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The metastable pitting behaviors of mild steel in bicarbonate and nitrite solutions containing Cl^-

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Abstract

The metastable pitting behaviors of mild steel in $NaHCO_3 + NaCl$ and $NaNO_2 + NaCl$ solutions were studied with electrochemical methods. In $NaHCO_3 + NaCl$ solution the potential range between metastable pitting potential E_m and pitting potential E_b is relatively large, and most of the current fluctuations are individual. While in $NaNO_2 + NaCl$ solution the E_m and E_b values are much higher and the potential range between them is very narrow, leading to overlapped current peaks. The changes of E_m and E_b with chloride concentration follow similar tendency. In both testing solutions, the repassivated metastable pitting sites are prone to become preferential sites for following metastable pits to nucleate, leading to accumulated corrosion damages on the surface. Mild steel shows stronger passivity in $NaNO_2 + NaCl$ solution than in $NaHCO_3 + NaCl$ solution, which explains the higher pitting resistance of the steel in the former. In addition, the competitive adsorption of NO_2^- anions also plays an important role in the increase of E_m and E_b, especially in inhibiting nucleation of metastable pits.

Keywords: Metastable pitting; Mild steel; Current fluctuations; Passivity

1. Introduction

Metastable pitting of metals and alloys have been studied by many authors [1–6] in order to understand the early mechanism of localized corrosion, and to find a potential method to predict pitting tendency of metals, because of the close relationship between metastable and stable pitting behaviors. It is well accepted that the current fluctuations before pitting are the results of nucleation, growth and repassivation of metastable pits on the metal surface. Most of the published papers in this area were on stainless steels and aluminum, however, in some systems carbon steels also show current fluctuations. Hashimoto et al. [4–6] studied the potential fluctuation during passive film breakdown and repair of pure iron in $NaNO_2 + NaCl$ solution by electrochemical noise measurement (EN), and pointed out that peak potential changes with the logarithm of chloride ion concentration, and the spatial distribution of pits followed a Poisson distribution. Cheng and Dong et al. [7–9] studied current and potential fluctuations for A516-70 and 16Mn carbon steel in $NaHCO_3 + NaCl$ solutions by EN, respectively. It was suggested that the quick rise and slow recovery of the current fluctuations reflect the initiation, growth and repassivation of metastable pits. While potential fluctuations reflect the response of the electrode capacitance to the pit growth charge. The "transient" in ECN had generally characteristic of "fast down and slow recovery". The amplitude and lifetime of transients in ECN increased with the addition of Cl^-.

However, in some biological solutions without chlorides or other halogen ions, pitting corrosion were also observed. For 316L stainless steel and iron, It was reported [10–12] that bacteria resulted in the formation of active sites and anodic currents, leading to local dissolutions which had the shapes as the agglomerates of bacteria. For carbon steel in an iron oxidizing bacteria solution [13], pitting corrosion

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was initiated by active anodic dissolution under oxides deposits. It seems that the formation of active sites and development of local dissolution are the key steps for initiation of metastable or stable pitting, no matter in solutions with or without chlorides. In our previous reports [14,15], metastable pitting behaviors of mild steel in $NaHCO_3 + NaCl$ and $NaNO_2 + NaCl$ solutions were studied, respectively. The statistical patterns of some current fluctuation parameters including frequency, peak current and decline rate of the current were obtained. It was found that during metastable process of mild steel, repeated local dissolution may result in accumulated corrosion damages on the surface. In this paper, metastable pitting behaviors of mild steels in bicarbonate and nitrite solutions were comparatively studied. The purpose of this study was to further understand the effects of passivity on local dissolution and metastable pitting behaviors of carbon steel in different solutions.

2. Experimental methods

2.1. Materials and preparation

The test material was mild steel with the chemical composition (wt%): C, 0.19; Si, 0.22; Mn, 0.56; P, 0.0086; S, 0.022. Specimens were manually finished up to 800 grit SiC abrasive papers, and rinsed with de-ionized water and degreased in alcohol. The specimens were coated with epoxy resin, leaving a working area of 0.04 cm^2 exposed to the solution.

