ELECTRODISSOLUTION KINETICS OF IRON AND ITS ALLOYS CONTAINING TITANIUM IN CHLORIDE SOLUTIONS

I. ACIDIC SOLUTIONS

By

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SYNOPSIS

The dissolution kinetics of iron and its alloys containing Ti has been investigated by galvanostatic polarization. An anodic Tafel slope of approximately 60mV/decade was obtained to corroborate the halide inhibited mechanism in concentration from 0.05 to 0.6mol / liter Cl$^-$. The following rate expression for iron dissolution and hydrogen evolution have been determined from the experimental data.

$$i_a = K_a C^{-1}_{Cl^-} C^{0.4}_{OH^-} \exp (FE / RT)$$
$$i_c = -K_c C_{H^+} \exp (-FE / 2RT)$$

In the range of Cl$^-$ concentration from 1.0 to 3.0mol/liter, an increase in the chloride ion concentration at a constant pH, increased the dissolution rate of iron and its alloys due to the direct participation of chloride ions in their dissolution.

The alloy specimen (0.02%Ti) of which Ti content is just enough to scavenge C, N and O in electrolytic iron in fact simulates the corrosion behavior of pure iron and exhibits the minimum corrosion rate.

1. Introduction

The effect of anions on the kinetics of metallic dissolution has been reviewed by Kolotyrkin[1]. Foley has reviewed the specific case of the effect of chloride ions on the dissolution of iron[2].

Lorenz studied the dissolution of iron in 0.5N H$_2$SO$_4$ in the absence and presence of KCl[3]. He found that below 0.1N, chloride ions did not affect the anodic polarization behavior of iron. An anodic Tafel slope of 30mV/decade was obtained. For concentrations greater than 0.1N, increasing the chloride ion concentration decreased the rate of iron dissolution and changed the anodic Tafel slope to 60mV / decade. At zero or low chloride ion concentration, Lorenz[3] interpreted his results for iron dissolution in terms of the Heusler mechanism[4].

Kolotyrkin and co-workers investigated the dissolution of iron in H$_2$SO$_4$–Na$_2$SO$_4$ and HCl-NaCl solutions[5,6]. In both types of solutions an increase in anion concentration increased the dissolution rate of iron. This increase in the rate of dissolution could not be attributed solely to a change in the solution pH. It was

concluded that both the sulfate and chloride ions participate in the dissolution of iron, and both have an accelerating effect. By addition of KCl to 0.1N H_2SO_4, the dissolution rate of iron was found to decrease with increasing KCl concentration up to 0.1N, similar to the observation of Lorenz[3] and Heusler and Cartledge[7]. However, further increase in KCl concentration increased the dissolution rate. Kolotyrkin's interpretation of these results were based on the competitive adsoption of chloride and sulfate ions on the iron surface. The retarding effect observed when chloride ions were added to H_2SO_4 was attributed to the displacement of sulfate ions by chloride ions on the iron surface.

In the subsquent study by Lorenz and co-workers, it was concluded that the SO_4^{2-} ions did not participate directly in the dissolution of iron.[8].

On the other hand, it is recognized that the electrochemical behavior of iron during corrosion is influenced by its purity, structure and heat treatment[9], [10]. According to Vijh, halogen ions have rather small effect on the anodic behavior of Ti and it essentially retain its passivity in media of high Cl^- concentration.

In this study the effect of chloride ions, at constant pH, on the kinetics of iron and its alloys (containing Ti) dissolution is investigated by using galvanostatic polarization techniques. The pH effect is also examined under potetiostatic steady-state conditions to maintain a constant Cl^- concentration in the solutions and vary Ti concentration in the alloys.

2. Experimetal

The materials used were electrolytic iron and its dilute alloys of Ti(0.02 to 0.5% as shown Table 1.), being prepared by melting and casting in vacuum. These ingots were first hot-rolled to 6 mm in thickness and then cold-rolled down to 0.8 mm in thickness. These plates were cut into 10x10x0.8 mm, and after chemical polishing the surface they were annealed at several elevated temperatures for various adequate periods in order to obtain a certain grain size. These specimen was covered with epoxy resin to leave 10x10mm uncovered, chemically polished with a H_2O_2-HF solution and degreased its uncovered surface.

