Research Paper

The Electrochemical Behavior of Iron in Phosphoric Acid Solutions

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The electrochemical behavior of zone-refined iron in 3*N* phosphoric acid and sodium salt solutions has been investigated by the measurement of the corrosion potentials, the corrosion currents, the steady state polarization curves and the pH dependences. The super-scrupulous experiment was made to obtain reproducible data and to minimize the experimental errors. A mercurous phosphate electrode was used as a reference electrode. The corrosion potentials and currents were lineally related to the pH's of the bulk solutions and the relations were discussed by employing the mixed potential theory. The steady state anodic polarization curves represented the two Tafel slopes, i. e., 40 mV/decade at the low current densities and 60 mV/decade at the high current densities. The anodic behavior of iron in phosphoric acid was similar to those in sulfuric acid. The cathodic polarization study, however, showed the different behavior from the case in sulfuric acid. A insulating film was formed during the cathodic polarization and assumed to be a ferrous phosphate film. The dissolved oxygen did not affect the dissolution mechanism of iron in phosphoric acid.

1 Introduction

The study of corrosion of metals in aqueous solutions is one of the most challenging subjects from viewpoints of industrial importances as well as of scientific interests. The electrochemical approach of this problem seems to be one of the best ways to obtain the fundamental informations for understanding the corrosion mechanism. The electrochemical behavior of iron in 1*N* H₂SO₄ with and without organic inhibitors has recently investigated by authors^{1)~4)}. To obtain further informations of the iron dissolution mechanism in aqueous solutions, the electrochemical behavior of iron in phosphoric acid has been studied in this investigation.

The reaction between metals and phosphoric acid has been studied in many technical papers in the field of chemical surface treatments of metals, known as phosphating. The scientific studies on this problem, however, have hardly been found in literatures because of the complexity of the problem. In the case of iron in phosphoric acid, the dissolution mechanism of iron in an acidic media should be fully worked out at first, and then, the information about the adsorption of

phosphoric acid and iron phosphate as well as water molecules on iron surfaces is a necessity for solving the problem. In addition, the formation of phosphate films at the surface may occur and play an important role in the corrosion behavior of iron in phosphoric acid.

In this investigation, the study of electrochemical behavior of zone-refined iron has been conducted in phosphoric acids to obtain the fundamental informations of both corrosion of iron in aqueous solutions and chemical surface treatment of iron.

2 Experimental

The electrochemical technique employed in this investigation was steady state galvanostatic polarization. As mentioned below, the super-scrupulous experiment was made to obtain reproducible data and to minimize the experimental errors. All chemicals including water except NaOH used in this research were purified thoroughly by recrystallization or rectification.

The zone-refined iron* used was donated by Ameri-

* Authors like to express thier appreciation toward professor K. Nobe who presented them with the zone-refined iron.

can Iron and Steel Institute, and prepared and fabricated to a half-inch rod by Battelle Memorial Institute. The sample rods were cut to cylindrical electrodes by a water wetted abrasive wheel, the surface was polished by wetted emery papers and degreased with hot benzene in a Soxhlet extraction apparatus. The electrodes were annealed at 700°C for one hour under vacuum of 10^{-5} mmHg followed by slow cooling in the annealing oven, polished by water wetted emery papers (up to No. 1500) and degreased with hot benzene again in a Soxhlet apparatus. The samples then were stored in a dessicator with silica gel until used.

The electrochemical cell was a 500 liter flask with a reference electrode compartment and with a cell for pre-electrolysis of electrolytes, all of which were connected through fine-polished ball joints (grease free) each other, so that the cleaning of the cell assembly could be easily and thoroughly performed. The parts were cleaned, before each experimental run, by a chromic acid cleaning solution and by an acid cleaning solution (equal parts of H_2O , H_2SO_4 and HNO_3), rinsed by purified water and dried in air. The cell was placed in a constant temperature bath of 25.0°C. The reference electrode made from purified chemicals was also maintained at the constant temperature. Nitrogen gas purified on activated copper catalysis⁵⁾ was saturated with water vapor, and introduced to the cells through glass tubes (without use of rubber tubes). The glass used in this experiment was pyrex glass beside only the places where platinum wires were sealed were substituted by regular hard glass. The electrode assembly was specially designed to eliminate leaking of the electrolyte between the electrode and teflon seals as described in a previous

paper⁷⁾.

