Corrosion Science 53 (2011) 161–167

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Corrosion resistance of lamellar aluminium pigments coated by SiO_2 by sol–gel method

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ARTICLE INFO

Article history:
Received 25 June 2010
Accepted 3 September 2010
Available online 16 September 2010

Keywords:
A. Aluminium pigment
B. Erosion
C. Paint coatings

ABSTRACT

The aluminium pigments were coated with SiO_2 by sol–gel method to improve their stability. The effects of formulation factors, such as medium of reaction, adding sequence of catalyst and number of coating, were investigated. The stability of the coated aluminium pigments in acid was examined by measuring the hydrogen generation amount. It was found that the coating layer formation is due to the condensation of tetraethyl orthosilicate (TEOS) to form a dense 3D cross-linked layer on the surface of aluminium. The optimized sequence of adding catalysts would be hydrochloride first, then ammonia. Stability tests confirmed that the aluminium pigments have better corrosion resistance after coating with SiO_2.

1. Introduction

Lamellar aluminium pigments have been widely used in plastic, printing, ink, dope and painting industries for many years due to their shiny appearance, excellent mechanical properties, and lower price [1,2]. The lamellar aluminium pigments usually are very thin, with thickness of about 0.2 μm, and its diameter of 10–50 μm. The aluminium pigments are produced by grinding atomized aluminium powder in a ball mill with a solvent. A subsequent filtration makes the ultra-thin lamellar aluminium flakes exist in the form of paste with volatile organic compounds [3–5].

The utilization of aluminium pigments is restricted in some applications by its active chemical properties, agglomeration form, and incompatibility with organic matters. Further, the reactions of aluminium pigments in aqueous acidic or alkali painting environments cause severe corrosion, which results in generation of flammable hydrogen gas. The main corrosion reactions are:

$$2Al + 3H_2O \rightarrow Al_2O_3 + H_2 \uparrow \quad (1)$$

$$2Al + 6H_2O \rightarrow 2Al_2(OH)_3 + 3H_2 \uparrow \quad (2)$$

$$2Al + 6HCl \rightarrow 2Alcl_3 + 3H_2 \uparrow \quad (3)$$

The hydrogen evolution from the corrosion reaction may lead to dangerous pressure build-up in containers. Therefore, corrosion inhibition is necessary. There are various inhibition methods described in the literatures [6,7], which can be divided into three categories: organic modification [8–15], inorganic coating [16–20] and organic–inorganic mixed coating [21–22]. However, commonly established methods (chromate treatment and stabilization with organic phosphorus compounds) show some disadvantages like reduced inter-coat adhesion after humidity test (organic phosphorus compounds). The chromate treatment is also undesirable because chromium (VI) is carcinogenic. The investigation of alternative and especially non-toxic methods for the inhibition of the corrosion reaction becomes critical for the success of using aluminium pigments.

A variety of surface coating technologies, such as heterogeneous flocculation, copolymerization, chemical vapor deposition, mechanical milling method, thermal decomposition–reduction, have been developed to insulate the aluminium pigments from the corrosive medium. So far, the sol–gel process shows very promising results – it creates coating layers with high purity and good chemical uniformity at low temperature. In addition, the adhesion between sol–gel coatings and metal or metal oxide surfaces is especially favorable because covalent bonds are formed between the metal surface and the coating film.

Recently, the coating of SiO_2 on the surface of aluminium flakes by the sol–gel method with tetraethyl orthosilicate (TEOS) was reported [17,18,21,23]. In general, the aluminium flakes are originally covered with some organic solvents during the manufacturing process [24]. If there is no pre-cleaning step, the solvent on the surface of the aluminium flakes could have negative effect on the corrosion resistance function of the coatings. For example, SiO_2 can not be coated to the surface of the aluminium flakes due to the presence of organic solvents. Few literatures, however, can be found on the topic of aluminium pre-treating before the coating process. In this paper, the aluminium flakes were washed with acetone in order to remove the impurity. Then, the aluminium pigments were coated

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doi:10.1016/j.corsci.2010.09.012

by TEOS in a sol–gel process. The effects of different medium of reaction, the sequence of adding catalyst, and multi-layer coatings, on corrosion resistance were studied.

2. Experimental

2.1. Pretreatment of aluminium

The lamellar aluminium pigments (median particle size of 30 μm) were washed with acetone, then filtered and dried. Raw materials used in the experiments are listed in Table 1.

2.2. Single coating process of SiO_2 on aluminium pigments

First, 4 g of lamellar aluminium pigments and 100 ml of ethanol were put into a three-neck round bottom flask. Second, three solutions were prepared: solution A (3.9 ml $NH_3{\cdot}H_2O$ + 20 ml H_2O + 20 ml TEOS), solution B (1.95 ml HCl + 19 ml H_2O + 20 ml TEOS) and solution C (12 ml TEOS + 10 ml EtOH). Stir the solution in the flask while solution B and C were added into it, then solution A was added. The solution was kept under stirring at 40 °C for 10 h. Three days later, the precipitate was filtered and washed with distilled water, and then it was washed twice with ethanol. Finally, the wet cake was dried in an oven at 100 °C for 12 h.