The electrolytic solutions were composed of 0.5 mol / liter Na_2SO_4 as a supporting electrolyte and sodium chloride of various concentrations from 0.05 to 3.0 mol / liter. The pH of the solution was adjusted with H_2SO_4 and NaOH to be in the ranges of 1-5. Corrosion tests were performed in the H-type cell at 25°C. After dipping the specimen into the electrolytic solution which had been deaerated by bubbling pure nitrogen gas, anodic and cathodic currents were measured by keeping the potential constant vs. SCE. The polarization curves were first obtained by the steady-state method to derive the potential region for dissolution, and then the dissolution potentials were measured versus SCE by using the constant current pulse method. Tafel's slopes and corrosion currents were obtained from these polarization curves.

Table 1 Chemical composition of Fe-Ti alloys

Alloy	C(%)	Si(%)	Mn(%)	Ti(%)	Ave. G. S. (mμ)	
No. 1				——	A	As-rolled
					B	20
No. 2				0.02	″	″
No. 3				0.05	″	″
No. 4	<0.01	<0.01	<0.01	0.10	″	″
No. 5				0.15	″	″
No. 6				0.20	″	″
No. 7				0.30	″	″
No. 8				0.50	″	″

3. Results and Discussion

The chemical analysis of specimens used are shown in Table 1. Figure 1 gives the typical polarization curves for these specimens in 0.6 mol / liter NaCl solution at pH 1. As is evident from Fig. 1, the corrosion current for Fe-Ti alloys first decreases with Ti content up to 0.02% to exhibit the minimum there and then increases with increasing Ti content up to 0.05%. Above this content it increases asymptotically. This variation of corrosion current with Ti concentration is quite similar to that of the flow stress with Ti concentration. The alloy specimen of which Ti content is just enough to scavenge C, N and O in electrolytic iron in fact simulates the corrosion behavior of pure iron and exhibits the minimum corrosion rate.
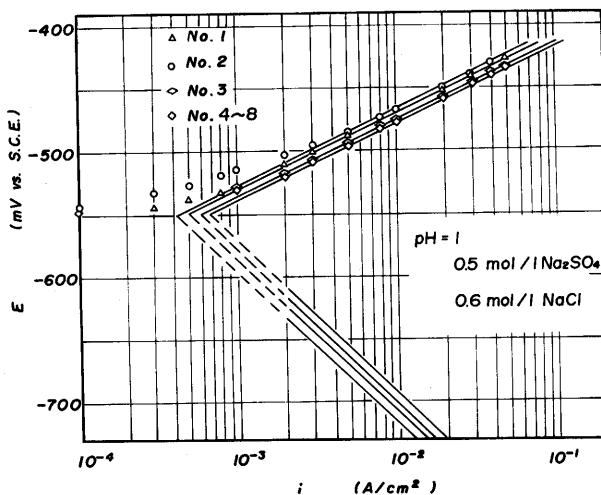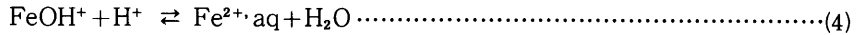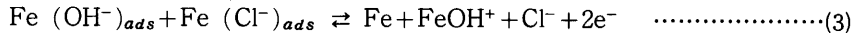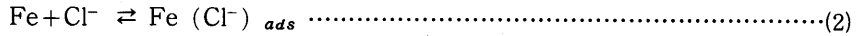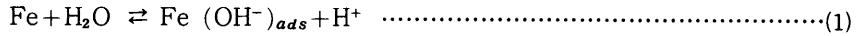

Fig. 1   Polarization curves.

