AN EVALUATION OF NI-P AND NI-P/NANO-SIO₂ COATINGS ON SWEET CORROSION OF API-5L-X70 PIPELINES STEELS

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Carbon and low alloy steels are the most commonly used construction materials for oil and gas pipelines. In order to improve their performance, various types of coatings are frequently applied on them. Electroless nickel composite coatings containing nano-particles are widely used on steel substrates. In this paper, CO₂ corrosion of X70 carbon steel coated with Ni-P and Ni-P-nanoSiO₂ in 3%Wt NaCl electrolyte, saturated with CO₂ at 85°C and pH 6.5 in 1bar CO₂ pressure for 72 h, was investigated and the results were compared against each other. SEM and XRD techniques were used for investigating the corrosion products morphology and composition, respectively. In addition, the corrosion process was studied using EIS technique. The experimental results showed that the formation of FeCO₃ protective film on coated samples was limited. Moreover, the addition of SiO₂ nano-particles to Ni-P coating improved corrosion resistance of the substrate, which also showed the ability of nano-particle addition to the Ni-P coating in decreasing the corrosion rate.

Keywords: CO₂ corrosion; electroless Ni-P/nano-SiO₂; FeCO₃ film; Electrochemical impedance spectroscopy.

1. Introduction:

CO₂ corrosion (sweet corrosion) is one of the most important problems in the oil and gas industries which cause many failures in the pipelines and equipments^{1,2}. These pipes were made from low alloy carbon steels. These kinds of steels can be protected by two methods: (i) by precipitating iron carbonate layer on the surface, (ii) by depositing a metallic coating such as electroless coating method.

(i): Under special circumstances Iron carbonate (FeCO_3) can precipitate as a layer on the steel surface. This layer can be protective and decrease the rate of corrosion. The morphology has a strong effect on the protective properties of this layer³. Water is the most common impurity in oil and gas, which usually contains CO_2 . Carbon dioxide gas hydrates in water and changes to carbonic acid, which causes the internal corrosion in oil and gas pipelines. This kind of corrosion is known as sweet corrosion or CO_2 corrosion.

(ii): Nickel-phosphorous (Ni-P) is widely used as an electroless coating in different industries because of its high hardness, excellent corrosion and wear resistances and its uniform coating thickness. Co-depositing another metallic or non-metallic elements or abrasive/lubricate particles or combination of them in binary Ni-P matrix can further enhance these properties⁴.

It can be rationally anticipated that the inclusion of nano-sized particles in electroless Ni-P alloy coating would be significant for broadening the scopes of the coating in engineering, because various types of nano-particles have special natures much different from that of bulk counterparts and could endow the coating with special functionality⁵.

In this context, the present work aims to study and comparing the effects of precipitating Iron Carbonate layer at it's optimum producing condition and depositing electroless Ni-P and Ni-P/nano- SiO_2 on corrosion protective behaviors.

2. Experimental Methods

2.1 Preparing samples for electroless coating and precipitating iron carbonate layer:

The samples were made of API5L-X70 steel with the nominal composition shown in Table 1. The shape of samples was cylindrical with the exposed surface area of 5.4 cm^2 . They were polished using 60 up to 2000 grit silicon carbide papers, then degreased in acetone using an ultrasonic cleaning device.

Table 1. Chemical Composition of the Steel (wt %)

C	Si	Mn	P	S	Cr	Ni	Cu
0.037	0.141	1.291	0.006	0.013	0.011	0.156	0.024
Mo	Nb	Co	Al	B	Ti	V	Fe
0.207	0.018	0.015	0.055	0.006	0.017	0.039	97.964

2.2 Depositing electroless Ni-P and Ni-P/nano- SiO_2 coatings on X70:

After preparing naked X70 samples, a commercial electroless nickel bath (SLOTONIP 70 A from Schlotter) with sodium hypophosphite as reducing agent was used to obtain the coatings. This bath provided Ni-P deposits with a high phosphorous content, 9–10% P. Temperature changed within 88– 93 °C and pH changed within 4.5–4.7 range, during coating process. The SiO_2 used for co-deposition was fumed type oxide by Degussa, with a mean diameter of 12–20 nm and concentration in the bath equal to 7g SiO_2 /l.

Prior to the co-deposition, a Ni-P coating was first deposited for 0.5 h. Then SiO₂ nano-particles were added to the plating bath by ultrasonic dispersion for 15 min, followed by deposition for 2 h under magnetic agitation at a speed of 300 rpm. For a comparison, pure Ni-P coating was prepared under the same conditions.

2.3 preparing circumstances for investigating CO₂ corrosion on X70 and electroless coated samples:

The experiments were carried out in a glass cell filled with 2.5 L of deionized water and 3%wt NaCl at atmospheric pressure in the temperature 85 °C and pH 6.5 for 72 h. An image of the test set-up is shown in Fig. 1. Before commencing the tests, the solution was deoxygenated by purging CO₂ for at least 2 h. Then Specimens prepared in sections 2.1 and 2.2 were put in the holder. In each experiment only one sample was used. Furthermore, CO₂ purging was continued throughout test. For adjusting pH, sodium bicarbonate (NaHCO₃) or hydrochloric acid (HCl) was used.

