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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.

Key words: 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 oxidation 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 α -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 3 min 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 30 min, the potential is swept in the positive direction with a scan rate of 100 mV/min, starting from the open-circuit potential

All the experiments are carried out at 25 ± 1 °C.

2 Results and Discussion

Fig 1 (a ~ f) show the $E \sim i$ 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

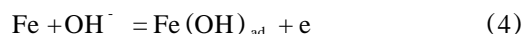
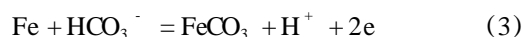
larger than i_1 , and the two peaks are so close that the initial current peak and the initial passivation zone are difficult to be observed. When the concentration of HCO_3^- is 0.2 mol/L, the two peaks are separated obviously, and $i_1 > i_2$. With the increase in HCO_3^- concentration, i_2 becomes 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:

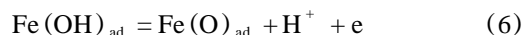
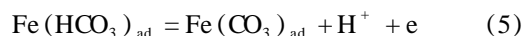
A-B-C-D is the initial active-passive transition. At beginning, the current increases with increasing anodic potentials until a maximum current (i_1) is reached, after which the current decreases with increasing anodic potentials, and then keeps unchanged for a very short potential range. A-B represents the active dissolution of steel, the reaction occurred is:



With the potential change in positive direction, more and more OH^- and HCO_3^- ions are adsorbed on the steel surface, resulting in formation of $\text{Fe}(\text{HCO}_3)_{\text{ad}}$ 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

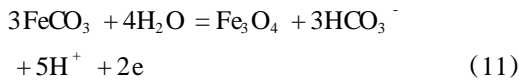
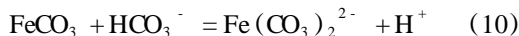
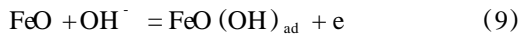


Meanwhile, desorption reaction of H^+ ion may take place in this potential region



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], $\text{Fe}(\text{CO}_3)_2^{2-}$, 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



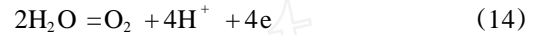
At F-G potential range, Fe₂O₃ is believed to form:



The maximum current (*i*₂) of second peak may indicate the attack of HCO₃⁻ ions on FeCO₃ 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.



In order to get further understanding of the above processes, the compositions of film formed in 0.5 mol/L HCO₃⁻ solution are analyzed using XPS. During the potential scanning, when the potential reaches just after the second peak, which corresponds to

