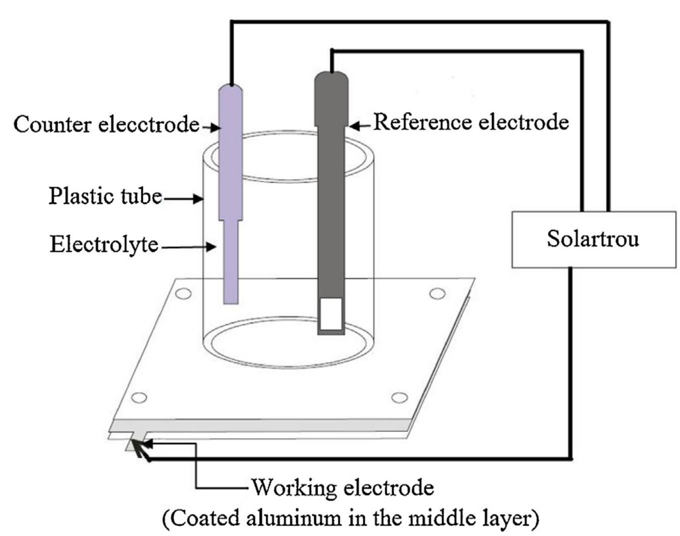

Fig. 1. Three-electrode system used for impedance measurements on 2024 Al-alloy coated silicone-epoxy hybrid coating.

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