The commercial phosphoric acid, even if it is reagent grade, was not pure enough to perform the electrochemical experiments. The phosphoric acid used in this study was prepared like follows. (1) Reagent grade P_2O_5 was sublimated under an oxygen atmosphere at 800°C. Iron pipes used for the sublimation apparatus, similar to others designed by Finch⁸⁾. (2) Purified water was added gradually over P_2O_5 powder placed in a glassy carbon beaker with a long neck to make 3N H_3PO_4 . All the phosphate must be converted to H_3PO_4 instead of poly-phosphoric acid formation during this process⁷⁾. (3) The H_3PO_4 was stocked in a pyrex flask and the pH was adjusted by adding reagent grade NaOH pellets in the acid when necessary. (4) The test solution was electrochemically purified (pre-electrolysis) by using a platinum anode and an iron cathode and then transferred to the test cell without opening the apparatus to the atmosphere.

Potentials were measured with a high impedance (10^{12} Ohms) pH meter, type KPH-51B by Yokogawa Electric Works. Car-batteries of 100 V were used as a power supply.

The reference electrodes used in this investigations were a mercurous phosphate electrode⁹⁾ and a saturated calomel electrode. The voltage of the cell (1) were measured over the temperature range from 0 to 45°C, and the potential of the mercurous phosphate electrode has been determined by Equation (2), where the potential is referred to a normal hydrogen electrode. The electrode potential has been constant for more than ten months, up to the end of this series of experiments; therefore, the electrode can be satisfactorily used as a reference electrode.

Fig. 1 Corrosion potential of zone-refined iron in 3N H_3PO_4 as a function of immersion time

Fig. 2 Corrosion potential of zone-refined iron in 3N H_3PO_4 as a function of pH

Fig. 3 Corrosion current versus pH

$$E_p = (0.6493 \pm 0.0004) - 4.0 \times 10^{-4}(t - 25) \text{ [V]} \quad (2)$$

The electrode potential value of a saturated calomel electrode was taken from the textbook by Ives and Janz²⁹. The potentials measured with the mercurous phosphate electrode are represented by (vs. N.H.E.) in the following figures. The liquid junction potentials between the reference electrode and the experimental solutions have been ignored in the discussion of this investigation.

3 Results

The corrosion potentials of zone-refined iron in 3N H_3PO_4 are plotted against immersion time in Fig. 1. The potential right after the immersion was positive, but the sudden decrease was observed within one or two minute immersion. After a minimum was recorded, the potential changed slowly in positive direction and reached a steady state after about 15 hours immersion. The steady corrosion behavior of zone-refined iron in 3N H_3PO_4 seemed to be achieved after this period: therefore, all samples in the following experiments were etched in deaerated 3N H_3PO_4 for 20 hours before the experimental runs.

The steady corrosion potentials were linearly related to the pH's of the bulk solutions, as shown in Fig. 2, and the relation of Equation (3) was given as a solid line.

$$E_{\text{corr}} = -0.246 - 2.30 \frac{3RT}{4F} \text{pH} \quad (\text{V vs. N.H.E.}) \quad (3)$$

The corrosion currents measured by the extrapolation of the steady state anodic polarization curves to

Fig. 4 Potential transient during anodic polarization

the corrosion potential were plotted against the pH values of the electrolytes in Fig. 3. The curve of Equation (4) is given as a solid line in the figure.

$$\log i_{\text{corr}} = \log 1.6 - (1/8)\text{pH} \quad (\text{mA/cm}^2) \quad (4)$$

The steady state anodic overpotential of iron in 3N H_3PO_4 was achieved within 10 minutes as shown in Fig. 4, in contrast to a much shorter time of about 5 seconds in 1N H_2SO_4 . After the polarization the shift of the open circuit potential toward negative direction was observed and more than 10 minutes were required to reach the original potential (the corrosion potential before the polarization). There are two Tafel regions in the steady state anodic polarization curve, as shown in Fig. 5. The anodic Tafel slope at the low current densities was 40 mV/decade and 60 mV/decade at the high current densities. The reproducibility was good

and no hysteresis effect on the anodic polarization behavior was observed, i. e., the polarization curves for increasing applied currents were the same as those for decreasing applied currents. The anodic Tafel lines were displaced by changing electrolyte pH's, but exhibit two Tafel slopes as shown in Fig. 6. At the pH value of 5, the passive film was formed by the anodic polarization of only 1 mA/cm^2 and the polarization potential changed toward positive. More than two runs were made for each case and the reproducibility was excellent.

