Photo-electrochemical analysis of passive film formed on X80 pipeline steel in bicarbonate/carbonate buffer solution

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Abstract

Photo-electrochemical measurement was used to explore the formation potential, formation time, chloride ions concentration, applied potential and pH value of the solution on the electronic property of passive film formed on X80 pipeline steel in 1 M $NaHCO_3$/0.5 M Na_2CO_3 buffer solution. The results showed that the photocurrent is positive, indicating an n-type semiconductor character of the passive film, the photocurrent increased with increasing the formation potential, prolonging the formation time, decreasing chloride ions concentration, rising applied potential and decreasing the pH value of the solution. Capacitance measurement exhibited a positive slope of Mott-Schottky plot, and the slopes of Mott-Schottky plots increased with the increasing formation potential, showing a decrement of the donor density of the passive film.
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Keywords: Passive film; Photo-electrochemical measurement; Capacitance measurement; Mott-Schottky analysis

1. Introduction

Passive film formed on metals or alloys play an important role in acting as a reacting ion barrier between metal surface and aggressive environment in corrosive solutions, and thereby protect metals from further corrosion. The electrochemical behaviors of passive films are controlled by their composition and structure, and can be related to their semi-conductive properties [1,2]. Therefore, in order to better understand the corrosion resistance property of passive film on metals and alloys, one need to know more about the semi-conductive properties of passive films and factors which affect the semi-conductive properties of passive film, such as formation potential, formation time, chloride ions, etc.

Many researches have been investigated the properties of the passive film formed on iron, stainless steel, chromium and other metals [3–9]. According to Cheng [10], the passive film formed on A516-70 carbon steel in chromate solution shows

characteristics of an amorphous n-type semiconductor with a 10^{26} to 10^{27} m^{-3} value of the donor density. From capacitance measurement, Hamadou [11] found the passive film formed on carbon steel behaves as highly doped n-type semiconductor above -0.5 V, the donor density is in the order of magnitude of 10^{21} cm^{-3} and decreases with increasing formation time and potential. Zeng and Luo [12] studied the passivation of X70 pipeline steel in 0.5 M $NaHCO_3$ solution, found the capacitance and donor density decrease with increasing the formation potentials and decreasing the chloride ion concentration in the $NaHCO_3$ solution. Ge et al. [13] found the sulfide can change the composition and structure of the passive film formed on 316 L stainless steel, and thereby decrease the corrosion resistance of the film.

Photo-electrochemical analysis is a powerful measurement widely used to examine the in situ semi-conductive properties of the passive film formed on metals and alloys. The application of the photo-electrochemical can obtain the composition and structure of the passive film, Jang [14] found the passive film formed on Ni in pH 8.5 buffer solution was consisted of an inner NiO film and an outer $Ni(OH)_2$ film using photo-electro-chemical measurement. Similarly, Kim [15] investigated the passive film of Cr in deaerated 8.5 buffer solution and concluded a single or duplex layer structure depending on the

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film formation potential. Comparison with the passive film formed on iron, stainless steel and other metals, few papers reported the passive film formed on X80 pipeline steel in bicarbonate/carbonate solution (high pH value), even, X80 pipeline steel may be suffered stress crack corrosion (SCC) in this environment.

The objective of this paper is to investigate the effect of formation potentials, formation time, chloride ions concentration, pH value of solution and applied potential on the photocurrent spectra of passive film on X80 pipeline steel in bicarbonate/carbonate solution using photo-electrochemical measurement and Mott-Schottky analysis.

2. Experimental

A conventional three-electrode electrochemical cell was used, the counter electrode was a Pt wire, and all potentials were measured against a saturated calomel electrode (SCE). The working electrodes were cut into a wafer with geometric area of 0.1256 cm^2, was embedded in two-component epoxy resin and mounted in a PVC holder. The exposed face of the electrode was abraded with 2000 grit SiC paper, polished with $0.5 \mu m$ Al_2O_3 powder and cleaned using double-distilled water. The working electrodes were initially reduced potentiostatically at -1.2 V (vs. SCE) for 20 min to remove the oxide formed on the electrode surface before experiments, and then were passivated at various potentials, respectively. The polarization curve was performed in the potential region of -0.8 V to 1.1 V (vs. SCE) with a 2 mV/s scanning rate. The photocurrent measurement was made of a conventional three-electrode cell of 1-multineck flash with a quartz window as a photon inlet, a 300 W Xenon arc lamp was used as a light source, and a monochromatic light with a wavelength from 200 nm to 800 nm was provided by a scanning digital monochromator controlled by a stepping motor at a scan rate of 5 nm/s, auxiliary focusing lens were used to raise the intensity of photons toward the monochromator.

