CORROSION SCIENCE AND TECHNOLOGY, Vol.2, No.5(2003), pp.233~237

An Investigation of Mild Steel with Nitrogen-containing Inhibitor in Hydrochloric Acid

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Pickling inhibitors can be used to form an adsorbed layer on the metal surface to hinder the discharge of H^+ and dissolution of metal ions. Nitrogen-containing inhibitors were selected as corrosion inhibitors for mild steel (MS) in pickling acid process. In this study, the addition of inhibitor, the pickling temperatures and the pickling times were the parameters to investigate the effects on the inhibition efficiency (IE) for MS by using weight loss measurement. Preliminary results show that the IE increased with the increase in pickling time from 10 minutes to 60 minutes, and the IE also increased with the increase in temperature at room temperature and 40°C. At the higher temperature, the IE values are higher and almost independent with the pickling time. Furthermore, the potentiodynamic polarization, open circuit corrosion potential-time and corrosion current-time studies show that nitorgen-containing inhibitor behaves predominantly as cathodic polarization. The roughness test and SEM investigation are also studied in this paper.

Keywords : *pickling inhibitors, mild steel, inhibition efficiency, potentiodynamic polarization, SEM.*

1. Introduction

Inhibiting the electrochemical corrosion of mild steel in acid environment or in steel making process is of economic importance. In pickling process of mild steel in acid solutions, the major features of the corrosion of mild steel are that it is rapidly corroded without formation of a passive layer of corrosion products, and that the cathodic reaction consists mainly the hydrogen gas evolution. Therefore, in recent years scientists have been concerned with the use of certain compounds as corrosion inhibitors in metal-corrodent systems. The use of organic inhibitors for mild steel corrosion has been reported by several authors.[1)-6)] Amines are widely used as corrosion inhibitors in the steel making process and the inhibition mechanism is poorly understood.[7)-9)] The aim of this paper is to study the influence of the nitrogen-containing compounds, as inhibitors in pickling process, on the corrosion properties and inhibition mechanism of mild steel in hydrochloric acid solution using several different techniques.

2. Experimental

2.1 Material preparation

The mild steel used for this study were mechanically press-cut into 2.0 x 2.0 cm samples of thickness 0.10 cm from China Steel Co., Ltd. Chemical composition (in wt %) of metal had the following composition: 0.08%C, 0.003%Si, 0.346%Mn, 0.001%P, 0.001%S, and 0.035% Ni, Cu, with the balance in Fe. These samples were used as supplied and without polishing, but the surface treatment made use of degreasing in distilled water and drying in acetone. The treated samples were then stored in a moisture-free desicator. These samples were used for weight measurement and electrochemical studies. Nitrogen-containing inhibitors were selected as corrosion inhibitors with concentration 2.5wt%(inhibitor A) and 0.4 wt% (inhibitor B) , all reagents were analytical grade and double-distilled water were used for preparing test solutions of 12% HCl for all experiments.

2.2 Weight loss measurements

Previously weighed mild steel samples were immersed in 12% HCl solution with and without inhibitor contained in different beakers kept at room temperature (25±2°C) and in two thermostat-controlled baths maintained at 40 °C and 80°C, separately. The immersion time were 10, 20, 30, 40,and 60 minutes. The difference in weight defined as:

$$\triangle W = W_i - W_f$$

was taken as the weight loss measured in g. Wi is the initial weight at time t=0, W_f is the final weight at time t.

The percentage inhibition efficiency (%IE) was calculated using the following equation:

%IE = [(Uninhibited corrosion rate - Inhibited corrosion rate) / Uninhibited corrosion rate] x 100

2.3 Electrochemical studies

For potentiodynamic polarization studies, the mild steel exposure area was 4 cm^2. All chemicals are commercially available and the hexamethylene tetramine used as inhibitor was supplied by the China Steel Co., Ltd. Solutions were not stirred and the experiments were carried out at 25±2℃ according to ASTM G3-89[10] and ASTM G5-94.[11] Potentiodynamic polarization studies were carried out using an EG&G Princeton Applied Research PAR model 273A potentiostat/galvanostat, a Schlumberger FRA1255 (Frequency Response Analyzer). The scan rate is 1mV/s from open circuit potential(OCP). A graphite electrode was used as auxiliary electrode, and a saturated calomel electrode (SCE) was used as a reference electrode. Analytical reagent-grade HCl and double-distilled water were used for preparing test solutions of 12% HCl for all experiments.