To obtain the quantitative correlation between anodic currents and hydroxyl ion activities, the polarization current at a constant potential of -300 mV were plotted against the electrolyte pH's in Fig. 7 (a) and (b). In the figure, the current densities were obtained by

Fig. 5 Steady state anodic polarization curve

Fig. 6 Steady state anodic polarization curves in H_3PO_4 of different pH's

Fig. 7 Polarization current versus pH at a constant potential

Fig. 8 Polarization potential versus pH at a constant current

Fig. 9 Potential transient during cathodic polarization

the extrapolation of the Tafel lines to the potential of -300 mV. As a matter of convenience the discussion will be made separately for the low current densities region (L) and the high current densities regions (H), which are shown in Fig. 5. As the slopes of the curves in the figures show, the anodic current at (L) was first-order in hydroxyl ion activity and half-order at (H). As the conclusion, the anodic current at (L) and at (H) were given by Equations (5) and (6), respectively.

$$i_a = i_{ka} a_{(\text{OH}^-)} \exp \frac{3F\varepsilon}{2RT} \quad (5)$$

$$i_a = i_{ka} a_{(\text{OH}^-)}^{1/2} \exp \frac{F\varepsilon}{RT} \quad (6)$$

Fig. 8 (a) and (b) show the relation between polarization potential and pH at a constant anodic current of 1 mA/cm^2 . The results coincide the equations.

The cathodic polarization behavior of iron in $3N \text{ H}_3\text{PO}_4$ was quite different from that in $1N \text{ H}_2\text{SO}_4$. The cathodic overpotentials during galvanostatic polarization were not reached a steady state within one hour and the reproducibility was poor. For an example as shown in Fig. 9, the overpotential during the applied current of 3.0 mA/cm^2 decreased with the polarization time, but, after 20 minutes polarization, the overpotential started increasing up to the end of the polarization. The electrode was observed to become black, at the same time, when the evolution of hydrogen gas was seen. Hysteresis, therefore, occurred during the cathodic polarization measurement and was related to the changes of the open circuit potentials (the potentials immediately after the applied current were recorded and shown as open circles in Fig. 10).

Fig. 10 Cathodic polarization curve

Fig. 11 Steady state anodic polarization curve in aerated $3N \text{ H}_3\text{PO}_4$

The effect of oxygen dissolved in the electrolyte on the anodic polarization curves of iron in H_3PO_4 was none, as shown in Fig. 11. The corrosion potential in the aerated solution was almost the same value as that in the deaerated solution. However, when the aerated electrolyte was stirred, the corrosion potential was shifted in 10~15 mV toward positive direction, showing that the diffusion of oxygen in the aerated electrolyte toward the electrode controlled the cathodic reaction.

4 Discussion

The corrosion potential of zone-refined iron in (3 N H_3PO_4) as a function of pH values was given by Equation (3). However, the corrosion potential in (1 N H_2SO_4) has been given by Equation (7), which was

$$E_{\text{corr}} = -0.233 - 2.303 \frac{RT}{F} \text{pH} \quad (7)$$

measured by Kelley¹⁰⁾ and checked by authors. Here, the parentheses of acid represent the mixture of the acid and the sodium salt. The corrosion current in (3N H_3PO_4) as a function of pH represented by Equation (4), was also quite different from the result obtained in (1N H_2SO_4). The difference will be made clear by the discussion of both the anodic reaction and the cathodic reaction of zone-refined iron in acids.

The mechanism of the dissolution of iron in acid solutions has been discussed in a number of papers. For the annealed zone-refined iron in H_2SO_4 , the following mechanism expressed by equations (8)~(12), was proposed and confirmed by experiments¹⁰⁾; where the steady state Tafel slope is 40 mV/decade and the reaction is the first order dependency on the hydroxyl ion activity (See Reference 1, on the detail discussion of this point). The kinetic analysis of zone-refined iron dissolution in H_3PO_4 gives the result that the dissolution mechanism proposed for the iron in H_2SO_4 is applicable for the iron in H_3PO_4 ; that is, Equation (5) shows the Tafel slope of 40 mV/decade and the first order dependency on the reaction on the hydroxyl ion activity. The difference between H_3PO_4 and H_2SO_4 , however, can be seen in magnitude of the anodic currents. The anodic current in H_3PO_4 was approximately fifty per cent of that in H_2SO_4 at the same pH and the same polarization potential. It can be concluded that the place where a hydroxide is adsorbed as an intermediate of the dissolution reaction, may be occupied by an adsorbed phosphate in the degree of about fifty per cent. In this way, phosphoric acid inhibits the anodic dissolution of iron to a small extent.