Fig. 1. An image of test set-up

2.4. Morphological and micro-structural investigations:

The morphology and microstructure of the samples were analysed using scanning electron microscopy SEM, (CAMSCAN MV2300). X-ray diffraction (XRD) patterns were obtained using Philip's Xpert pro type X-ray diffractometer with a cobalt target and an incident beam mono-chromator).

2.5. Electrochemical measurements:

Corrosion behavior of Iron Carbonate layer, Ni-P and Ni-P/nano-SiO₂ composite coated X70 steel was studied by using electrochemical impedance spectroscopy (EIS) during the experiments running. The tests were carried out in a three-electrode cell using an EG&G potentiostat/galvanostat, model 273A. Platinum plate and Ag/AgCl electrode were used as counter and reference electrodes, respectively. The EIS tests were undertaken using a Solartron Model SI 1255 HF Frequency Response Analyzer (FRA) coupled to a Princeton Applied Research (PAR) Model 273A Potentiostat/Galvanostat. The EIS measurements were obtained in a frequency range from 0.01Hz to 100 kHz with an

applied AC signal of 5mV (rms) using EIS software model 398. The equivalent circuit simulation program (ZView2) was used for data analysis.

3. Results and discussion:

3.1. Morphological and micro-structural Analysis:

SEM micrographs of samples are depicted in Fig. 2. Fig. 2(a) shows that Iron Carbonate layer formed at 85 °C and pH = 6.5 consist of rhombohedral crystals which are dense and compact that distributed uniformly on the surface of the steel.

Fig. 2(b,c) show the SEM images of the surface morphologies of electroless Ni-P and Ni-P/nano-SiO₂ composite coatings with 7g/l nano-SiO₂ concentration after exposing the samples to the tests conditions.

Fig.2.The SEM micrographs of the specimens exposed at 85 °C at pH=6.5 (a) FeCO₃, (b) Ni-P and (c) Ni-P/Nano-SiO₂ for 72 h.

SiO₂ nano-particles had been embedded in the Ni-P matrix via co-deposition, and some of the SiO₂ nano-particles were agglomerated to a certain degree even in the presence of ultrasonic and magnetic agitation.

3.2. Phase analysis of the composite coatings

Fig. 3 shows the XRD patterns of samples exposed at 85 °C pH=6.5. From Fig. 3(a) it is evident that characteristic peak's intensity of Iron Carbonate layer is so high that demonstrate test's conditions for producing a uniform and dense layer is at optimum level. Fig 3(b) shows the XRD patterns of Ni-P and Ni-P/nano-SiO₂ composite coatings. It is seen that both types of coating have amorphous structures and X-ray diffraction pattern of nano-composite coating is similar to that of particle free coating and sweet corrosion does not effect electroless coated sample's structure.

Fig.3 . XRD patterns of specimens exposed at 85 °C at pH 6.5 for 72 h (a) FeCO₃ (b) Ni-P and Ni-P/nano-SiO₂ coating.

3.3. Electrochemical corrosion performance:

3.3.1. EIS investigation of Iron Carbonate covered specimen:

Fig. 4 shows the EIS spectra of naked and Iron carbonate covered X70 steels that were exposed at 85 °C at pH 6.5 for 72 h. According to the mechanism of carbon dioxide (CO₂) corrosion of carbon steels proposed by researchers and with respect to the main reaction processes of carbon steels in deoxygenated aqueous environments containing carbon dioxide mentioned, due to the sediment of corrosion products, such as FeCO₃, surface film is formed on the surface of carbon steels. In general, the formation of the surface film can significantly reduce the CO₂ corrosion rate of carbon steels. Many literatures report that the additions of film-forming corrosion inhibitors can also decrease the CO₂ corrosion rate of steels in oil industry.

Fig. 4. Nyquist plots recorded on the naked and Iron carbonate covered sample exposed at 85 °C at pH 6.5 for 72 h.

As shown in Fig. 4, Iron Carbonate covered specimen's Nyquist plots have two semicircles. The first one (in high frequency region) expanded significantly with the development of exposure time of the electrode in the corrosive environment, which revealed that the variation in the electrochemical kinetics occurred during the period of

exposure. This phenomenon was attributed to the formation of the surface film and the continuous strengthening of its protective ability.

