Electrochemical Behavior of Titanium in HCl Solutions Containing Ferrous and Ferric Ions*

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Polarization of commercially pure titanium with reference to the reversible potential of the hydrogen electrode has been determined in deaerated HCl solutions containing ferrous and ferric ions at 35°C.

Titanium was corroded in solutions containing a low concentration of ferric ions, but it remained inactive at high concentrations.

The static potential of titanium reached the oxidation - reduction potential of the solution when the titanium was passivated.

The optimum concentration of ferric ions in a deaerated solution of HCl at 35°C to prevent corrosion of the titanium was determined empirically.

Because titanium has excellent resistance to corrosion in solutions containing an oxidizing agent, its demand in the chemical process industries has a bright future.

On the other hand, unsatisfactory resistance to non-oxidizing solutions is a drawback. Improvement in the corrosion resistance in such an environment has been studied by some authors^{1)~4)} and it has been claimed that addition of ferric or cupric ions to the solution inhibits corrosion. Such a process is a modification of the technique employed for steel and stainless steel by Markrides¹⁾ but detailed discussion of the process is lacking.

This paper will describe the mechanism of the electrochemical behavior of

ferric ions at the surface of titanium in an acid solution.

1. Experiment

Nitrogen gas for deaeration of the electrolytic solution was introduced into a glass cell of about 0.5 l volume through a sintered glass filter at the bottom of the cell as shown in Fig. 1.

A potentiostat, Yanagimoto Seisakusho, Type VE 101 was used for potential measurement in conjunction with a calomel electrode (3.3 N-KCl) as the reference electrode. The observed potential however was calibrated against the standard hydrogen electrode scale.

The scanning velocity of the potentiostat was about 100mV/min.

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for a solution containing 0.01 mole/l of Fe²⁺ and 0.05 mole/l of Fe³⁺, and the other for a solution containing 0.05 mole/l and 0.08 mole/l of Fe²⁺ and Fe³⁺ respectively.

The sign (I) in the figure indicates the cathodic current and (II) indicates the anodic current. Three mixed potentials appeared as shown by the signs 1, 2, and 3 in the figure. The reversible potential of the oxidation- reduction process for ferrous and ferric ions:

$$\text{Fe}^{2+} = \text{Fe}^{3+} + e, E^{\circ} = 0.771\text{V}$$

at 25°C

(1)

is about 0.814V in a solution containing 0.01 mole/l of Fe²⁺ and 0.05 mole/l of Fe³⁺ at 35°C. It is much more noble than any mixed potential, that is, 1.195V, 0.933V and 0.386V greater at the points 1, 2, and 3. The reduction process of ferric ions is, then assumed to take place at the local cathode, and assuming a diffusion controlled process. The reduction rate is described by the following equations:

$$i = Fk_d a_{\text{Fe}^{3+}} \exp (-2. \eta \cdot F / R T)$$

(2)

$$t i = F D / \delta \cdot\left(a_{\text{Fe}^{3+}}^{\circ}-a_{\text{Fe}^{3+}}\right)$$

(3)

$$1 / F K_d \ll\left|t / D \cdot \exp (-2. \eta \cdot F / R T)\right|$$

(4)

K_d is the rate constant of the backward process of the reaction (1). D is the diffusion coefficient of Fe³⁺, δ is the thickness of the diffusion layer, and a_{Fe³⁺} and a[°]_{Fe³⁺} are the activities of Fe³⁺ near the electrode surface and the bulk of the solution, respectively.

The parameter t is the transference coefficient of foreign ions of Fe³⁺ and has a value close to unity in this case because of the low concentration of Fe³⁺.

Then we have the following equation:

$$i_L = F d / \delta \cdot a_{\text{Fe}^{3+}}^{\circ}$$

(5)

where i_L is the limiting current density for Fe³⁺, and also the current density of the local cathode at the titanium surface. The limiting current density for the reduction of Fe³⁺ was determined with a platinized platinum electrode of 1 cm² area. The results are shown in Table 2.

Table 2. Limiting Current Density for the Reduction of Ferric Ions

the concentration of Fe ³⁺ (mole/l)	the concentration of Fe ²⁺ (mole/l)	the limiting current density (μA/cm ²)
0.05	0.01	2.50 x 10 ²
0.08	0.05	3.82 x 10 ²
0.117	0.01	1.05 x 10 ³

These values are related to the anodic polarization curve of titanium in a de-aerated solution of 6N-HCl, and the mixed potential is obtained from the cross-point of both lines as shown in Fig. 4

- (1) indicates -0.319V vs. N.H.E.
(2) indicates -0.100V vs. N.H.E.
(1') indicates -0.279V vs. N.H.E.
(2') indicates -0.109V vs. N.H.E.
(IV), (V), (VI) indicates the limiting current densities for the reduction of ferric ions at conc of 0.05mole/l 0.08 and 0.117 respectively

Fig. 4 Partial polarization curves of titanium in a deaerated solution of 6 N-HCl containing ferrous and ferric ions at 35°C.

These values agree with the experimental data in Table 3 (see also Fig. 2 and Fig. 3)

Table 3. Comparison of the Experimental and Calibrated Values of the Mixed Potential

the concentration of Fe^{2+} (mole/l)	the concentration of Fe^{3+} (mole/l)	the calibrated (V vs. NHE)	the experimental (V vs. NHE)
0.01	0.05	(1) -0.319	-0.386
		(2) -0.100	-0.119
0.05	0.08	(1) -0.279	-0.349
		(2) -0.109	-0.189

Thus it can be considered that the mixed potential (1) in Fig. 2 consists of the anodic dissolution of titanium and the cathodic reduction of ferric ions to ferrous. Since the mixed potential (1) is close to the static potential of titanium in the solution containing 0.08 mole/l of Fe^{3+} , titanium is active in a solution of Fe^{3+} concentration lower than this value.

