Anodic Polarization Behaviors of Carbon Steel in Bicarbonate Solution

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Abstract: The anodic polarization curves of mild steel were measured in sodium bicarbonate solution of various concentrations, and the surface products were analyzed by XPS. Two anodic current peaks and two passive zones are observed in all the curves. When HCO_3^- ions concentration is below 0.1 mol/L, the two peaks are so close that the first passive zone is difficult to be observed. When HCO_3^- ions concentration is above 0.1 mol/L, the first peak appears clear, while the second becomes smaller. The XPS results indicate that the out layer of film formed at a higher potential is mainly composed of Fe_2O_3, and the inner film is a mixture of ferrous and ferric oxide.

Keywords: Anodic polarization, Carbon steel, Bicarbonate solution

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Introduction

Earlier work on the anodic passivation of iron and steel in carbonate and bicarbonate solutions has involved investigations using galvanostatic, potentiostatic and potentiodynamic measurements and different shapes of polarization curves were observed.

Hancock and Mayne[1] and Gilroy and Mayne[2] studied the passivation of iron in carbonate solutions with galvanostatic method and observed two arrests in potential. The initial arrest was ascribed to the formation of a film consisting of ferrous carbonate and hydroxide, and the second to the oxidation of the former film to ferric oxide.

Potentiostatic studies by Clerbois and Massart[3] of the passivation of iron in carbonate solutions have shown two oxidization peaks to be present in the polarization curves.

Thomas et al[4] found two distinct current maxima in the polarization curve for iron in carbonate solutions. The initial oxidation peak was attributed to the formation of a film consisting mainly of an oxide of iron, probably magnetite, and also ferrous carbonate. The second oxidation peak was thought to be related to the oxidation of the ferrous carbonate present in the film to -ferric oxide.

However, the studying, potentiodynamically, of anodic polarization of steel in sodium carbonate and bicarbonate solutions by Armstrong[5] and Von Fraunhofer[6] showed only one current peak and one passivation zone which was attributed to the formation of film of Fe_2O_3 or Fe_3O_4.

From the above it is apparent that there is need for further investigation on behavior of steel electrode in HCO_3^- solutions. In this paper, polarization

curves of carbon steel in HCO_3^- solutions of different concentrations are measured by potentiodynamical method and the film compositions are analyzed by XPS.

1 Experimental

1.1 Test Solutions

The solution studied is x mol/L $NaHCO_3$ solution with a pH value of 8.5, open to the air, where x is 0.05, 0.1, 0.2, 0.5, 0.75, 1.0 respectively. Analytical-grade $NaHCO_3$ and distilled water are used in preparing the solutions.

1.2 Materials and Preparation

A rod of mild steel is mounted into epoxy resin and used as working electrode with 0.785 cm^2 apparent area. The composition of the steel has already been described in previous publication[7]. The working electrode is initially polished with silicon carbide paper up to 800 grit, then cleaned with acetone and repeatedly rinsed in distilled water. Finally, the electrode is cathodically polarized in the test solution for 3min at 1300 mV (SCE) to remove an air-formed oxide layer from the surface.

1.3 Polarization Measurements

Current potential curves are obtained potentiodynamically using a potentiostat (EG & G Princeton Applied Research M273A). The counter electrode is a large area platinum sheet, and the reference electrode is a saturated calomel electrode (SCE) to which all potentials are referred. After the working electrode is immersed in the solution for 30min, the potential is swept in the positive direction with a scan rate of 100mV/min, starting from the open-circuit potential.

All the experiments are carried out at 25 ± 1 .

2 Results and Discussion

Fig 1 (a f) show the E i polarization curves for steel in $NaHCO_3$ solutions of different concentrations. It can be seen that all the anodic curves are characterized by two current peaks and two passivation zones. The maximum currents of two peaks are denoted as i_1 and i_2 respectively. When the concentration of HCO_3^- is lower than 0.1 mol/L, i_2 is much
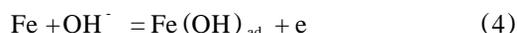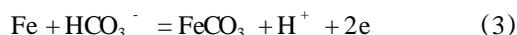
larger than i_1, and the two peaks are so close that the initial current peak and the initial passivation zone are difficult to be observed. When the concentration of HCO_3^- is 0.2 mol/L, the two peaks are separated obviously, and i_1 i_2. With the increase in HCO_3^- concentration, i_2 becomes smaller than i_1.