2.4 SEM examination and roughness test

Mild steel specimens surface were examined by SEM after immersed in 12% HCl solution for 10 minutes at 25℃, 40℃, and 80℃, separately. SEM analysis was carried out using a Camscan SEM with BE detector and EDX. And the mild steel specimens were also selected for detailed analysis after pickling process by step-height profiler(ie,α-step analyzer).

3. Results and discussion

3.1 Corrosion by HCl solution and the effect of pickling temperature

The weight loss measurement of mild steel in 12% HCl solution with and without inhibitor at room temperature as a function of time is shown in Fig. 1. The result in Fig. 1 shows that the weight loss of mild steel in 12% HCl solution without inhibitor increases with the increasing pickling time, and from the non-uniformity of the plot reveals that mild steel corrosion by HCl solution occurs not only by simply homogeneous process but by a heterogeneous one involving several steps.[7] From the weight loss measurement of mild steel in 12% HCl

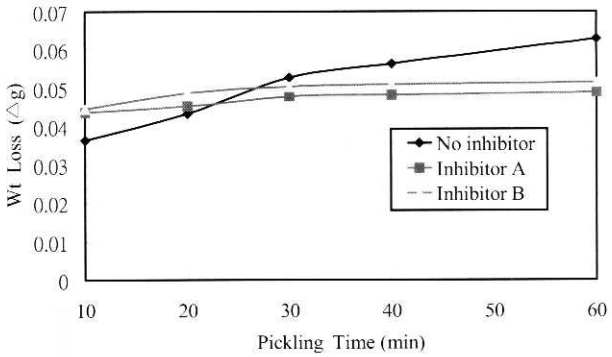


Fig. 1. Variation of weight loss with pickling time in 12% HCl solution at 25℃.

solution with inhibitors, the smaller weight loss exhibits the inhibition effect, and the inhibitors' action is due to the chemical adsorption onto the metal surface. It is observed that the inhibitor A and inhibitor B almost have the same tendency in weight loss.

Fig. 2 and Fig. 3 show that the weight loss measurement of mild steel in 12% HCl solution as a function of picking

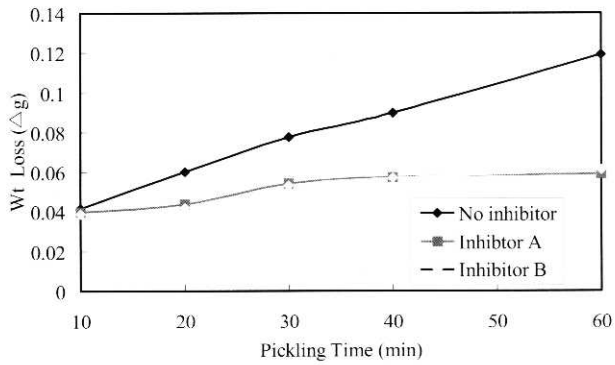


Fig. 2. Variation of weight loss with pickling time in 12% HCl solution at 40℃.

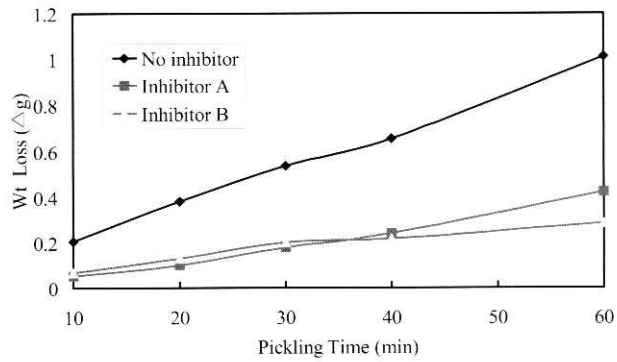


Fig. 3. Variation of weight loss with pickling time in 12% HCl solution at 80℃.

time at 40℃ and 80℃, respectively. The weight loss of mild steel in 12% HCl solution increases with the in creasing temperature from room temperature to higher temperatures.

