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A novel antiscaling and anti-corrosive polymer-based functional coating

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ABSTRACT

Carbon nanotubes (CNTs), as a carrier of diethylenetriaminepenta(methylphosphonic acid) (DTPMPA), combining with flake zinc and PVDF powders, were used to fabricate a novel organosilicon epoxy resin-based (EP) composite coating (EP/iDCNTs/Zn/PVDF) for antiscaling and anti-corrosion purposes. Compared with EP coating, the EP/iDCNTs/Zn/PVDF composite coating exhibited unique antiscaling properties with the $CaCO_3$ deposition on the coating surface decreased by 81.6%. It was mainly because the coating surface contains DTPMPA, and Zn^{2+}released by corrosion of Zn powder, which jointly inhibited the deposition behavior of $CaCO_3$. Meanwhile, the fabricated composite coating hardly adhered by $CaCO_3$ crystals which was due to its higher hydrophobicity. Moreover, anti-corrosion tests proved that the prepared composite coating's impedance modulus was about 2 orders higher than that of the EP coating. This was ascribed to the improving shielding effect of fillers and high hydrophobicity of coating, preventing the water and oxygen molecules from penetrating into the composite coating.

1. Introduction

Since various kinds waste water produced by petrochemical industries contains abundant corrosive and fouling ions such as Cl^-, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^-, metal pipelines and equipments are inevitably suffered from grievous contamination and corrosion dilemma in the process of transporting wastewater, which reduces the service life and efficiency of pipelines, and leads to the cost increase of equipment and operating [1–3]. Therefore, antiscaling and anti-corrosion technologies are imperative approaches to overcome these problems [4–6].

At present, a tremendous effort has been made to decrease the deposition of scaling on metal surface [7–9]. Using scale inhibitors is one of the commonly methods in scale inhibition technology. Zahra Kiaei found that Ca-DTPMP inhibitors can effectively delayed the precipitation of $CaCO_3$ and increased the final Ca^{2+} concentration in bulk solution [10]. R. Ketrane's examined the inhibitory effect of commercial inhibitors on precipitation of $CaCO_3$ in hard water, and results showed phosphonate had the best inhibitory effect on $CaCO_3$ [11]. These researches employed the traditional methods by adding scale inhibitors into the scale solution, to achieve the purpose of antiscaling. However, it cannot be ignored that the disadvantage of traditional methods was that the inhibitor molecules in the solution that may leave rapidly in the flowing system, reducing the contact time between the scale inhibitors and the metal surfaces. As a result, it leads to low scale inhibition efficiency, high cost of subsequent separation and the negative effects on the environment. Anti-scaling coating technology can effectively prevent the scaling on metal pipeline surface. Therefore, it is an attractive proposition to uniformly immobilize the scale inhibitors on the coating through the carrier for antiscaling.

Recently, zinc powders have got rapidly development and application in coatings due to its antiscaling and anti-corrosion properties [12–14]. The unique abilities are ascribed to the release of Zn^{2+} on coating surface, which can effectively inhibit the growth rate of $CaCO_3$ scaling and change the $CaCO_3$ morphology on the coating surface [15,16]. Wang et al. [17] prepared a composite coating by blending 50% zinc-graphite alloy powders with silicone epoxy resin for antiscaling in geothermal water. Although the composite coating effectively inhibited the deposition of $CaCO_3$ scaling, the excessive addition of inorganic particles decreased the adhesive capability of the coating owing to particle aggregation [18]. Beyond that, it had been shown that the superhydrophobic coatings with low surface energy substances like F and Si elements can also effectively reduce fouling adhesion on the coating

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surface. Li et al. [19] prepared a superhydrophobic coating with antiscaling properties by electrodeposition, solution soaking, and fluorination modification. Dowling et al. [20] evaluated the antifouling properties of different atmospheric plasma deposition coatings. Results indicated the adhesion of the $CaCO_3$ scaling to the TCFS (2, 4, 6, 8-Tetramethylcyclotetrasiloxane (TC) and 1H, 1H, 2H, 2 H-Perfluorooctyltriethoxysilane (FS) mixtures) coated steel surface reduced dramatically compared with that of the uncoated steel. Superhydrophobic coatings with good scale inhibition and corrosion protection performance were mainly rely on air cushion forming by bubbles and the relatively low surface energy [21,22]. Nevertheless, the durability of superhydrophobic coatings is always sacrificed in practical applications [23]. Most superhydrophobic surfaces will spontaneously turn into water-wet status owing to the liquid impregnation caused by pressure or temperature under continuous dynamic or static water flow conditions [24,25]. That's an unavoidable shortcoming for long-term scale inhibition and anti-corrosion of superhydrophobic coatings.

With comprehensive considering the above-mentioned issues, a novel antiscaling and anti-corrosion EP/iDCNTs/Zn/PVDF composite coating was designed and fabricated by a simple one step spraying technique. Firstly, acidified CNTs were used as the carriers of scale inhibitor to evenly fix antiscaling agent DTPMPA on the surface. In addition, for the first time, the modified CNTs was added to the polymer coating in combination with metal powder (zinc powder) and low surface energy substance (PVDF) for long-term antiscaling and corrosion protection of metals. The use of small amount of fillers greatly improved the scale resistance and corrosion resistance of epoxy coating without affecting the adhesion. Comparing with the commercial organosilicon epoxy resin coating, the EP/iDCNTs/Zn/PVDF composite coating manifested excellent antiscaling and anti-corrosion performances, which were discussed in detail later. This paper has significance references for antifouling and anti-corrosion, especially for equipments with requirements of antiscaling and anti-corrosion simultaneously, such as heat exchangers, various evaporators, geothermal mining pipelines and some marine devices.