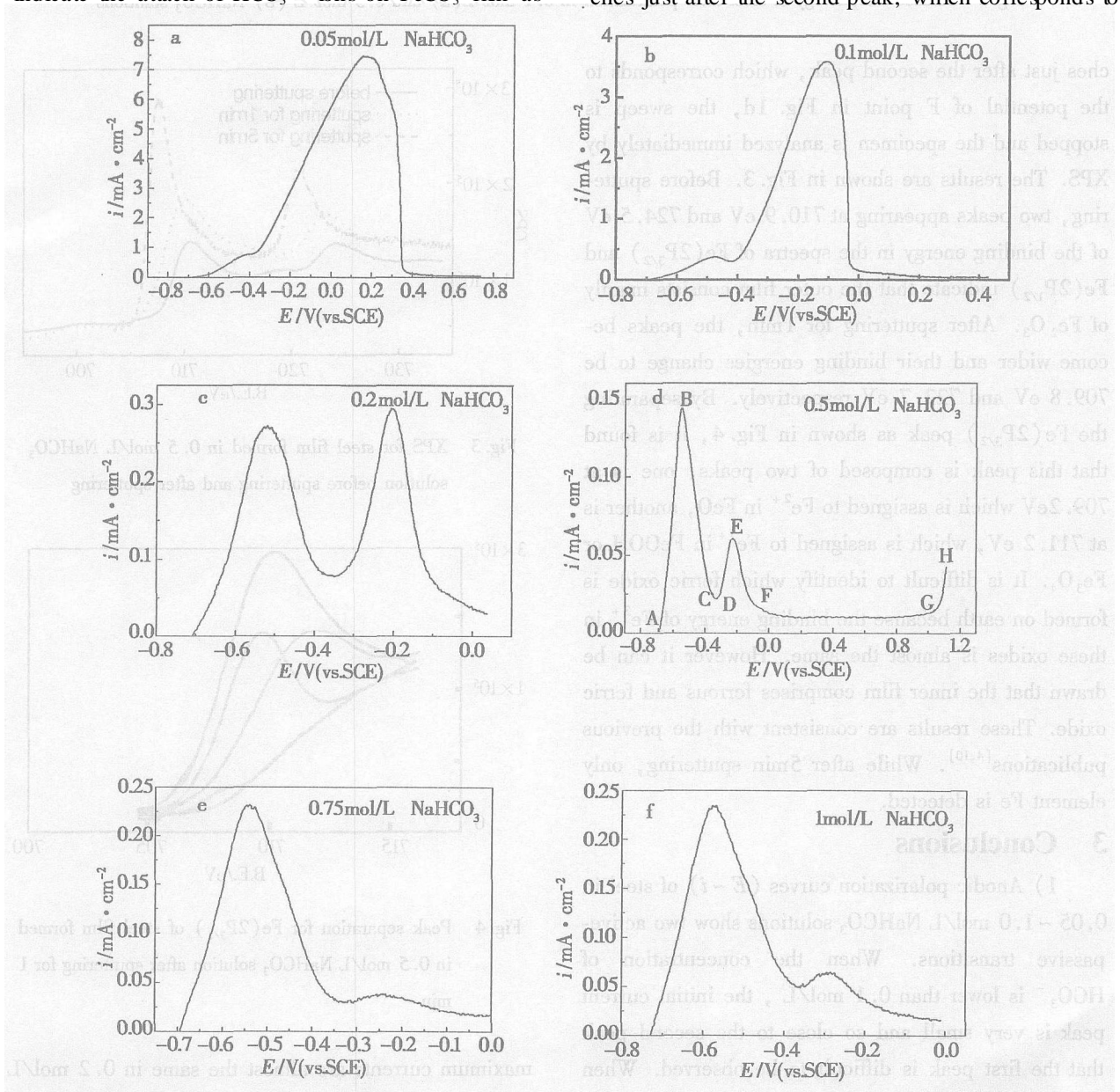


Fig 1 The polarization curves of steel in 0.05 ~ 1.0 mol/L NaHCO₃ solutions

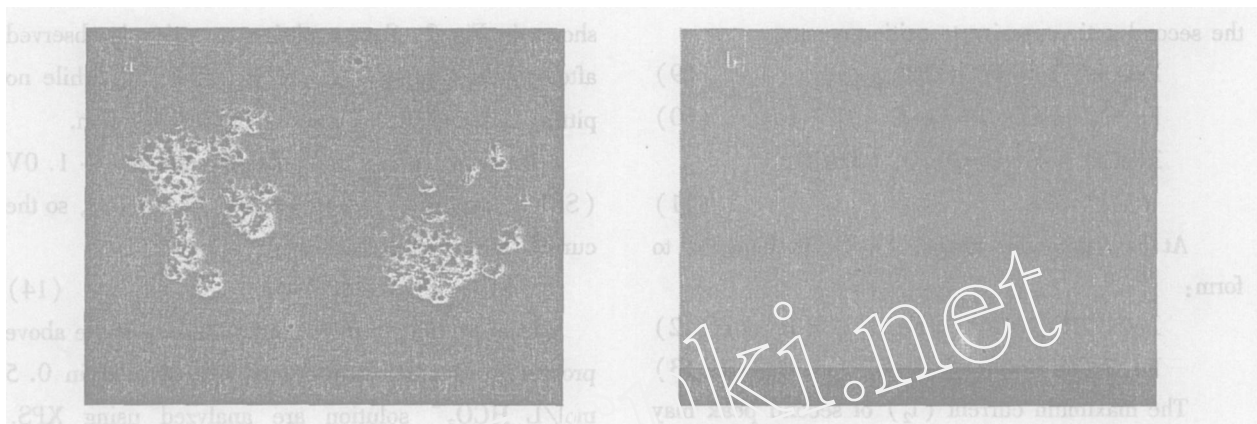


Fig 2 Surface morphology of steel after polarization in 0.1 mol/L (a) and 0.5 mol/L (b) NaHCO_3 solutions