The mixed potential (2), on the other hand, may show the passive state of titanium for the same reason as described above.

Fig. 5 show the results for solutions

Fig. 5 Polarization curves of platinized platinum and titanium in a deaerated solution of 6 *N*-HCl containing 0.01 mole/l of Fe^{2+} ions and 0.117 mole/l of Fe^{3+} ions at 35°C.

containing 0.01 mole/l of Fe^{2+} and 0.11 mole/l of Fe^{3+} .

Fig. 6 Static potentials on platinum and titanium electrodes in a deaerated solution of 6 *N*-HCl containing Fe^{3+} ions at 35°C.

The solid lines with closed points show the polarization curve of titanium and the broken lines are for the platinized platinum electrode in the same solution. Fig. 6 shows the static potential of titanium and platinized platinum electrodes. It is clear that the static potential of titanium reaches the value of the platinized platinum electrode in the solution in which the concentration of ferric ions is more than 0.115 mole/l, while the potential of titanium is quite less noble than the platinum electrode in more dilute solutions of Fe^{3+} . The anodic and cathodic polarization curves for the platinized platinum electrode in the deaerated solution of 6*N*-HCl containing ferrous and ferric ions have been determined at 35°C. and are shown in Fig. 7. It is evident that the anodic polarization depends on the concentration of ferrous ions and the cathodic polarization is a function of the concentration of ferric ions.

Both the cathodic and anodic polariza-

Fig. 7 Dependence of polarization curves of platinized platinum upon the concentration of Fe²⁺ ions and Fe³⁺ ions at 35°C.

zation potential are linear with respect to the log current density with slopes of 0.131 and 0.120 V/decade, respectively. These values correspond to values of 0.47 and 0.51 for α and $1-\alpha$, respectively, where α is the transfer coefficient for the cathodic process. According to Vetter's description, the oxidation-reduction process for a species S is represented as follows (5):

$$Z_{r1} S_1 + Z_{r2} S_2 + \dots = Z_{rj} S_j + \dots + S_R \tag{6}$$

$$S_R = S_o + e \tag{7}$$

$$S_o + Z_{oj} S_1 + \dots = Z_{oj} S_j + \dots \tag{8}$$

Therefore, the orders of the electrochemical reaction for both directions, Z_{rj} and Z_{oj} , are represented as follows:

$$\left(\frac{d \log i_+}{d \log c_j}\right) \text{ at constant O.V.} = Z_{rj} \tag{11}$$

$$\left(\frac{d \log i_-}{d \log c_j}\right) \text{ at constant O.V.} = Z_{oj} \tag{12}$$

A linear relationship exists between log current density and log concentration of ferrous and ferric ions at a given over-voltage over 60mV and the slope is almost unity.

It is also clear that the reaction rates for anodic and cathodic processes are independent of the concentrations of ferric and ferrous ions, respectively. From this discussion, it may be concluded that the reversible reaction of ferrous and ferric ions may be taking place at the surface of titanium in an acid solution containing 0.115 mole/l or more, and thus titanium will act as a passive or durable electrode. The last discussion concerns the mixed potential (3). This potential is less noble than the reversible potential of the system Fe²⁺/Fe³⁺ obtained with the platinized platinum electrode in a solution containing a low concentration of ferric ions, but it reaches the reversible potential in the concentrated solution of ferric ions as shown in Table 3. Thus the main reaction in a concentrated solution might be a ferrous- ferric redox reaction. The mechanism in dilute solution can not yet be described in detail.

Table 4. Mixed Potentials on Titanium and Reversible Potential on Platinized Platinum in Deaerated Solutions of 6N HCl Containing Ferrous and Ferric Ions

the concentration of Fe ²⁺ (mole/l)	the concentration of Fe ³⁺ (mole/l)	the mixed potential (V vs. NHE)	the reversible potential (V vs. NHE)
0.01	0.05	(3) 0.451	0.670
0.05	0.08	(3) 0.541	0.603
0.01	0.117	(3) 0.654	0.663
0.01	0.210	(3) 0.679	0.685

4. Conclusion.

The reversible, the static and the polarization potentials of titanium and platinized platinum electrodes have been de-

terminated in solutions containing various amount of ferrous and ferric ions at 35°C and the data have been discussed from the view of the electrochemical behavior of titanium in HCl.

1. Titanium is corroded in HCl containing a very low concentration of ferric ions by a local cell reaction.
2. When the concentration of ferric ions in solution is more than 0.115 mole/l, the reduction of ferric to ferrous may be the local cathode reaction, and the titanium becomes passive.
3. The static potential on titanium in the passive state reaches the value for the platinum electrode, on which the reversi-

ble potential for the system of $\text{Fe}^{2+} = \text{Fe}^{3+} + e$ is maintained.

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Deposition of Silicon Dioxide Films by the Reaction of SiCl_4 or SiHCl_3 with Water Vapor*

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Silicon dioxide films are deposited on silicon substrates in the temperature range 800~1250°C by the reaction of SiCl_4 or SiHCl_3 with water vapor. The deposition rate of a silicon dioxide film as a function of the molar ratio of SiCl_4 or SiHCl_3 to water vapor and temperature was investigated and the apparent activation energies for the reaction of SiCl_4 and SiHCl_3 with water vapor were 45 and 25 kcal/mole respectively. Physical properties of these films, such as refractive index, density, etching rate and infrared absorption were measured as a function of the deposition temperature. Dielectric properties of films obtained above 1100° were as good as those of thermally grown silicon dioxide films, but films formed at lower temperatures were less dense. From these observation, the reaction kinetics have been discussed.

*The original written in Japanese can be seen in *Denki-Kagaku* **35**, 120 (1967).