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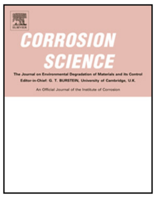

The influence of the chemically bonded interface between fillers and binder on the failure behaviour of an epoxy coating under marine alternating hydrostatic pressure

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ABSTRACT

The failure behaviour of epoxy resin-based modified mica (MM) coating has been investigated under marine alternating hydrostatic pressure (AHP). The results indicate that the chemically bonded interface forms between MM fillers and epoxy binder, which significantly enhances the compactness and the mechanical properties of coating by promoting the dispersion of fillers and reducing the defects of coating. The improvement of the fillers/binder interface weakens the permeation of water and the deterioration of coating structure which are caused by the drawing force of AHP. Hence, the performance of epoxy coating is promoted under AHP environment.

1. Introduction

With drastic consumption of global resources, the deep ocean has drawn more public attentions because of the abundance of marine resources. However, harsh and complex conditions of deep ocean environment pose an enormous challenge to the corrosion protection of exploration facilities. One of the major factors is the hydrostatic pressure varying with ocean depth [1,2]. Employing organic coatings is one of the most widely used methods for protecting metals from corrosion. Recently, some studies have focused on the organic coatings applied to deep ocean environment. Wang et al. [3] investigated the evolution of impedance models of epoxy coating/907A steel system at 25 atm hydrostatic pressure and proposed three equivalent electrical circuits for different immersion stages. Liu et al. [4] compared the failure behaviour of nano-SiO_2 fillers epoxy coating under hydrostatic pressure with that under atmospheric pressure, the results indicated that high hydrostatic pressure accelerated the failure of organic coating by promoting diffusion of water in the coating. They also [5] considered that high hydrostatic pressure changed the electrochemical behaviour of the coated steel and deteriorated coating protectiveness through accelerating water absorption and changing diffusion type.

Besides, another more realistic pressure condition is alternating hydrostatic pressure (AHP), which is common for machinery moving up and down in the ocean, such as the bathyscaphe. In previous study, the failure behaviour of an epoxy glass flake coating/steel system under AHP has been studied [6]. The results indicated that AHP deteriorated both interfaces in the system, including the coating/steel interface and the inorganic fillers/organic binder interface. The coating/steel interface was destroyed which led to the detachment of coating from the steel and the rapid spread of water at the interface. The deterioration of the fillers/binder interface increased the quantity of defects and promoted the transport of water in the coating. The weak parts of the coating/steel system are the two interfaces above, the improvement of these two interfaces is significant for prolonging the protective lifetime of the coating.

Inorganic fillers are an important part of the protective coatings. One of the main functions of inorganic fillers is to improve the barrier properties of the coating against electrolyte permeation [7–12]. The diffusion paths in the coating are effectively lengthened by the fillers, therefore the electrolyte has to reach the surface of substrate through more winding paths. However, the distinct differences of

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both physical and chemical properties between inorganic fillers and organic binder contribute to a bad interfacial compatibility [13]. Our previous studies indicated that a large number of defects on the coating surface such as pores were generated by the addition of inorganic fillers [4–6]. Moreover, high surface energy of inorganic fillers would form agglomeration which lead to the degradation of coating mechanical properties [14–16]. These reasons make the protective performance of the traditional coatings far from meeting the demand of the deep ocean application. According to the survey of application of the coatings in practical deep sea environment, the coatings which showed good protective performance in shallow sea often rapidly deteriorated and lost the protective function in deep sea, at least, it is the case in China. Our prior research also revealed that deep sea environment accelerated the failure of organic coating [4–6]. Many surface modification technologies of the inorganic particles have been extensively employed to change the physical and chemical properties of the particle surfaces, such as surface deposition method, coupling agent method, esterification method and surface grafting method [17–21]. A new idea which is to make modified fillers with surface grafting method has been initiated in our group. Applying the same epoxy resin to modify inorganic fillers. The modified fillers are then added into the epoxy resin binder to form the coating. During the cross-linking reaction, the same epoxy resin warrants a superior compatibility between the fillers and the coating polymer. The chemical bond will form at the fillers/binder interface. However, it is still uncertain whether the chemically bonded interface can effectively improve the combination ability of the interface and increase the protective properties of the coating, especially under AHP.

In this study, the failure behaviour of epoxy resin-based MM coating/steel system has been compared with that of epoxy resin-based unmodified mica (UM) coating/steel system under AHP. The coating involved in this work was a model coating system with a single component pigment, not a commercial product. Therefore, the preparation process of the coating did not entirely follow the industrial manufacture. However, the same preparation procedure for coatings in our lab was performed so that unbiased and objective experimental results can be provided. The compactness, mechanical properties and adhesion of the coatings have been studied by electrochemical impedance spectroscopy (EIS), gravimetric test, tensile experiment, pull-off adhesion test, scanning electron microscopy (SEM) observation and FT-IR spectra. The influence of chemically bonded interface between fillers and binder on the protective performance of epoxy coating under AHP has been discussed in details.