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 $\text{Fe}(2\text{P}_{3/2})$ and $\text{Fe}(2\text{P}_{1/2})$ indicate that the outer film consists mainly of Fe_2O_3 . After sputtering for 1 min, the peaks become wider and their binding energies change to be 709.8 eV and 722.7 eV respectively. By separating the $\text{Fe}(2\text{P}_{3/2})$ peak as shown in Fig 4, it is found that this peak is composed of two peaks, one is at 709.2 eV which is assigned to Fe^{2+} in FeO , another is at 711.2 eV, which is assigned to Fe^{3+} in FeOOH or Fe_3O_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 5 min sputtering, only element Fe is detected

3 Conclusions

1) Anodic polarization curves ($E \sim i$) 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 separate obviously, and the two maximum currents are almost the same in 0.2 mol/L

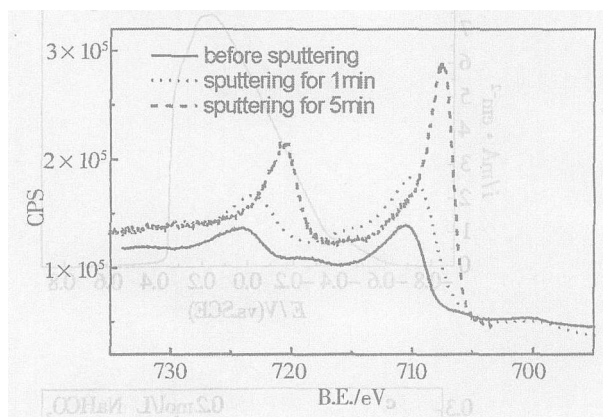


Fig 3 XPS for steel film formed in 0.5 mol/L NaHCO_3 solution before sputtering and after sputtering

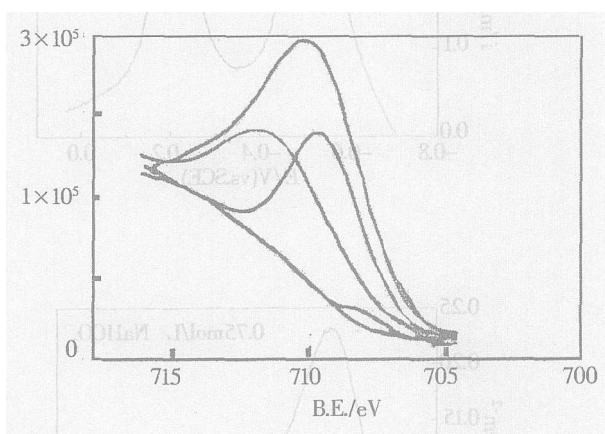


Fig 4 Peak separation for $\text{Fe}(2\text{P}_{3/2})$ of steel film formed in 0.5 mol/L NaHCO_3 solution after sputtering for 1 min

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, $\text{Fe}_3\text{O}_4/\text{FeOOH}/\text{Fe}_2\text{O}_3$ 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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碳钢在 NaHCO_3 溶液中的阳极极化行为

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摘要: 研究碳钢在 NaHCO_3 溶液中的阳极极化行为。极化曲线测试表明,在 $(0.05 \sim 1.0 \text{ mol/L}) \text{NaHCO}_3$ 浓度范围内,碳钢的阳极极化曲线都显示 2 个电流峰和 2 个钝化区,当 HCO_3^- 浓度低于 0.1 mol/L 时,两电流峰相距很近,致使第 1 个钝化区不易观察到。而当 HCO_3^- 浓度 $> 0.1 \text{ mol/L}$ 后,其第 1 电流峰峰电流愈加上扬,而第 2 电流峰峰电流反而下降。XPS 分析表明,在较高电位下碳钢形成的表面膜,其外层主要成分为 Fe_2O_3 , 而内层组成主要含 $\text{Fe}(\text{II})$ 和 $\text{Fe}(\text{III})$ 氧化物。

关键词: 阳极极化; 碳钢; NaHCO_3 溶液