Mott-Schottky plot measurement was carried out at EG&G Model 273 potentiostat/galvanostat with M5210 lock-in amplifier, the scanning potential is from -0.4 V to 1 V (vs. SCE) with a 40 mV/s scanning rate. The electrochemical impedance spectrum was measured from 100 kHz to 10 mHz with a 10 mV amplified potential.

3. Results and discussions

3.1. Effect of formation potential on photocurrent spectra

To obtain the passive potential range, the polarization curve of X80 pipeline steel in 1 M $NaHCO_3$/0.5 M Na_2CO_3 buffer solution was measured. Fig. 1 shows the result of polarization curve, it exhibits that X80 pipeline steel is in stable passive state in the potential range of 0 V (SCE) to 0.8 V (SCE) with a current density of 7.97E−5 A cm^{-2}.

Moreover, it can be seen that a current peak appeared at about -0.5 V in the polarization curve, it might be related to electrochemical reactions in solid state involving the transition
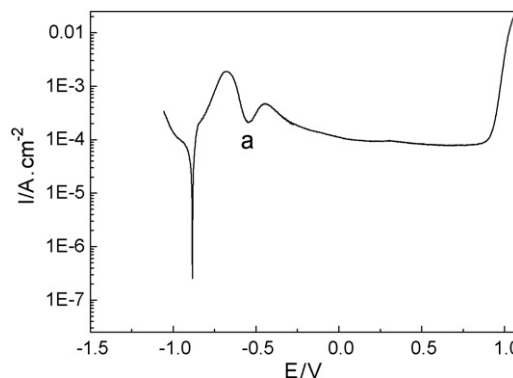

Fig. 1. Polarization curve of X80 pipeline steel in 1 M $NaHCO_3$/0.5 M Na_2CO_3 buffer solution.

to higher oxidation state of Fe [16]. The potential corresponding to this current peak it presents can be expected to have an influence on the photocurrent spectra of the passive film.

It is generally that the formation potential has a remarkable influence on the composition and structure of the passive film formed on metals or alloys. To investigate the photocurrent spectra dependence on the formation potential, the working electrode was polarized at 0 V, 0.2 V, 0.4 V and 0.6 V, respectively. The influence of formation potential on the photocurrent spectra was shown in Fig. 2. In which, Fig. 2(c) is the photocurrent versus photon energy plot of passive film formed at 0 V for 2 h, and Fig. 2(d) is its corresponding $(i_{ph}h\upsilon)^{0.5}$ versus photon energy plot. Fig. 2(e), (g) and (i) are the photocurrent versus photon energy plots of passive films formed at 0.2 V, 0.4 V and 0.6 V for 2 h, respectively, and Fig. 2(f), (h) and (j) are the corresponding $(i_{ph}h\upsilon)^{0.5}$ versus photon energy plots of Fig. 2(e), (g) and (i). Obviously, all the photocurrents are positive, this indicating the passive films formed at various potentials have an n-type semi-conductive character, and the photocurrent increases with raising the formation potential. All photocurrent spectra for the passive films began to increase at about 2.535 eV, exhibiting a shoulder at about 2.79 eV, and showing a peak at about 3.51 eV, respectively. The passive film formed on iron was reported to be as a double-layer structure consisting of an outer maghemite (γ-Fe_2O_3) and an inner magnetite (Fe_3O_4) layers [17–19]. For X80 pipeline steel, the major component is iron, then it can be considered the passive film formed on carbon steel is described of an outer maghemite (γ-Fe_2O_3) and an inner magnetite (Fe_3O_4) layers. It is significantly that the photocurrent spectra can be divided into two photocurrent spectra (a and b), one photocurrent peak at about 3.05 eV, and another photocurrent peak at about 3.51 eV, respectively. Therefore, the two divided spectral components in Fig. 2(c), (e), (g) and (i) may be originated from the γ-Fe_2O_3 and Fe_3O_4 oxides, respectively.

The band gap E_g of the passive film has been estimated from the photocurrent spectra according to Eq. (1) on assumption of the proportional relationship between photocurrent and the optical absorption [20]:

$$i_{ph} = \frac{A(h\upsilon - E_g)^n}{h\upsilon} \qquad (1)$$