3.2 Inhibition efficiency

Fig. 4 and Fig. 5 show the inhibition efficiency (%IE) from weight loss measurements for inhibitor A and inhibitor B in 12% HCl solution at different temperatures. From the result it was found that IE increased with the increase in temperature from room temperature to the higher temperature for the two different inhibitors. The inhibition efficiency of inhibitor A decreased by increasing the duration of the pickling time from 10 min to 60 min. The decrease in inhibitor effectiveness at longer pickling times was caused by various factors such as an increase cathodic or hydrogen evolution kinetics or an increase in concentration of ferrous ions.[12] The variation in inhibition efficiency mainly depends on the type and nature of the substituents present in the inhibitor molecules.[13] Inhibitor B gave the better performance in IE, this can be explained by its π-electrons in conjugation with adjacent polar group, this polarization reaction favored greater adsorption on the metal surface.[14)-16)]

3.3 Electrochemical studies

The corrosion rates (mpy, mili-inch per year) of mild steel in 12% HCl with and without nitrogen-containing inhibitors are given in Table 1. The corrosion rate values decreased significantly in the presence of inhibitors.

The galvanic current and potential of mild steel immersed in 12% HCl solution were measured as a function of time, the results are shown in Fig. 6 and Fig. 7. Results

Table 1. Corrosion rate of mild steel in HCl solution.

Solution	Corrosion Rate (mpy)
12% HCl	6.704×10^3
12% HCl + inhibitor A	24.3
12% HCl + inhibitor B	14.47

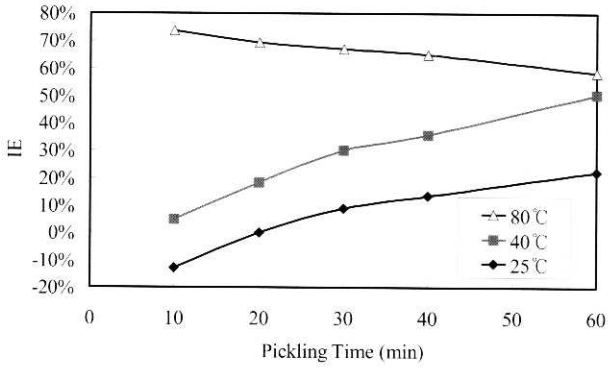


Fig. 4. The inhibition efficiency of mild steel in 12% HCl containing inhibitor A at 25℃, 40℃, and 80℃.

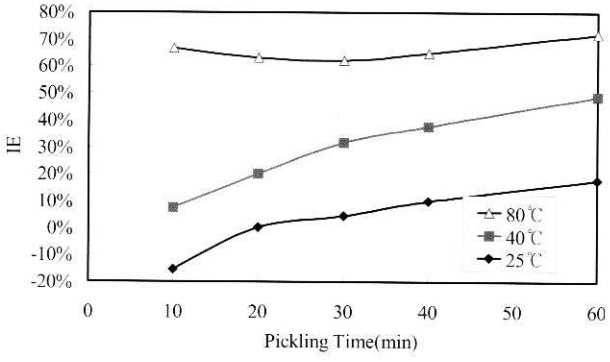


Fig. 5. The inhibition efficiency of mild steel in 12% HCl containing inhibitor B at 25℃, 40℃, and 80℃.

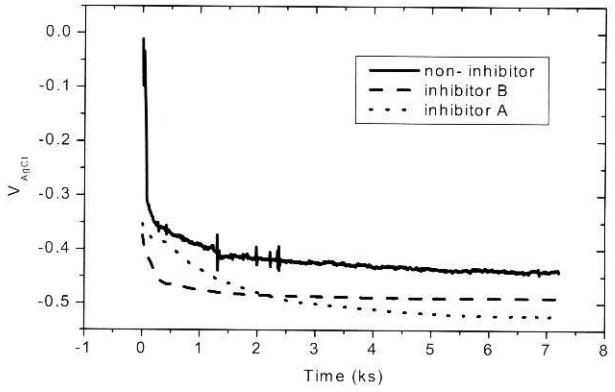


Fig. 6. Variation of potential of mild steel in 12% HCl solution with/without inhibitor.

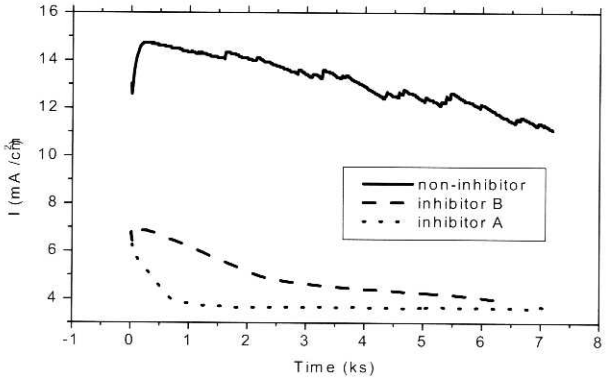


Fig. 7. Variation of current of mild steel in 12% HCl solution with/without inhibitor.