The anodic dissolution of zone-refined iron at the high current densities was quite different from that in the low current densities. The steady state anodic Tafel slope was 60 mV/decade and the reaction was the half order dependency on the hydroxyl ion activity as given by Equation (6). From the kinetic analysis of the above experimental results, one may elucidate the anodic dissolution reaction as the mechanism shown by Equation (13)~(15).

The different activation energy of the spontaneous dissolution of Ferrovac E iron in phosphoric acid from the activation energy of the anodic dissolution was reported by Smith and Hatfield¹¹⁾, and they concluded that a change in activation energy by the anodic polarization is indicative of a change in the rate controlling mechanism rather than a change in the oxidation state of iron. The result seems to be consistent with our elucidation, that is, the dissolution mechanism changes by the anodic polarization of iron and an adsorbed phosphoric acid acts as an intermediate of the dissolution reaction under anodic polarization. The transition of the anodic reactions from at low current densities to at high current densities was determined by the current density, but not by the polarization potential. The reason could not be made clear, however, it may be related to the limiting current.

The cathodic reaction of iron in 3N H_3PO_4 was not a simple hydrogen evolution reaction, in contrast to the case in H_2SO_4 . Although the hydrogen evolution was observed on the cathodically polarized iron, the surface becomes black and the increase of the overpotential was observed during the cathodic polarization. An insulating film must be formed during the cathodic polarization, which may be a ferrous phosphate film. The films was gradually dissolved into 3N H_3PO_4 after the polarization. Krutikov¹²⁾ concluded from the electro-phosphating study that the formation of phosphate coatings proceeds at the cathodic portion of the metallic surface. He assumed that the pH value of the solution increases by the cathodic polarization, which leads to the formation of the slightly soluble phosphate as given in Equation (16).

In addition, positively charged particles formed in the phosphating bath crystallize on the cathodic portion of the surface.

Another possible explanation on the peculiar behavior of the cathodically polarized iron in H_3PO_4 might be made by assuming that phosphoric acid is reduced on the cathodically polarized iron, just like the case of nitric acid; indeed, the authors¹³⁾ has been observed the reduction of phosphoric acid when a polyphosphoric acid solution was electrolyzed. The reduced phosphate might play an important role for the formation of insulating films.

By employing the mixed potential theory, the corrosion potential and current can be discussed. The corrosion potential and current were computed from Equations (3) and (4), respectively, as the fittest curves in Fig. 2 and 3 by the trial and error method with Equation (5). ($\partial \varepsilon_{\text{corr}}/\partial \text{pH}$) and ($\partial i_{\text{corr}}/\partial \text{pH}$) are quite different from those¹⁰⁾ obtained for the case of H_2SO_4 . The difference is mainly due to the different cathodic reactions between in H_2SO_4 and in H_3PO_4 .

Dissolved oxygen in phosphoric acid did not affect the dissolution mechanism of iron. It seemed that the oxygen inhibited the formation of the cathodic films (possibly the phosphating coatings); because, the in-

crease of the overpotential was not observed during cathodic polarization in aerated phosphoric acid. The result opposes the well-known assumption that the phosphoric acid reacts with iron oxide on the surface as a preliminary interfacial reaction for a phosphate coating process of iron. It should be noted, however, that the electrolyte used in this experiment is quite different from a phosphate coating bath.

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Research Paper

Kinetic Studies on Phosphidation of Iron by Phosphorus vapor

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The Phosphidation of α -iron sheets by phosphorus vapor has been kinetically investigated between 715°C and 860°C at phosphorus partial pressures of 1.3 to 25 Torr in a flow system. The phosphidations proceeded generally with growth of phosphide mounds. Each phosphidation was found to follow parabolic behavior, and to be independent of the partial pressure of phosphorus vapor. The parabolic rate constant K_p increased with an increase of temperature, and its values have fallen into the category of order of 10^{-8} to 10^{-7} g²/cm⁴-min. The Arrhenius plot of K_p has given a curve, so that constant values of activation energy could not be evaluated. From the resulted X-ray diffraction patterns it has been found that the surfaces of the specimens phosphidized appear to be made up of mixtures of FeP and Fe₂P, and that Fe₂P is formed at the phosphide/metal interface.