2.2. Polarization and EIS measurement

Potentiodynamic polarization curves of the steel in $NaHCO_3 + NaCl$ and $NaNO_2 + NaCl$ solutions were measured by a Model 273A potentiostat, with a scan rate of 0.3 mV/s. When the current density reached 50 $\mu A/cm^2$, the potential scanning was reversed at the same rate until the current density returned to the background. Electrochemical impedance measurements were conducted with a potentiostat (Galvanostat Model 273A) and a 5210 lock in amplifier. A perturbation potential of 10 mV amplitude was applied over the frequency range of 10^{-2}–10^5 Hz. In addition, current–time curves of mild steel in $NaHCO_3 + NaCl$ and $NaNO_2 + NaCl$ solutions were recorded by a potential step test. The potential of the specimen was raised from −500 mV(SCE) to −180 mV quickly and the current transient was recorded.

2.3. Current fluctuations measurement

Slow potentiodynamic polarization tests were carried out to study the current fluctuations during metastable pitting process of mild steel in $NaHCO_3 + NaCl$ (pH 8.8) and $NaNO_2 + NaCl$ solutions. The current was recorded against time. Specimens were first cathodically polarized for 3 min at potential 400 mV below open circuit, then anodic polarization was carried out in a potential scanning rate of 0.1 mV/s until stable pitting occurred. The lower limit of current detection in the study was 0.02 μA. We denote the potential when the first apparent current fluctuation occurs as metastable pitting potential E_m, and the potential when current rises continuously as pitting breakdown potential E_b. After polarization tests the surface morphology of the specimens was examined by scanning electronic microscope.

A conventional three-electrode system was used for all the electrochemical tests. The specimen of mild steel was used as the working electrode and a Pt plate as counter electrode. The potentials reported were relative to a saturated calomel electrode. All the solutions were made from analytical grade reagents and de-ionized water. The tests were conducted at ambient temperature.

3. Results and discussion

3.1. Polarization curve measurements

Polarization curves were measured for the specimens in 0.3 M $NaHCO_3$ + 0.05 M Cl^- and 0.3 M $NaNO_2$ + 0.05 M Cl^- solutions, as shown in Fig. 1. In the two solutions mild steel showed similar open circuit potentials and passive current densities, but the passive regions and pitting breakdown potentials are quite different. In $NaHCO_3$ solution the pitting potential E_b is 15 mV, while in $NaNO_2$ solution E_b is 252 mV. It is also seen that in $NaHCO_3$ solution the difference between E_b and repassivation potential E_p is 343 mV, while in $NaNO_2$ solution the value of $E_b - E_p$ is only 162 mV. The results indicate that better passivation and pitting resistance are obtained for mild steel in $NaNO_2$ solution than in $NaHCO_3$ solution. Also, the different hysteresis loops on the polarization curves show that in $NaHCO_3$ solution it is more difficult for the growing pits to repassivate.

It is also seen in Fig. 1 that on the polarization curve in $NaHCO_3 + NaCl$ solution, current fluctuations occurred in the potential region near pitting potential. Slow potential

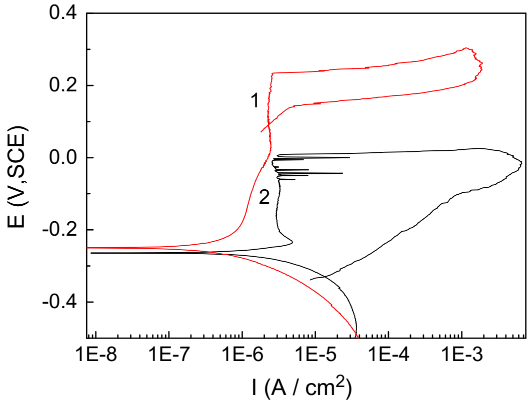

Fig. 1. Polarization curves of mild steel in: (1) 0.3 M NO_2^- + 0.05 M Cl^-, (2) 0.3 M HCO_3^- + 0.05 M Cl^-.