2.3. Characterization and testing

Fourier transformation infrared (FTIR, QB-08) measurements were used to characterize the functional groups of the coated aluminium flakes. The samples were ground with dried potassium bromide (KBr) powder, and tablet pressed into a disc. The KBr disc was subjected to analysis by an IR spectrophotometer. X-ray diffraction (XRD, D/Max 2550) spectra were performed to show the element characteristics of the coating layer. The scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) analysis were done with a FEI Sirion200 FEG SEM and a Gensis EDS, respectively. BET method was used to measure the specific surface areas of the samples by nitrogen adsorption at −196 °C. The transmission electron microscope (TEM, FEI Tecnai G^2 20ST) method was used to characterize the approximate thickness of coating layer. Thermogravimetric (TG) analyses and differential scanning calorimetry (DSC) were performed under atmospheric condition to test the thermal stability of the samples by using STA449C/3/MFC/G simultaneous thermal analysis at a heating rate of 10 °C/min.

The effectiveness of the coating was estimated by measuring the generation amount of hydrogen in an acid. The test was carried out with 0.5 g of the coated or uncoated aluminium pigments that were well dispersed in 40 ml HCl (1 mol/L) solution. The suspension was stored at glass bottles at room temperature for several hours.

Table 1
Raw materials used in the experiments.

Materials	Grades
Aluminium pigments	–
Acetone	⩾99.5%, AP
Ethanol	⩾99.7%, AP
Isopropanol	⩾99.7%, AP
1-butanol	⩾99.0%, AP
Tetraethyl orthosilicate (TEOS)	SiO_2 ⩾ 28.0%, AP
Ammonia ($NH_3{\cdot}H_2O$)	NH_3 25–28%, AP
Hydrochloric acid (HCl)	HCl 35–37%, AP

3. Results and discussion

3.1. Effect of the medium of reaction on coating quality

Usually, alcohol, not water, is selected as the medium of reaction in the sol–gel method because TEOS can react with H_2O. Moreover, TEOS can be dispersed uniformly in alcohol. In order to evaluate the effect of media, three media: isopropanol, 1-butanol and ethanol, were selected in the sol–gel experiments.

Fig. 1 shows the hydrogen generation trends of uncoated and coated aluminium pigments in 1 mol/L HCl aqueous solution. As can be seen, 556.4 ml of hydrogen in total was generated by 0.5 g uncoated lamellar aluminium after 10 h, while SiO_2 coated aluminium released almost no hydrogen when the medium of reaction was 1-butanol. Apparently, the coating layer on the surface of aluminium pigments prevented aluminium from reacting with the corrosive media, and it also indicated that 1-butanol was the best choice of medium of reaction among the three. This can be explained by the hydrophile–lipophile balance number of 1-butanol, which can disperse on the oil–water interface, being conducive to the formation of low interfacial tension so as to promote the combination of SiO_2 and aluminium.

3.2. Effect of catalysts

Both acid and alkali can be used as catalysts in the sol–gel processing. As can be seen in Fig. 2, sample D4 (adding hydrochloride first and ammonia later) had the least amount of hydrogen generation (38.7 ml), and sample D3 (adding ammonia first and hydrochloride later) yielded 133.7 ml hydrogen. However, both sample D1 (adding ammonia separately) and D2 (adding hydrochloride separately) had obviously inferior corrosion resistance. It might be explained that the mixed catalysts can form a dense and even coating than single catalyst. It was also found that less hydrogen would be generated during the quality test if hydrochloride was added prior to ammonia. That could be explained by the relationship between catalyst and hydrolysis-condensation of TEOS.

The mechanism of hydrolysis-condensation of TEOS is directly affected by the category of catalysts. Therefore, the structure of SiO_2 coated on the surface of aluminium pigments and the coating quality would be different. TEOS would condense rapidly and hydrolyze slowly in the condition of acid, while it will experience

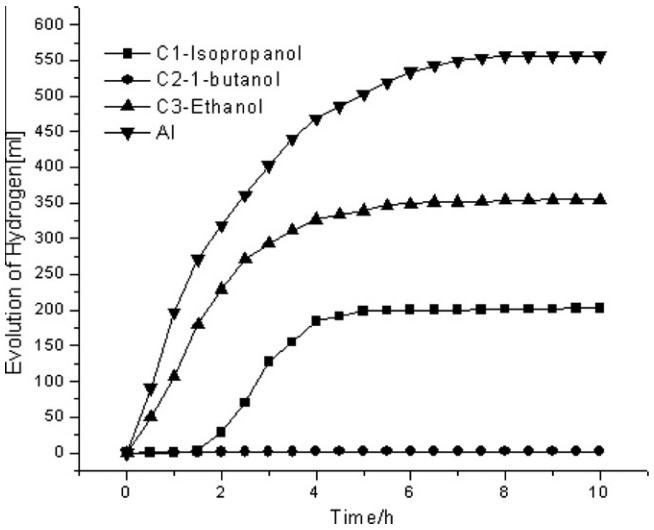

Fig. 1. Relationship between volume of hydrogen and different medium of reaction (Amount of sample: 0.5 g).