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Facile fabrication of antiwax conversion coatings based on water film theory

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ABSTRACT

Wax deposition is a detrimental problem that happens during the crude oil production and transportation. To inhibit wax deposition, a conversion coating with excellent antiwax property is developed using a quite simple and environmentally friendly method. The surface morphology, composition and wetting behaviors were characterized by SEM, EDS, FTIR and contact angle meter. A possible mechanism of antiwax is proposed, which can be calculated from water film theory. Due to the simple fabrication and excellent performance, this conversion coating is expected to widely apply in petroleum industry.

1. Introduction

In the modern society, crude oil plays a very important role for the wide application in energy, synthetic and many other areas. It is meaningful to ensure the adequate supply of crude oil. Wax deposition is a detrimental problem that happens during the crude oil production and transportation, which reduces the cross area and leads to short supply [1–3]. It is necessary and exigent to develop an efficient method for antiwax. Various methods have been employed to inhibit wax deposition, but most of them are either inefficient or costly [4–7].

Antiwax coatings have attracted much attention due to the simple fabrication and wide application. Many researchers have committed to develop efficient antiwax coatings in recent years [8–12]. But they are all complex and not environmental friendly. Chemical conversion method is a very simple and common method used in fabricating functional coatings. In previous work, chemical conversion coatings with different surface morphology and containing different elements were fabricated on carbon steels to prevent wax from deposition, and good performance was investigated [11]. But the conversion treatment would destroy the initial surface structure and reduce the corrosion resistance, which greatly limit practical applications. Phytic acid conversion is the most commonly used method in chemical conversion for low cost, easy fabrication and environmentally friendly [12]. However, nobody has employed it in antiwax applications.

In this work, phytic acid conversion coating was fabricated on Zn coated carbon steel to inhibit wax deposition. The Zn coating is fabricated by a simple electrodeposition method and the conversion coating comes from chemical conversion by directly immersing method. The prepared conversion coatings with porous hierarchical structure exhibit superhydrophilicity and underwater superoleophobicity. Excellent antiwax property was investigated in wax deposition test and the mechanism was discussed, which can be calculated to water film theory. Meanwhile, compared to the previous antiwax coatings, the conversion coating in this work is pretty simple and ecologic. This prepared conversion coating is expected to widely apply in petroleum industry.

2. Experimental procedure

The Zinc coating was prepared by electrodeposition method in the bath containing 2 M $ZnSO_4 \cdot 7H_2O$, 0.04–0.05 M $Al_2(SO_4)_3 \cdot 18H_2O$, 0.08–0.1 M $KAl(SO_4)_2 \cdot 12H_2O$ and 0.02 M surfactant. The conversion process was carried out in a phytic acid solution containing phytic acid, Na_2MoO_4, Na_2SiO_3 and TEA. All the chemicals used were of analytical grade without further treatment. A3 carbon steels with the size of 20 mm × 50 mm × 2 mm were used as substrates. The A3 carbon steels were polished by sandpaper and rinsed by deionized water, degreased by acetone,

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and then etched in the aqueous solution of 30% HCl for 30 s. The crude oil for wax deposition test was from Daqing Oilfield, which contains about 50 wt% water.

The wax deposition procedure was simulated in the laboratory using the method mentioned in the previous literature [13]. The quantitative determination of the wax prevention deposition weight, DW in abbreviation, was calculated according to Eq. (1):

$$DW = \frac{(W_t - W_0)}{S_0} \times 100\% \tag{1}$$

Where W_t is the weight of the wax deposited sample; W_0 is the weight of the original sample; S_0 is the surface area of sample [14].

A scanning electron microscope (SEM, JSM-7500F, JEOL Ltd., Japan) was used to observe the surface morphology of the obtained samples. The contact angles were measured using a contact angle meter (DSA 20, Krüss Instruments GmbH) on five different positions for each surface. The volume of an individual droplet in all measurements was 5 μL. The contact angles of crude oil on the samples underwater were measured by the underwater oil contact angle test (OCA). The samples were upside down in a water-filled glass container because the density of oil was lower than water. The images were also captured by the contact angle meter. Digital images of the samples before and after the wax deposition test were obtained by a digital camera (Olympus, E-PL1).

3. Results and discussion

It is widely known that the surface morphology greatly influence the antiwax property by affecting the wetting behaviors [15]. For pH value is important influence factor on the conversion coating morphology, the SEM images, CAs and OCAs digital images attained at different solution pH values were measured and shown in Fig. 1. Fig. 1 (A) shows the SEM image of the Zn coating, which present typical Zn particle shape with diameter of about 3–4 μm. The corresponding CA and OCA digital images were shown in Fig. 1 (E) (a) and (F) (a), indicating that the Zn coating present hydrophilicity with CA of about 52.5° and underwater oleophobicity with OCA of about 130.6°. The surface was covered by a layer of conversion coating after immersing in the conversion solution, as shown in Fig. 1 (B–D). The change of pH values leads to decrease of CAs and increase of OCAs, as shown in Fig. 1 (E) and (F). For the pH value close to 4.0, the coating surface was completely covered by conversion coating with porous hierarchical structure, which is prone to be hydrophilic. The prepared conversion coating shows superhydrophilicity with CA of 0° and superoleophobocity with OCA of about 162.3°. The consistency of hydrophilicity in air and oleophobicity underwater can be explained by Eq. (2) [16]:

$$\cos\theta_3 = \frac{\gamma_{o-g}\cos\theta_1 - \gamma_{w-g}\cos\theta_2}{\gamma_{o-w}} \tag{2}$$

Where $\gamma_{\text{o-g}}$ is the oil/gas interface tension, θ_1 is the contact angle of oil in air, $\gamma_{\text{w-g}}$ is the water/gas interface tension, θ_2 is the contact angle of water in air, $\gamma_{\text{o-w}}$ is the water/oil interface tension, and θ_3 is the contact angle of oil in water. For the superhydrophilicity and underwater superoleophobocity are the characteristic property of antiwax coatings [16], the pH value of 4.0 is suitable in this work.

