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Modification effect of high-temperature ball milling condition to iron oxide corrosion protective coating

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ABSTRACT

Grinding time and grinding rotation speed of iron oxide surface modification using high-temperature ball milling method were studied on the basis of the optimal grinding temperature. The modification effect of iron oxide improved with the grinding time extended from 1 h to 5 h and with the grinding rotation speed increased from 300 r/min to 516 r/min. The content of iron oxide to the corrosion performance of epoxy coatings was also investigated. The results show that the modified iron oxide can improve the corrosion performance of epoxy coating, and the optimal content of modified iron oxide in epoxy coating is about 10 wt.%.

1. Introduction

Pigments are often used in epoxy resin coatings to enhance the barrier performance and corrosion protective property [1–3]. Fe_2O_3 as one of anticorrosive pigment can reduce the permeability of oxygen, water and chloride ions in coatings, protecting coatings from degradation by sunlight, corrosive medium [4,5]. Small concentrations of nano-Fe_2O_3 can improve the corrosion resistance of the coating [6]. Jin [7] studied the anti-corrosion mechanism of different content nano-Fe_2O_3 in epoxy resin coatings on the surface of magnesium. Whereas nano-Fe_2O_3 particles disperse badly in the epoxy coating, and they have poor compatibility with the epoxy resin, resulting in the existence of micro-voids in polymer matrix/nano-particles interface [8]. Sathiyanarayanan [9] modified Fe_2O_3 with polyaniline by using the chemical oxidative method, and found that the coating with modified Fe_2O_3 offered more effective protection than the coating with unmodified Fe_2O_3. According the literatures motioned above, the compatibility and dispersibility of Fe_2O_3 in epoxy resin were important for anticorrosive property of coating. In order to improve the compatibility and dispersibility of Fe_2O_3 in epoxy resin, the Fe_2O_3 particles should be modified properly.

In general, high-energy ball milling treatment is utilized to modify the crystal structure and microstructure of materials [10,11], to improve the compatibility and dispersion of organics and inorganics [12–16], and to promote grafting reactions [17–19] as a consequence of strong compressive and shear forces. By using high-energy ball milling, some researchers [20–22] synthesized nano-structures which could not be realized by chemical approach. The corrosion resistance of copper/polyurethane (Cu/PU) coating was improved via the surface modification of Cu with silver by using a ball-milling method [23]. Many researchers [24–26] achieved the phase transfer and grain refinement of Fe_2O_3 powder at room temperature by using high-energy ball milling. Then, we succeeded in modifying iron oxide with epoxy resin by using high-energy ball milling treatment in the early stage of our work [27]. Meanwhile, we explored the effect of grinding temperature on iron oxide surface modification, and got the optimal grinding temperature [28].

Other grinding conditions were also considered in our research like grinding time and grinding rotation speed. We wondered how could those factors affect the modifying of iron oxide using epoxy resin? So, in this paper, we studied the modifying effects of grinding time and grinding rotation speed to iron oxides. Furthermore, the content of iron oxide in epoxy coating was also investigated for corrosion protective property.

2. Experimental

2.1. Experimental process

The iron oxide, epoxy resin (E-44), other reagents and materials

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used in the experiment were described as the same as our previous paper [27]. The iron oxide used in this paper was purchased from paint market with particle size of 350 nm. The epoxy resin and curing agent polyamide (PA) were both purchased from Phoenix Resins Inc. (Wu xi, China), the commercial numbers of the epoxy resin (E44) was 6101, and the epoxy equivalent was 0.44 mol/100 g. The solvent used to dissolve epoxy resin and curing agent polyamide was a mixture of dimethylbezene and *n*-butyl alcohol with weight ratio of 7:3. Carbon steel panels (60.18% C; 60.050% S; 60.045% P, in mass%) used as the substrates were grit blasted (near white blast).

The high-temperature planetary ball milling [27] was used to modify iron oxide. A temperature-regulating device and electrical heating system combined with the planetary ball milling formed the high-temperature planetary ball milling. The modification process of the iron oxide was described as [27], the mixture of iron oxide and epoxy resin with mass ratio of 1:1 underwent grinding tests in the high temperature planetary ball milling. Agate grinding medium with ball to the mixture ratio of 5:1 was used in this grinding work. The grinding temperature was chosen as 120 °C, grinding time was chosen with 1 h, 3 h, 5 h and 7 h, and the grinding rotation speed was chosen with 300, 400, 516 and 576 r/min which was almost the maximum speed of our ball milling machine. After grinding, the mixture slurry was filtered repeatedly at least 3 times with the solvent, and extracted with the solvent for 24 h, then dried in a vacuum oven at 60 °C for 24 h. If epoxy resin grafted on iron oxide surface, epoxy resin cannot be washed away from the iron oxide surface.