Fig 1d is a complete polarization curve which is measured in 0.5 mol/L HCO_3^- solution. The following reactions are derived in Fig 1d:
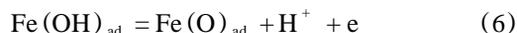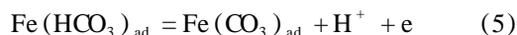
. A-B-C-D is the initial active-passive transition. At beginning, the current increases with increasing anodic potentials until a maximum current (i_1) is reached, after which the current decreases with increasing anodic potentials, and then keeps unchanged for a very short potential range. A-B represents the active dissolution of steel, the reaction occurred is:

$$Fe = Fe^{2+} + 2e \qquad (1)$$

With the potential change in positive direction, more and more OH^- and HCO_3^- ions are adsorpted on the steel surface, resulting in formation of $Fe(HCO_3)_{ad}$ and $FeCO_3$ according to the following equations, which may retard the active dissolution[8]. So the initial active-passive transition and passive zone (C-D) appear.
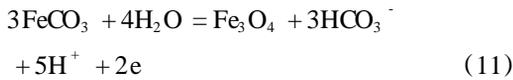
$$Fe + HCO_3^- = Fe(HCO_3)_{ad} + e \qquad (2)$$

$$Fe + HCO_3^- = FeCO_3 + H^+ + 2e \qquad (3)$$

$$Fe + OH^- = Fe(OH)_{ad} + e \qquad (4)$$

Meanwhile, desorption reaction of H^+ ion may take place in this potential region.

$$Fe(HCO_3)_{ad} = Fe(CO_3)_{ad} + H^+ + e \qquad (5)$$

$$Fe(OH)_{ad} = Fe(O)_{ad} + H^+ + e \qquad (6)$$

$$Fe(CO_3)_{ad} = FeCO_3 \qquad (7)$$

$$Fe(O)_{ad} = FeO \qquad (8)$$

. D-E-F-G is the second active-passive transition with a broad passive zone. The concentration of HCO_3^- and OH^- adsorbed on the surface will increase further as the potential keeps increasing. High concentration of HCO_3^- ions can attack $FeCO_3$ film to form soluble carbonate[9], $Fe(CO_3)_2^{2-}$, so an increasing current is again observed. But the conversion from $FeCO_3$ to Fe_3O_4 can suppress the dissolution, so

the second active-passive transition occurs

$$FeO + OH^- = FeO(OH)_{ad} + e \qquad (9)$$

$$FeCO_3 + HCO_3^- = Fe(CO_3)_2^{2-} + H^+ \qquad (10)$$

$$3FeCO_3 + 4H_2O = Fe_3O_4 + 3HCO_3^-$$
$$+ 5H^+ + 2e \qquad (11)$$
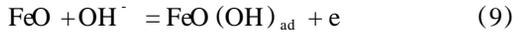
At F-G potential range, Fe_2O_3 is believed to form:

$$FeO(OH)_{ad} + FeO = Fe_2O_{3(ad)} + H^+ + e \qquad (12)$$

$$Fe_2O_3 (ad) = Fe_2O_3 \qquad (13)$$

The maximum current (i_2) of second peak may indicate the attack of HCO_3^- ions on $FeCO_3$ film as

shown in Fig 2. Severe pitting corrosion is observed after polarization in 0. 1 mol/L NaHCO₃, while no pitting is found in 0. 5 mol/L NaHCO₃ solution.