To further investigate the composition of the prepared conversion coating, the EDS pattern and FTIR spectrum were measured and the results were shown in Fig. 2. Fig. 2 (A) shows the EDS pattern of the conversion coating, indicating that O, P and Zn are detected. Vibration bands at 1002 cm^{-1} and 836 cm^{-1} in the FTIR spectrum (Fig. 2 (B)) are associated with the P–OH and C–P–O stretching bands in phytic acid, respectively. The broad vibration band at 1076 cm^{-1} would be characteristic of P=O and the intensive vibration bands at 3271 cm^{-1} is associated to OH in phytic acid. The results of EDS pattern and FTIR spectrum illustrate that after immersing in phytic acid, a layer of conversion coating was fabricated on the specimen. According to the previous literature [12], the formation for the conversion coatings can be speculated as follows:

$$RH_{12} + Zn^{2+} + 2H_2O \leftrightarrow RH_{10}Zn + 2H_3O^+ \tag{3}$$

To further investigate the antiwax property of the prepared conversion coatings, wax deposition test was carried out and the results were shown in Fig. 3. Fig. 3 (A) shows that the wax

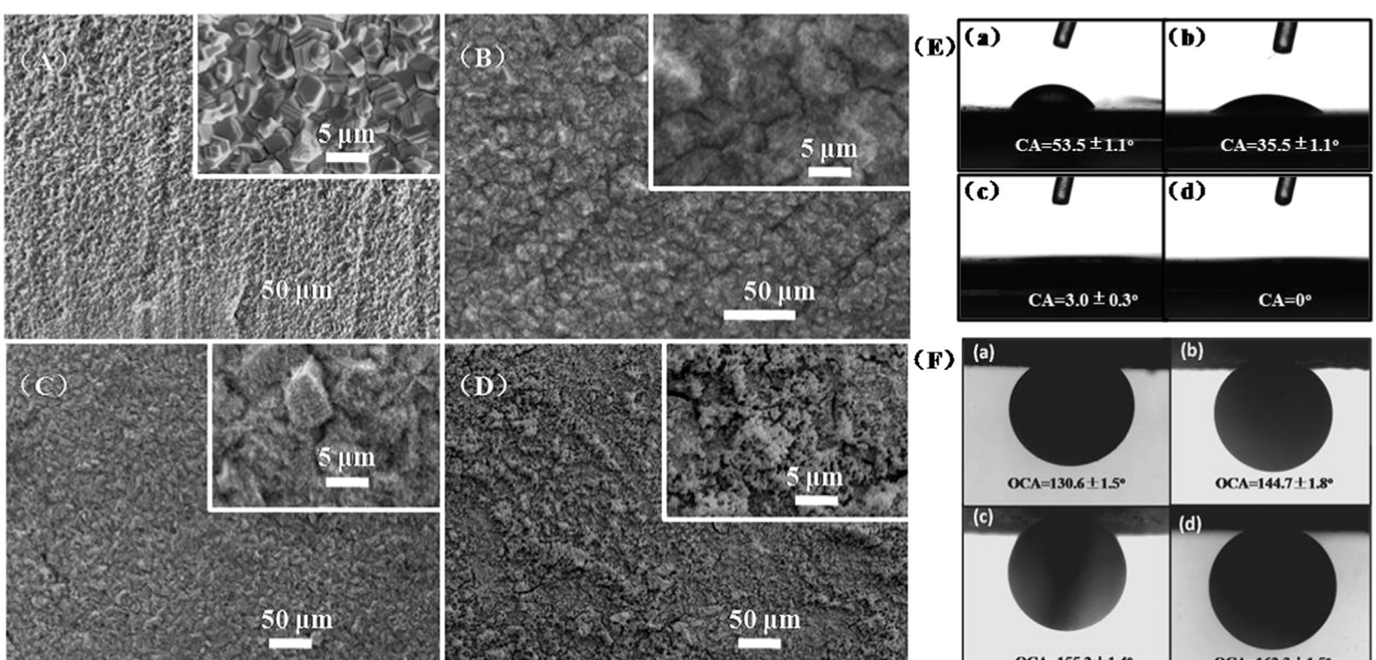

Fig. 1. SEM images of (A) Zn coating and prepared conversion coatings attained at different pH values: (B) 2.0; (C) 3.0 and (D) 4.0; (E) Digital images of contact angles of the corresponding conversion coatings in (A), (B), (C) and (D); (F) Digital images of underwater oil contact angles of the corresponding conversion coatings in (A), (B), (C) and (D).