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A study on effects of elastic stress on protective properties of marine coatings on mild steel in artificial seawater

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ABSTRACT

The effects of macro-elastic stress on protective properties of two marine coating systems applied on mild steel plates in artificial seawater at room temperature were investigated through the measurement of electrochemical impedance spectroscopy (EIS). One coating system contained zinc-rich epoxy primer, micaceous iron oxide anchor coat and aliphatic polyurethane top coat and the other was composed of zinc-rich epoxy primer, micaceous iron oxide anchor coat and acrylic polyurethane top coat. Two different elastic stress levels (tensile and compressed modes) were applied on coated substrates by using bent samples and non-bent coated samples were used as references. The obtained results indicated that elastic stress could have a significant influence on coating resistance, water absorption and diffusion coefficient, and meanwhile the extent of this influence depends on both the magnitude and direction of elastic stress. Furthermore, the disparity in the evolution of water uptake and diffusion coefficient with elastic stress was discussed, and a thermodynamic approach was employed to evaluate the enthalpic and entropic contributions of the water diffusion coefficient under various elastic stress levels.

1. Introduction

Stress constitutes one of the factors contributing to degradation of construction materials, limiting their lifetime and being of extreme importance in terms of safety aspects. Although attempts are undertaken towards stress minimization, it will always be associated with engineering practice [1]. Coating/metal systems also encounter such a problem on a regular basis.

Coatings have been used for a long time to protect steel structures against corrosion in marine environments. During the service life, coating systems on ship and marine structures usually experience various environmental loadings such as wind, waves and current, and the stress caused by welding, machining and operating force etc. is also inevitable. For such a coated structure, the mechanical load may affect the coating property by changing the polymer chain spatial distribution. Many previous studies on coating degradation mainly focused on the influence of UV radiation or temperature [2–7], and some authors [8,9] also reported on the influence of intrinsic stress related to volume contraction during curing process on the coating quality. Up to now, less information concerning the effect of elastic stress on actual marine coating systems is available in the literature.

Bastos and Simoes [10] investigated the influence of uniaxial strain on the barrier properties of coil-coatings, and it was found that anticorrosive protection rapidly decreased with the degree of elongation. A similar work about the effect of non-uniform strain on the protective properties of organic coatings was done by Deflorian et al. [11], and it was concluded that the more the coatings were deformed, the more they were damaged. However, some other researchers hold different views. Kazimierz and Szocinski [1] investigated the impact of a cyclic mechanical load on the organic coating degradation, and it was found that coating behaviour upon mechanical load cycling could be segmented into three stages: an improvement stage, a relaxation stage and a deterioration stage. Fredj et al. [12–14] reported that both barrier property and initial relative permittivity of several marine organic coatings applied on mild steel changed significantly due to the stress in the visco-elastic domain of polymer, and meanwhile the influences of tensile and compressed stress were different due to the stress sign effect, thereby it was concluded that the mechanical state of polymer could affect the coating degradation process remarkably. However, a recent study by Dang et al. [15] has found that the applied visco-elastic stress, independent of its sign, allowed a better barrier property for the model polymer DGEBA/TETA coating applied on

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steel panels, and could delay the corrosion process of the metallic substrates.

Although some investigations about the effect of mechanical stress on the performance of coatings have been conducted, only small amounts of mechanical stress were considered in each previous study, and the stress levels were relatively low, resulting in an incomplete understanding about the influence mechanism of pure mechanical stress on coating performance. Moreover, the coatings used for this topic were generally monolayers or in the form of no additives (fillers, plasticizers or pigments), not belonging to the practical composite coating system which usually contains the primer coating and topcoat (with or without intermediate coat). Finally, no general trend concerning the relation between coating performance and mechanical stress has been proposed according to the several hypotheses provided by previous researchers, and thus more studies should be done on this topic.

In reality, the coating system on ship and marine structures is usually composed of primer, intermediate coat and topcoat, and meanwhile most of the stress level on structural surface could not be too low, although it should be in the elastic range of steel to meet the safety design of marine structures. The major objective of present study is to investigate the effects of mechanical stress in the elastic range of steel substrate on protective properties of two marine coating systems. One was composed of zinc-rich epoxy primer, micaceous iron oxide anchor coat and aliphatic polyurethane top coat and the other was composed of zinc-rich epoxy primer, micaceous iron oxide anchor coat and acrylic polyurethane top coat. Two marine coating systems were applied onto the Q235 steel plate and different elastic stresses were applied by bending the coated steel panels. The coated samples were immersed in artificial seawater at room temperature and the properties of protective coatings were regularly evaluated by employing electrochemical impedance spectroscopy (EIS) technique. The EIS data were analyzed by employing different approaches to determine whether the mechanical stress is really of substantial importance to the durability of coating/metal systems. It is anticipated that some concluding remarks achieved in this study would provide some insights into the mechanism of coating degradation due to the stress on structural surface and the optimization design of actual marine coating system.