. G-H: when the potential reaches + 1. 0V (SCE), oxygen-evolution reaction takes place, so the current increases dramatically.

$$2H_2O = O_2 + 4H^+ + 4e \qquad (14)$$

In order to get further understanding of the above processes, the compositions of film formed in 0. 5 mol/L HCO_3^- solution are analyzed using XPS. During the potential scanning, when the potential reaches just after the second peak, which corresponds to the potential of F point in Fig 1d, the sweep is stopped and the specimen is analyzed immediately by XPS. The results are shown in Fig. 3. Before sputtering, two peaks appearing at 710. 9 eV and 724. 3 eV of the binding energy in the spectra of Fe(2P_{3/2}) and Fe(2P_{1/2}) respectively, are consistent with those of Fe_2O_3. After sputtering for 1min, the peaks become wider and their binding energies change to be 709. 8 eV and respectively. Based on the Fe(2P_{3/2}) peak as shown in Fig. 4, it is found that this peak is composed of two peaks: one at 709. 2eV which is assigned to Fe^{2+} in FeO, and it is at 711. 2 eV, which is assigned to Fe^{3+} in $FeCO_3$, Fe_2O_3. It is difficult to identify which ferric oxide is formed on earth because, in native energy of these oxides is almost the same. However, it can be drawn that the inner film comprises ferrous and ferric oxide. These results are consistent with the previous publications[1,10]. While after 5min sputtering, only element Fe is detected.

3 Conclusions

1) Anodic polarization curves ($E - i$) of steel in 0.05 ~ 1. 0 mol/L NaHCO₃ solution show two active-passive transitions. When the concentration of HCO_3^- is lower than 0. 2 mol/L, the initial current peak is very small and so close to the second that the first peak is difficult to be observed. When
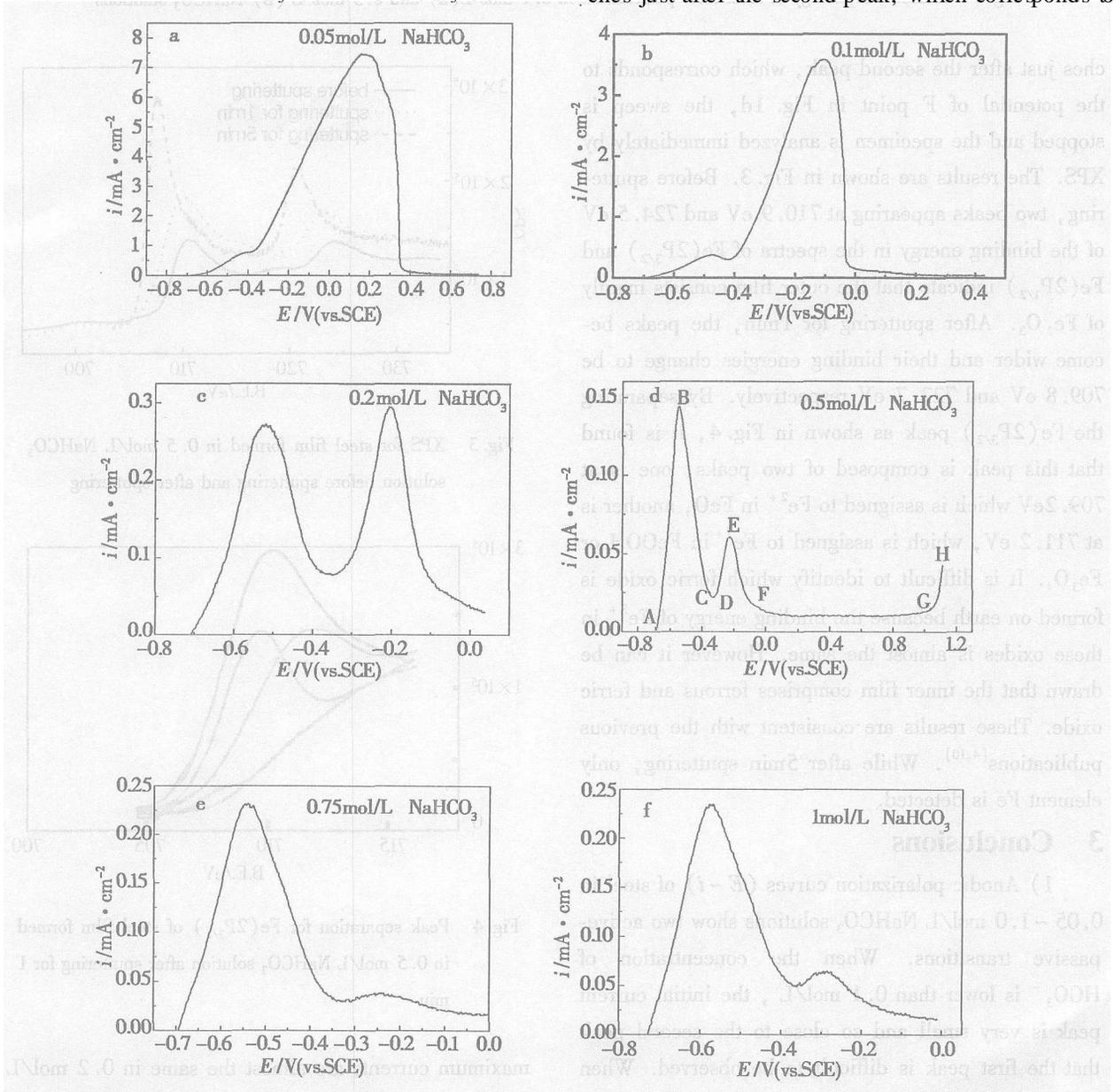