Electrical equivalent circuits are commonly used to describe the electrochemical behavior and to calculate the parameters of interest, such as electrolyte resistance (R_s), double layer capacitance (C_{dl}) and electrochemical charge transfer resistance (R_{ct}). The constant phase element (CPE) is widely used as scattered circuit element in equivalent circuits when non-ideal frequency response is present. The impedance of Z_{CPE} is shown in the following equation:

$$Z_{CPE} = A^{-1}(j\omega)^{-\alpha} \quad (1)$$

Where A is a proportional coefficient, $j^{1/2}$, ω is $2\pi f$. However, the use of α to describe the non-ideal capacitance behavior of the metal/solution interface is not well understood. $1/A$ is a constant comparable to a capacitance. CPE is usually used in the model in place of a capacitor to compensate for non-homogeneity in the system. Fig. 5 shows the proposed electrical equivalent circuit employed to analyze the impedance plots of Iron Carbonate covered specimen in this work. Here, R_{pore} is the resistance of the film in pore areas, R_s the solution resistance, Z_{CPE} the impedance of non-ideal capacitor, R_{ct} the charge transfer resistance and C_{dl} is the double layer capacitance. These parameters were calculated by fitting the EIS data into the circuit model, and the results are shown in Table 2.

Fig. 5. Equivalent circuit used to represent the impedance results of the Iron Carbonate covered sample.

Table 2. Evolution of the fitted parameters with sweet corrosion times

Time(h)	$R_{pore}(\Omega/\text{cm}^2)$	$R_{ct}(\Omega/\text{cm}^2)$	$Z_{CPE}(\text{S sec } \alpha/\text{cm}^2)$	$C_{dl}(\text{F}/\text{cm}^2)$
0	45	38.62	0.0022	0.158
72	999.2	938	0.0008	0.016

3.3.2. EIS investigation of Ni-P and Ni-P/nano-SiO₂ covered specimen:

Fig.6 show the Nyquist plots obtained for Ni-P and Ni-P/nano-SiO₂ composite coatings in sweet corrosion of test conditions. All the curves appear to be similar (Nyquist plots), consisting of a single semicircle in the high frequency region signifying the charge controlled reaction. However, it should be noted that though these curves appear to be similar with respect to their shape, they differ considerably in their size. This indicates that the same fundamental processes must be occurring on all these coatings but over a different effective area in each case ⁶⁻⁹

Fig. 6. Nyquist plot for electroless coatings prepared with various concentrations of SiO₂ nano-particles: (a) without SiO₂; (b) 7gr/l

To account for corrosion behavior of these coatings, an equivalent electrical circuit model given in Fig. 7 has been utilized to simulate the metal/solution interface and to analyze the Nyquist plot⁶⁻⁹.

Fig. 7. Equivalent electrical circuit model used to analyze the EIS data of Ni-P electroless coatings with and without nano-particles.

The charge transfer resistance R_{ct} and double layer capacitance C_{dl} obtained for Ni-P and Ni-P/nano-SiO₂ composite coatings are compiled in Table 3. The occurrence of a single semicircle in the Nyquist plots indicates that the corrosion process of these coatings involves a single time constant. The high values of charge transfer resistance (R_{ct}), obtained for the coatings of present study imply a better corrosion protective ability of Ni-P/nano-SiO₂ composite coatings than Ni-P electroless coating. The C_{dl} value is related the porosity of the coating. The low C_{dl} value confirms that the electroless composite coating of present study is relatively less porous in nature⁶⁻⁹.

Table 3. Electrochemical parameters from EIS data of Ni-P electroless coatings with and without nano-particles in CO₂ corrosion conditions.

Type of coating	R_{ct} (Ω cm ²)	C_{dl} (μ F/cm ²)
Ni-P	650	0.85
Ni-P/nano-SiO ₂ (7g/l)	1210	0.7

It is evident from literature reports on Ni-P coatings that preferential dissolution of nickel occurs at open circuit potential, leading to the enrichment of phosphorus on the surface layer. The enriched phosphorus surface reacts with water to form a layer of adsorbed hypophosphite anions (H₂PO₂⁻). This layer in turn will block the supply of

water to the electrode surface, thereby preventing the hydration of nickel, which is considered to be the first step to form either soluble Ni^{2+} species or a passive nickel film. By comparing the corrosion resistance of electroless Ni-P and Ni-P/nano-SiO₂ composite coatings, the latter coating type appeared to offer better corrosion protection. This seems to be logical, because even though the apparent area remains the same, the effective metallic area prone to corrosion is decreased considerably in the case of electroless composite coating⁶⁻⁹.

4. Conclusions:

1. The temperature of 85°C and pH 6.5 were the best conditions for the formation of protective iron carbonate layer.
2. Formation of Iron Carbonate layer improves corrosion resistance of X70 steels.
3. SiO₂ nano-particles have been successfully co-deposited with Ni-P matrix to generate Ni-P/nano-SiO₂ composite coatings in the absence of any surfactants.
4. Plain electroless Ni-P deposits seem to be smooth compared to the slightly nodular deposits obtained due to the particle reinforcement. Particle co-deposition was uniform through out the cross-section of the composite coating.
5. Corrosion tests performed showed that both electroless Ni-P and electroless Ni-P/nano-SiO₂ composite coatings demonstrated significant improvement of corrosion resistance.
6. Higher corrosion resistance was obtained for Ni-P/nano-SiO₂ over Ni-P coating, which can be ascribed to a reduction in the effective metallic area available for corrosion.

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