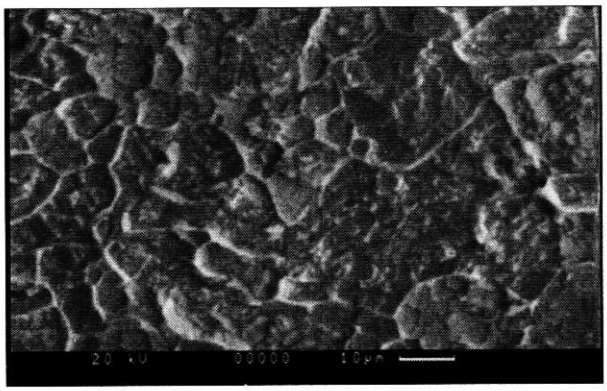
Table 2. Roughness of mild steel in 12% HCl solution.

Solution	Roughness(μm)		
	25℃	40℃	80℃
12% HCl	1.825	2.400	2.475
12%HCl + inhibitor A	1.925	1.600	1.775
12%HCl + inhibitor B	1.575	1.575	1.110

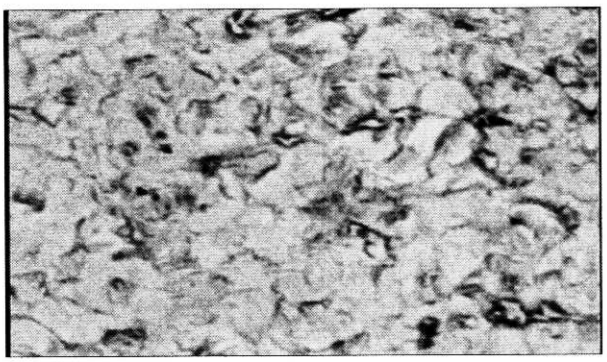
clearly showed that nitrogen-containing inhibitor behaved predominantly as cathodic for MS.

3.4 SEM and roughness comparisons

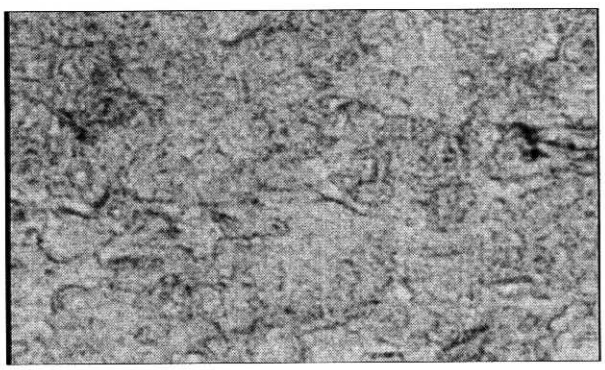
Fig. 8 shows SEM images of mild steel after immersion in 12% HCl solution at room temperature for 10 minutes. Fig. 9 and Fig. 10 show the analogous images of the same sample after immersion in 12% HCl solution with inhibitors A and B at 40℃and 80℃, respectively. The