In the 0.6 mol / liter NaCl solution at pH 1, the anodic slopes of polarization curves for the alloy specimens are identically 60mV / decade to corroborate the halide inhibited mechanism[12].

$$Fe + H_2O \rightleftarrows Fe\ (OH^-)_{ads} + H^+ \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$
$$Fe + Cl^- \rightleftarrows Fe\ (Cl^-)_{ads} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$
$$Fe\ (OH^-)_{ads} + Fe\ (Cl^-)_{ads} \rightleftarrows Fe + FeOH^+ + Cl^- + 2e^- \quad \cdots\cdots\cdots\cdots(3)$$
$$FeOH^+ + H^+ \rightleftarrows Fe^{2+\cdot}aq + H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

For the rate determining step (3) valid:

$$i_a = 2FK_3\theta_{Fe(OH-)}\theta_{Fe(cl-)}\exp\ (2\beta FE/RT) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$$
$$i_c = -2Fk_{-3}\ [1 - (\theta_{Fe(OH-)} + \theta_{Fe(cl-)})\ C_{FeoH^+}C_{cl}\text{-}\exp\ [-(1-\beta)FE/RT]$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

When the reaction (1), (2), (4) are all equilibrium conditions, i_a and i_c are expressed as follows,

$$i_a = 2FE(C_{OH-}/C_{cl-})\ \exp\ (2\beta FE/RT) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(7)$$
$$i_c = -2FkC_{Fe^{2+}}C_{OH-}C_{cl-}\exp\ [-2(1-\beta)FE/RT] \quad \cdots\cdots\cdots\cdots\cdots(8)$$

In these equations i_a represents the anodic current density, i_c the cathodic current density, $\theta_{Fe(OH-)}$ the surface coverage with $Fe(OH^-)_{ads}$, $\theta_{Fe(cl-)}$ the surface coverag with $Fe(Cl^-)_{ads}$, β the symmetry factor. By assuming $\beta = 0.5$, the surface coverage with $Fe\ (Cl^-)_{ads}$ near to one and Langmuir-type isotherm, the above mechanism predicts an anodic Tafel slope of 60mV /decade and reaction order with respect to chloride ion concentration of -1.
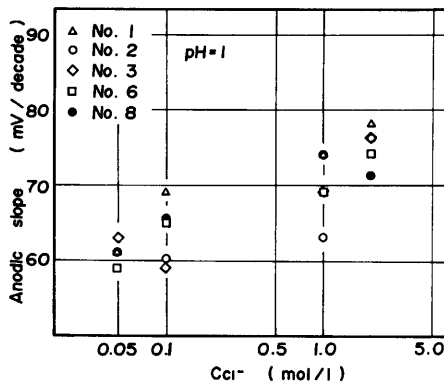

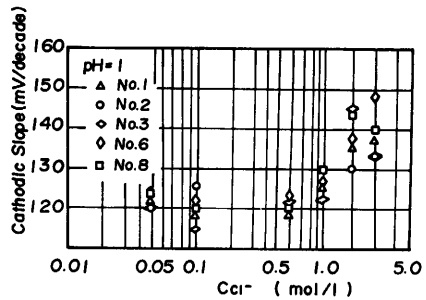Fig. 2 The effect of Cl⁻ concentration on the anodic slope

Fig. 3 The effect of Cl⁻ concentration on the cathodic slope

The changes in the anodic and cathodic Tafel slopes related to the chloride ion concentration are respectively shown in Fig. 2 and Fig. 3. It can be seen that the anodic slope of about 60mV / decade and the cathodic slope of about 120mV / decade are indicated in the range of 0.05 to 0.6 mol / liter Cl⁻, and then both slopes increase linearly with increasing the concentration of Cl⁻ in the range of 1.0 to 3.0 mole / liter Cl⁻. These support the assumption that the direct participation of chloride ions in