Fig 1 The polarization curves of steel in 0. 05 ~ 1. 0 mol/L NaHCO₃ solutions
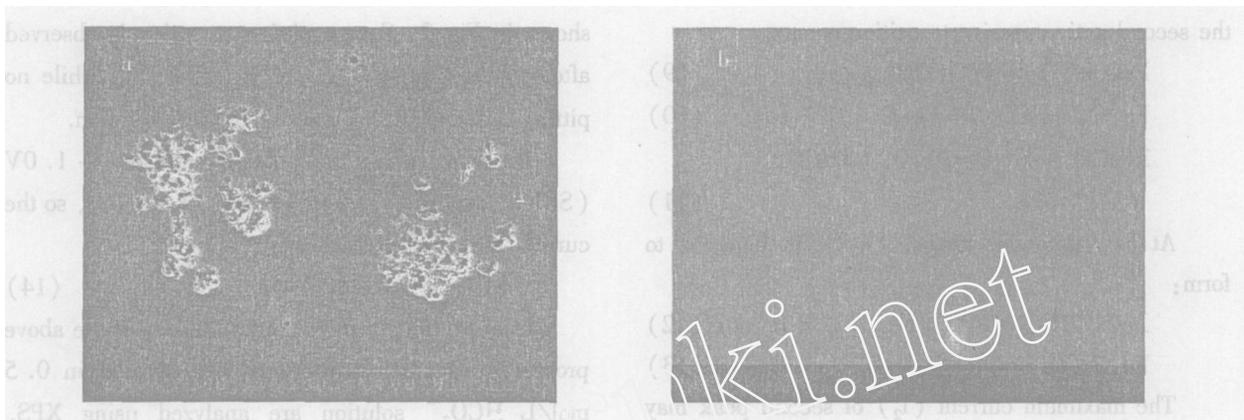
Fig 2 Surface morphology of steel after polarization in 0. 1 mol/L (a) and 0. 5 mol/L (b) NaHCO$_3$ solutions

the potential of F point in Fig 1d, the sweep is stopped and the specimen is analyzed immediately by XPS. The results are shown in Fig 3. Before sputtering, two peaks appearing at 710. 9 eV and 724. 5 eV of the binding energy in the spectra of Fe(2P$_{3/2}$) and Fe(2P$_{1/2}$) indicate that the outer film consists mainly of Fe$_2$O$_3$. After sputtering for 1min, the peaks become wider and their binding energies change to be 709. 8 eV and 722. 7 eV respectively. By separating the Fe(2P$_{3/2}$) peak as shown in Fig 4, it is found that this peak is composed of two peaks, one is at 709. 2eV which is assigned to Fe^{2+} in FeO, another is at 711. 2 eV, which is assigned to Fe^{3+} in FeOOH or Fe$_3$O$_4$. It is difficult to identify which ferric oxide is formed on earth because the binding energy of Fe^{3+} in these oxides is almost the same. However it can be drawn that the inner film comprises ferrous and ferric oxide. These results are consistent with the previous publications[4, 10]. While after 5min sputtering, only element Fe is detected.