8(a): 25℃

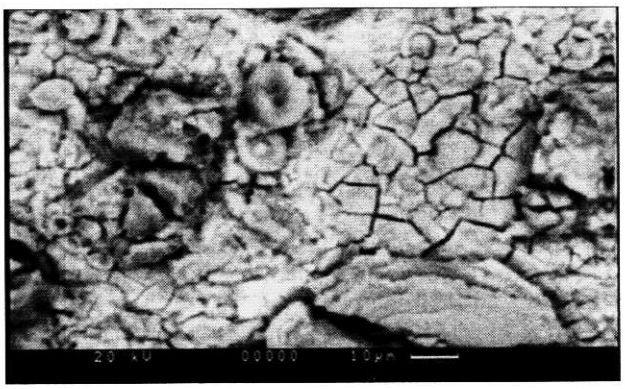


8(b): 40℃

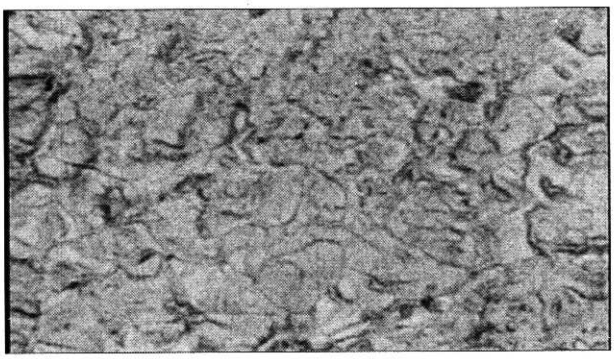


8(c): 80℃

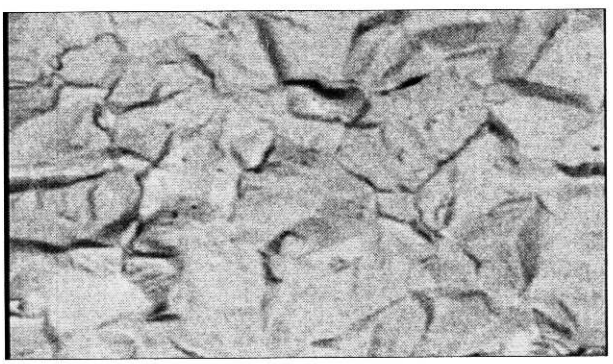
Fig. 8. Surface of mild steel after immersion in 12% HCl solution for 10 min.



9(a): 25℃

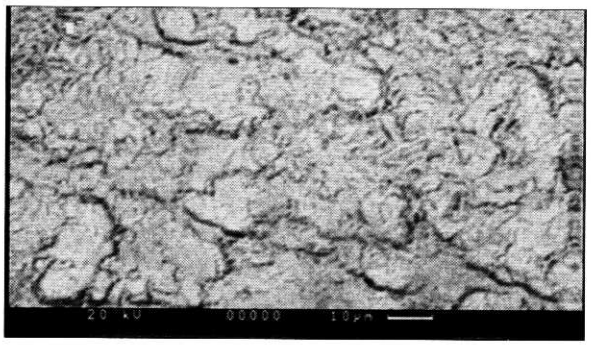


9(b): 40℃

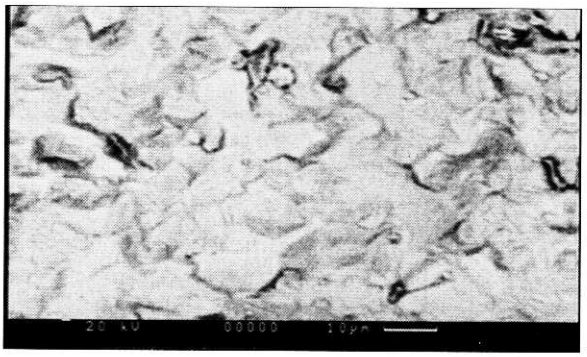


9(c): 80℃

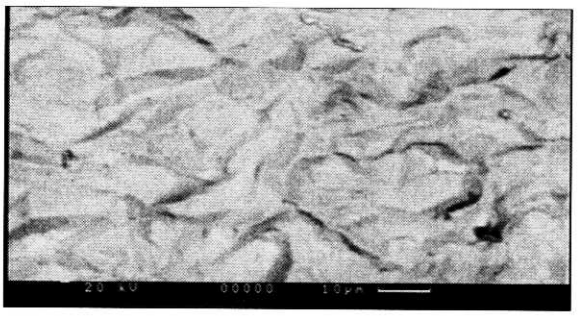
Fig. 9. Surface of mild steel after immersion in 12% HCl solution with inhibitor A for 10 min.



10(a): 25℃



10(b): 40℃



10(c): 80℃

Fig. 10. Surface of mild steel after immersion in 12% HCl solution with inhibitor B for 10 min.

images after acid pickling process (Fig. 8(a), 9(a) and 10(a)) show that the surface not exposed to the inhibitor solution is less smoothness. The step-height profiler measurement (roughness test) in Table 2 shows the same surface observation.

4. Conclusions

1) The corrosion rate of mild steel in 12% HCl solution without inhibitor increases with increasing pickling time and temperature.

2) The inhibition efficiency of mild steel in 12% HCl solution with nitrogen inhibitor increase with the pickling time.

3) Nitrogen-containing inhibitors behaved predominantly as cathodic type inhibitor for mild steel.

4) Roughness results were in good agreements with those images obtained from SEM for mild steel in hydrochloric acid with inhibitor and at higher temperatures, the surface roughness was lower.

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