In this research, epoxy resin coating with the pigment content of 5, 10, 20 and 30 wt.% was formulated, respectively. The preparation process of the iron oxide/coating was described in [27,28]. The resin added different content of iron oxide power was mixed with the calculated amounts of polyamide and solvent, and then applied to the ground carbon steel panels. The weight ratio of epoxy resin to curing agent polyamide was 2:1. Coatings were cured at 30 °C for 24 h, and then cured at 60 °C for 24 h. The thickness of the dry coating was 140 ± 10 μm. The coating containing 5, 10, 20 and 30 wt.% unground iron oxide powder was called 5, 10, 20 and 30-unmodified coating, the coating containing 5, 10, 20 and 30 wt.% ground iron oxide powder was called 5, 10, 20 and 30-modified coating, respectively. Meanwhile, the coatings were painted onto the silicon rubber board, and peeled off from the silicon rubber board after dry, then tailored in square with a certain area to measure water absorption of the coatings.

2.2. Characterization of iron oxide and corrosion resistant properties of the iron oxide/epoxy coatings

The particle size and sedimentation test were performed as paper [27]. The ground iron oxide slurry used for particle size and sedimentation test was dispersed in solvent by using ultrasound treatment for 10 min to produce suspension. The particle size was measured with NICOMP™ 380ZLS. Sedimentation test was performed in small bottles. The modification effect of the iron oxide powder was investigated using thermogravimetric analysis (TG, Q200). The infrared spectra of the ground powders were recorded on IR 200 spectrometer in KBr medium at ambient temperature in the region of 4000–500 cm^{-1}.

The corrosion resistant properties of the coatings were tested using water adsorption, adhesion measurement, and electrochemical impedance spectroscopy (EIS) measurement. Water adsorption and adhesion measurement of the coatings were described as the same as paper [28]. Weight change of the coating was used to represent water adsorption of the coating immersed in a 3.5% sodium chloride solution. Water absorption was calculated using the following relation:

$$M = \frac{m - m_0}{m_0} \times 100\% \quad (1)$$

where M is the water absorption in percent, m_0 is the initial weight, and m is the weight of the film after immersion for some time. Five films of each series were measured to calculate average data of the water adsorption, and the weight was measured to an accuracy of ± 0.01 mg. Adhesion strength was determined by PosiTest Pull-Off Adhesion Tester (DeFelsko Corporation, USA). The adhesion measurements were performed during exposure in a 3.5% sodium chloride solution at ambient

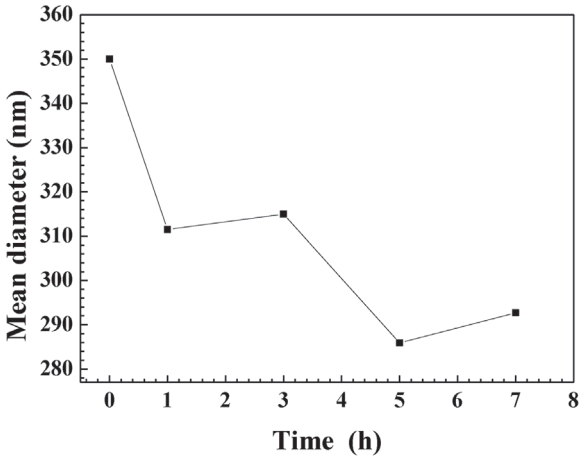

Fig. 1. Changes of iron oxide particle sizes with grinding time.

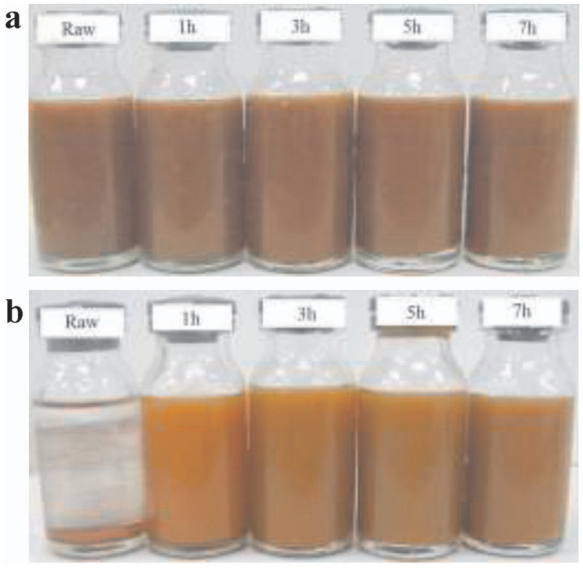

Fig. 2. Sedimentation of iron oxide at different grinding time: (a) 0 day, (b) 10 days.

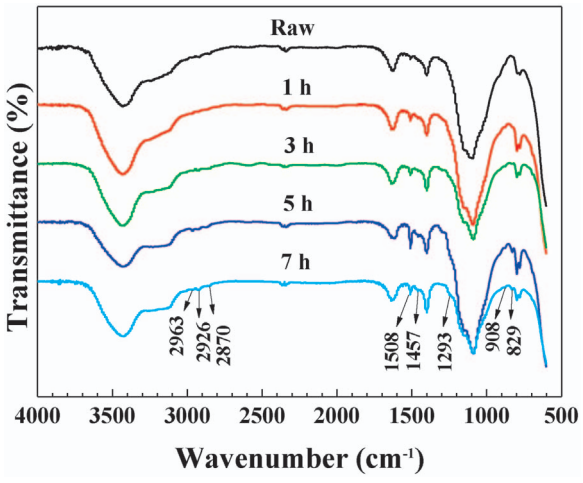

Fig. 3. FT-IR spectra of iron oxide at different grinding time.