2. Experiment

2.1. Materials

Commercial W304 organosilicon epoxy resin (EP) was manufactured from Hubei Xinsihai Chemical Company, China. Flake zinc powder (Dacromet level) was supplied by Jiangsu Curriculum Colored memorial Book Materials Co., Ltd. CNTs were bought by Guangdong Tianxin Reagent Factory of China. Commercial PVDF powders FR904 (average diameter of 25 µm, number-average molecular weight is 380,000 g/mol.) were obtained from Shanghai 3F Co., Ltd. (China), and DTPMPA ($C_9H_{28}O_{15}N_3P_5$) was purchased from Xuzhou Yuxin Chemical Technology Co., Ltd. Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, AR) was bought from Huadong Reagent Factory, Shenyang, China. Sodium bicarbonate ($NaHCO_3$, AR) was provided by Heng xing Chemical Reagent Factory of Tianjin (China). Sodium chloride (NaCl, AR) was purchased from Aladdin Reagent Co., Ltd (China). Q235 steel plates (C, Si, Mn, S, P) were used as base metal for the coatings during the experiment, all reagents were used analytical grade without further treatment.

2.2. Preparation of composite particles

Distilled water and DTPMPA with the volume ratio of 10:1 were added in a beaker, then an appropriate amount of acidified carbon nanotubes (CNTs) were ultrasonically dispraised in above solution for 2 h to form a uniform solution. Finally, the above mixture was kept at 80 °C in vacuum drying oven until solvent volatilizing was completed. The product of CNTs encapsulated by DTPMPA was abbreviated as iDCNTs.

2.3. Process of preparation epoxy-silicone resin coatings

The steel plate was polished with 800 mesh SiC papers, and then the metal substrate was ultrasonic treated for 30 min with absolute alcohol to remove grease on the surface. The 33.3% silicone epoxy resin was blended with 66.7% ethyl acetate to form a uniform solution follow by sprayed onto the metal base plate using an air spray gun at a pressure of 0.6 MPa. Thereafter, the sample was kept at 80 °C for 30 min and cured in oven at 200 °C for 3 h.

2.4. Preparation of EP/iDCNTs/Zn/PVDF composite coatings

Ethyl acetate and xylene solvent were used to mix silicone epoxy resin and filler (3% iDCNTs, 3%iDCNTs/10%Zn, 3%iDCNTs/10%Zn/15%PVDF) to prepare three kinds of coating precursors, which were separately sprayed on steel plates. The process of metal base plate processing and coating curing process were the same as for pure epoxy-silicone coating. The average thickness of all coatings was 85–90 µm.

2.5. Formation of calcium carbonate on coating's surface

Oversaturated calcium carbonate solution consists of $Ca(NO_3)_2{\cdot}4H_2O$ and $NaHCO_3$ solutions. As the $Ca(NO_3)_2/NaHCO_3$ solution includes supersaturated $Ca^{2+}$and HCO_3^-, when they mixed together, HCO_3^{-1} will instantly react with Ca^{2+} as soon as it becomes CO_3^{2-} to form $CaCO_3$ thus fouling in the bulk solution and on the specimens surface (Eq. (1)).

$$Ca(NO_3)_2 \cdot 4H_2O + 2NaHCO_3 \rightarrow CaCO_3 + 2NaNO_3 + 5H_2O + CO_2 \uparrow \quad (1)$$

There were two specific steps to test the fabricated coatings' antiscaling performance: I. Dispersed 3.5422 g $Ca(NO_3)_2{\cdot}4H_2O$ into 250 mL distilled water to form an uniform solution. Then the prepared coatings were vertically immersed into the $Ca(NO_3)_2{\cdot}4H_2O$ solution. II. 250 mL $NaHCO_3$ solution with a concentration of 10.08 g/L was slowly added into the $Ca(NO_3)_2{\cdot}4H_2O$ solution, then the above mix solution was heated in the thermostatic water bath at 60 °C. After a period of time, the samples were taken out slowly and gently rinsed with a small amount of distilled water then dried in a drying oven at 100 °C until the solvent volatilized completely.

2.6. Characterization

The surface properties of modified materials were characterized by Fourier transform infrared spectroscopy (FT-IR). Scanning electron microscopy (SEM) was utilized to investigate the morphology of calcium carbonate deposited on the surface of the coating. The shape of calcium carbonate on the coating was measured by X-ray diffraction (XRD). The corrosion resistance of the coating was examined in 3.5 wt.% NaCl solution using the electrochemical workstation (LK2010). A conventional three-electrode cell was used in this test, including coated steel specimens with an exposed area of 7 cm^2 served as working electrode, saturated calomel electrode as reference electrode and Pt wire as counter electrode. The impedance tests were carried out at a constant open circuit potential. The experiment was performed in frequency range of 100 kHz to 0.01 Hz, amplitude of 10 mV. All tests were implemented in a Faraday cage to minimize noise interference. Meanwhile, via neutral salt spray test in a salt spray chamber, according to ASTM B 117 procedure, was used to visually judge the corrosion resistance of the coatings.