the dissolution of iron and its alloys takes place at the concentration of 1.0 mol /liter Cl^-. However, definite conclusions can not be drawn here, because the set of electrochemical data is incomplete.
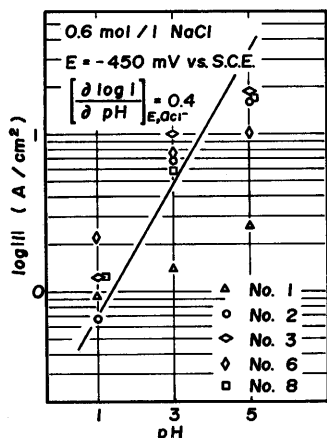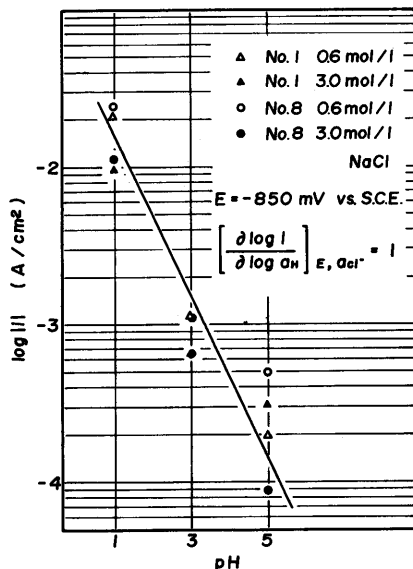
Fig. 4   The effect of pH
on the anodic current

Fig. 5   The effect of pH on the cathodic current

From the slope of straight line in Fig. 4, the anodic electrochemical reaction order related to hydrogen ion concentration is found as $n_{+,H^+}=-n^+,_{pH}=-0.4$. These experimental data described above lead the following rate expression for the anodic dissolution of iron in the range of 0.05 to 0.6 mol / liter Cl^-.

$$i_a = k_a \ (C_{OH-}^{0.4}/C_{cl-}) \quad \exp \ (FE \ / \ RT) \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \ (9)$$

As depicted in Fig. 5, the cathodic electrochmical reaction order related to the hydrogen ion concentration is found as $n_-,H^+=-n_-, pH=1$. This is a good agreement with that predicted from equation (8). However, the cathodic slope of 120mV /decade and the anodic reaction order of -0.4 related to hydrogen ion concentration are significantly deviated from the values which are calculated by expecting the halide inhibited mechanism. This seems to be due to the change in the reaction order related to hydrogen ion concentration from -1 indicated in equation (1) to an another value. The following emprical rate expression can be obtained.

$$i_c = -k_{c'}C_{H^+}\exp \ (-FE \ /2RT) \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \ (10)$$

Comparing Fig. 6 and Fig. 7 it can be seen that the corrosion rates for the specimens containing Ti in concentration up to 0.02% are smaller than those for the specimens containing Ti above 0.05% in the range of 0.05 to 0.6 mol /liter Cl^-. The corrosion rate is not affected, howerer, by alloying element Ti in chloride ion concentration above 1.0 mol / liter.
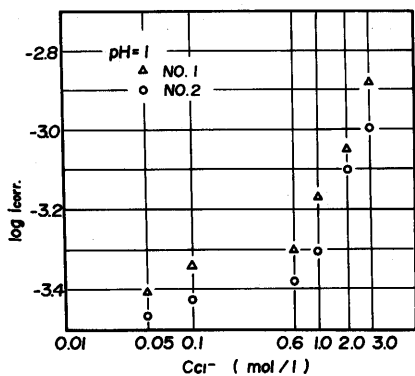
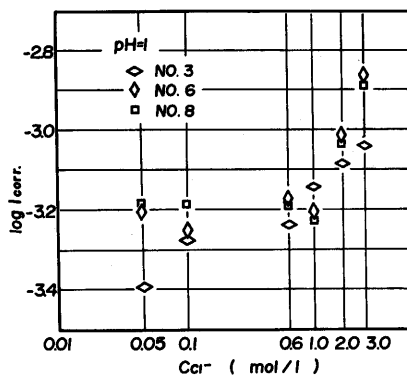Fig. 6   The effect of Cl⁻ concentration
on the corrosion current (1)

Fig. 7   The effect of Cl⁻ concentration
on the corrosion current (2)

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