3 Conclusions

1) Anodic polarization curves (E i) of steel in 0. 05 1. 0 mol/L NaHCO$_3$ solutions show two active-passive transitions. When the concentration of HCO$_3^-$ is lower than 0. 1 mol/L, the initial current peak is very small and so close to the second peak that the first peak is difficult to be observed. When the concentration of HCO$_3^-$ is higher than 0. 1 mol/L, two peaks seperate obviously, and the two maximum currents are almost the same in 0. 2 mol/L
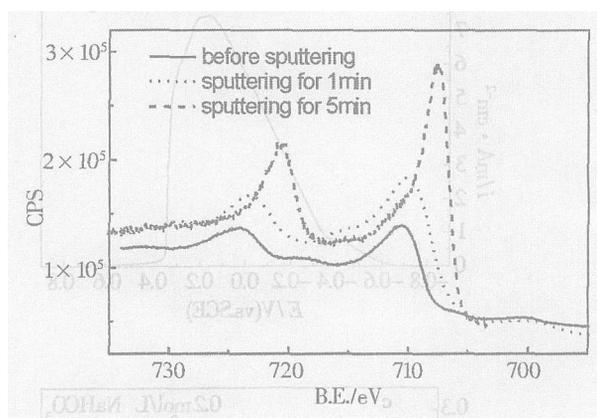

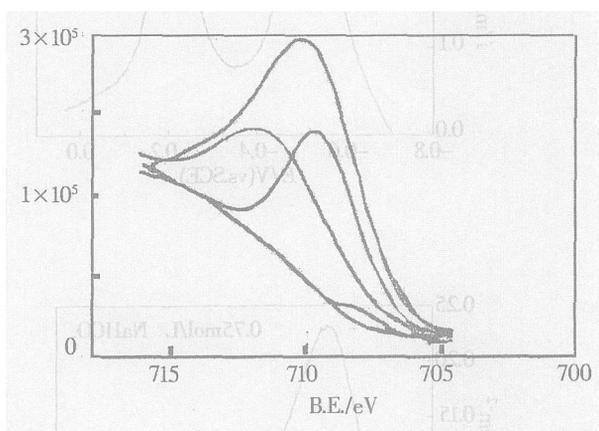Fig 3 XPS for steel film formed in 0. 5 mol/L NaHCO$_3$ solution before sputtering and after sputtering

Fig 4 Peak separation for Fe(2P$_{3/2}$) of steel film formed in 0. 5 mol/L NaHCO$_3$ solution after sputtering for 1 min

HCO$_3^-$ solution. With the increase of HCO$_3^-$ concentration, the current of first peak becomes larger

than that of the second peak.

2) A series of reactions on the surface of iron are responsible for the occurrence of current peaks. At lower potential, $FeCO_3$ /FeO are formed on the surface of steel, and at higher potential, Fe_3O_4 / $FeOOH$ / Fe_2O_3 are formed. The outer film formed at the second passive zone consists mainly of Fe_2O_3, and the inner film is a mixture of ferrous and ferric oxide.

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NaHCO₃

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:   NaHCO₃   .   , (0. 05   1. 0 mol/L) NaHCO₃
,   2   2   , HCO₃⁻   0. 1 mol/L   ,
,   1   .   HCO₃⁻   >0. 1 mol/L   ,   1   ,
2   . XPS   ,   Fe₂O₃,
Fe( )   Fe( )   .
:   ;   ; NaHCO₃