2. Experimental methods

2.1. Preparation of modified fillers

In this study, MM was produced for a good chemical bonding between the fillers and the E44 epoxy resin (bisphenol A, Wuxi Resin Factory, China) by surface grafting method. This surface modification technology are developed for many years, which has been reported in a series of literature [22–24]. According to this technology, we grafted epoxy group onto the mica surface, and the detailed procedures are as follows: the mica was dispersed in toluene with magnetic stirring, then the mixture was heated to 135 °C for 2 h in order to remove the adsorbed water molecules adequately. Adding toluene diisocyanate (TDI) to the mixture and keeping it in the reaction vessel. After this, dried E44 and toluene were added and the reaction was carried out at 90 °C for 2 h. The products were repetitively washed by acetone after the previous step to remove unreacted E44 epoxy resin. Finally, the mica-E44 particles were obtained by drying in the vacuum condition. According to the procedures, the schematic diagrams of the chemical reactions are shown in Fig. 1. FT-IR analysis of E44, UM and MM (mica-E44) were carried out to identify whether mica was indeed coupled with the epoxy group or not. Fig. 2 shows that the peaks at about 2922 cm^{-1} and 2970 cm^{-1} are related to the $-CH_2$ and $-CH_3$ anti-symmetric stretching vibrations. The peak at around 1509 cm^{-1} is assigned to the vibrations associated with the C=C of benzenoid (B) ring. The peak at around 915 cm^{-1} is assigned to the vibrations associated with the epoxy group. These results suggest that the chemical bonding has formed between mica and the epoxy group, and the existence of chemical bonds can effectively prove our idea. Some characteristic peaks of epoxy group are not intense in the plot of mica-E44, which is mainly because not all of the fillers have reacted with the epoxy resin.

2.2. Sample preparation

UM and MM were separately added as fillers into the epoxy resin to prepare two epoxy resin based coatings. Both coatings consisted of E44 epoxy resin as the binder, polyamide (TY-650, Tianjin Yanhai Chemical Co., Ltd., China) as the curing agent and xylene as the solvent, with a mass ratio of 1: 0.8: 0.4 for stoichiometric reaction. The amount of the lamellar mica particles (thickness: 2–5 μm, diameter: 10–15 μm, Shunjia Minerals Factory, China) is 20% in mass for both UM and MM coatings. The two paints were stirred separately by a commercial magnetic stirrer for 0.5 h, then let them stand for 0.5 h to partially cure before brushing.

Two kinds of samples were prepared, coating/steel sample and free film sample. The coating/steel sample was prepared by brushing the paints on the substrate, then it was cured in an oven with the following conditions: 40 °C for 4 h, 60 °C for 20 h, and then room temperature (25 °C, 30% RH) for 7 days. The substrate was hot-rolled steel sheets with composition (in wt.%): 4.67 Ni, 0.60 Cr, 0.46 Mo, 0.065 V, 0.54 Mn, 0.076 C, and Fe balance. The steel sheets were ground to 240-grit finish and then degreased and dewatered with a commercial acetone and ethanol, respectively. The surface roughness of the steel substrate, Ra = 15–20 μm. Ra is defined as the profile arithmetic average error, which is the most widely used one-dimensional roughness parameter. The dimensions of the steel substrate were 20 mm × 20 mm × 2 mm for electrochemical experiment and 30 mm × 30 mm × 2 mm for adhesion test. The steel substrate for electrochemical experiment was welded to copper wire firstly. Then put them on the bottom of plastic vessels and inject the epoxy resin paint into the vessels for curing. The frontage of substrate was ground with the exposed area of 4 cm^2, and the other sides were sealed by epoxy resin. Finally, brush the paints on the frontage of substrate, and the electrochemical specimens were finished. The free film sample was made by brushing the paints on a clean silica gel plate. After being cured in an oven with 40 °C for 4 h, the film was peeled off from the plate and was cut into two different dimensions for different purposes. One of the dimensions was 50 mm × 50 mm × 0.2 mm which was prepared for gravimetric experiment. Another was cut into a special dimension which was used for tensile test, and the details of the dimension can be found in Ref. [5]. Then the film continued to cure at 60 °C for 20 h and at room temperature (25 °C, 30% RH) for 7 days.

The coating thickness was measured by a hand-held electronic gauge (PosiTector 6000, Defelsko) according to ISO 2808 standard procedures [25], and an average thickness of 200 ± 20 μm was obtained.

2.3. Experimental setup

The experiments were performed in an Automatic Deep Sea Simulation System, and details of the setup have been reported in Ref. [6]. The simulated AHP condition was obtained by the alter-