2. Experimental procedures

2.1. Material and sample preparation

Two marine coating systems were studied: sample A contained zinc-rich epoxy primer, micaceous iron oxide anchor coat and aliphatic polyurethane top coat; and sample B contained zinc-rich epoxy primer, micaceous iron oxide anchor coat and acrylic polyurethane top coat. Both coating systems were applied onto the two sides of Q235 cold-rolled steel plate with the dimension as 200 mm × 100 mm × 1 mm.

Prior to coating application, the Q235 steel substrate panels were cleaned with ethanol, followed by degreasing, derusting and phosphating pretreatment. The degreasing and derusting process were simultaneously achieved by immersing the substrate panels in a degreasing and derusting solution (35.0 wt.% *N*-butyl alcohol, 25.0 wt.% isopropyl alcohol, 22.0 wt.% DI water and 18.0 wt.% Phosphoric acid) for 3.5 min, then rinsing them twice with tap water. After degreasing and derusting, the substrate plates were treated in ferric-based phosphating solution at room temperature for 15 min, and then dried at room temperature for the coating process. The coatings were applied by spraying with standard heavy duty airless spray equipment. The dry film thickness of the primer film was in the range of 42–48 μm, intermediate coat was 42–48 μm and the topcoat was 28–32 μm. The dry film thickness was measured using an Elcometer 456 coating thickness gauge and the average value was 120 μm for each coating system. Moreover, a metallic lead wire was electrically connected with each steel substrate panel through a bolt in order to conduct EIS measurements. Finally, for all the samples, an additional epoxy resin was deposited onto the coated panel edges and the whole surface of the bolt so as to avoid water ingress and protect the electrical connection.

2.2. Loading method

Various elastic stress levels were chosen and applied to the coated panels by bending the panels between two pieces of PVC mould. To obtain a specific stress, the suitable curvature radius of the PVC mould was determined by using numerical simulation and calibration test. The steel substrate panels affixed with adequate strain gauges were bent by employing a three-point bend loading experimental apparatus with two threaded rods, as shown in Fig. 1. Different stress levels can be obtained by adjusting the adjustable threaded rods. The value of the applied stress was accurately measured by the strain gauges, and then the corresponding curvature radius was approximately determined by recording the shape or displacement of the bent steel substrate. The distribution of stress on the whole bent coated panel with the curvature radius based on above bending test was simulated and evaluated by employing the finite element analysis software ANSYS, and an example of the stress distribution on the steel substrate with the restriction of displacement at the stress level of 200 MPa is as shown in Fig. 2. Finally, according to the qualified curvature radius, a series of PVC moulds were manufactured and then were validated or calibrated by the steel substrates affixed with adequate strain gauges again. All the mechanical states used in this study were in a plane stress state, under tension or compression, and the levels of the elastic stress were 0 MPa, 40 MPa, 80 MPa, 120 MPa, 160 MPa and 200 MPa (below the yield strength of Q235 steel), respectively.

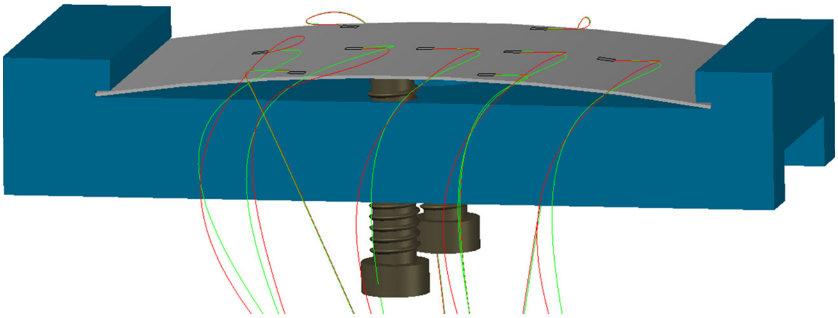

Fig 1. The three-point bend loading experimental apparatus with two threaded rods. Different stress levels can be obtained by adjusting the adjustable threaded rods.