Technical Paper

The Rate and Mechanism of the Reaction between Iron and Gaseous Phosphorus

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The rates of reaction of an α -iron sheet with gaseous phosphorus were determined by a sealed-tube method. An x-ray diffraction and an electron microprobe analysis showed that the exterior phosphide layer, the second, and the last which is in contact with metallic iron, were FeP_2 , FeP , and Fe_2P , respectively. The phosphidations were revealed to proceed according to the parabolic rate law, namely, the rate-determining step seems to be a diffusion process. The parabolic rate constants, K_p , have been determined to be the order of 10^{-8} – $10^{-7} \text{ g}^2 \text{ cm}^{-4} \text{ min}^{-1}$ at 700°C – 850°C under the phosphorus vapor pressures of 1–760 Torr. The Arrhenius plot yielded the activation energy of $31 \pm 2 \text{ kcal/mole}$ at 1 atm. The dependence of K_p on the pressure of P_4 and of P_2 vapor determined experimentally was given by the expression $K_p \propto P_4^{0.16 \pm 0.12}$ and $K_p \propto P_2^{0.32 \pm 0.04}$ at 700°C , respectively, which could be explained in terms of the mass action law with respect to the concentrations of binary cation vacancies and electron holes in the phosphide layers. This phosphidation was discussed also on the thermodynamic grounds.

1 Introduction

The phase diagram^{1),2)} of the iron-phosphorus system, the crystal structures of Fe_3P ^{3),4)}, Fe_2P ⁵⁾, FeP ⁶⁾ and FeP_2 ⁷⁾, and heats of formation⁸⁾ of these four phosphides have been studied already.

The authors reported previously⁹⁾ the rate of reaction of iron with gaseous phosphorus in a flow system at temperatures ranging from 715°C to 860°C under the partial pressures of 1.3 to 25 Torr. According to its results, the iron was parabolically phosphidized, but the dependence of the rate on the partial pressure was not recognized experimentally because of the narrow range of the partial pressure. The present study was undertaken to extend the reaction or growth mechanism by means of a sealed-tube method, a closed system, by which the wide range of pressure can be obtained.

2 Experimental

2.1 Materials

An iron sheet 0.5 mm thick, which was made by the Tohoku Kinzoku Kogyo Co. Ltd., was cut into coupons of approximately 6 by 25 mm. According to an analysis by the supplier, the impurity level of the sheet was as follows: Si, 0.19; Mn, 0.11; Al, 0.036; C, 0.016; P, 0.008; S, 0.007; Cu, 0.006 wt%. The coupons were finished by use of a 0/9 emery paper, followed by being degreased in a refined toluene.

Geometric surface areas of the coupons were measured and their weights were determined.

Red phosphorus was treated with a boiling 10% solution of sodium hydroxide for 7 hr, and with dilute hydrochloric acid. After being washed with distilled water, the refined red phosphorus was stocked in a desiccator containing phosphorus pentoxide.

2.2 Apparatus and procedure

The sealed tube containing the iron specimen and white phosphorus was prepared as follows. An appropriate amount of the refined red phosphorus was introduced into a one-side-closed silica tube (inside diameter: 7 mm) and some clean glass wool was packed. After the iron specimen was put in this tube, it was evacuated to 10^{-2} Torr at room temperature, then was filled to 1 atm with argon gas purified by passing through a heated active copper and phosphorus pentoxide, and finally was reevacuated. These procedures, evacuating and the filling, were repeated five times at 200°C in order to remove moisture, oxygen and other gaseous impurities. In this case, only the iron specimen placed near the open end of the tube was not heated. After these procedures, this tube was sealed under vacuum.

Since it seems reasonable for red phosphorus with a variety of structures not to give constant phosphorus pressures, a conversion from red to white phosphorus is necessary. In this study, the phosphorus vapor which was evolved by heating the red phosphorus in the sealed tube was condensed into white phosphorus by the cooling of the neighborhood of the packed glass wool with water.

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The vapor pressure, in Torr, of the white phosphorus is given as a function of the absolute temperature as follows¹⁰⁾:

$$\log P = 7.808 - 2.729 \times 10^3/T \quad (1)$$

$$349.6^\circ\text{K} (1 \text{ Torr}) \leq T \leq 553^\circ\text{K} (760 \text{ Torr})$$

which was used to obtain the selected pressures. The gaseous phosphorus molecule in the form of symmetrical P_4 tetrahedra dissociates into P_2 molecules according to the following equation¹¹⁾:

$$\begin{aligned} \log K_{\text{atm}} &= \log (P_d^2/P_t) \\ &= 7.5787 - 11489/T^\circ\text{K} \end{aligned} \quad (2)$$

where P_d and P_t denote the pressures, in atmospheres, of the diatomic and tetratomic molecules, respectively.

The phosphidation apparatus is schematically diagrammed in Fig. 1. It consists of two furnaces, of which the temperatures are regulated separately. The phosphidation temperatures were given by one furnace, whereas the minimum temperature, by which phosphorus vapor pressures are governed in the closed system, was maintained near the contact part of the two furnaces by adjustment of the temperature of the other furnace.

S: Sample sheet T: Sealed tube
P: White phosphorus F: Furnace
G: Glass wool C: Control T.C.

Fig. 1 Schematic diagram of the phosphidation apparatus

After the sample sheet was subjected to phosphidation, the tube was taken out of the furnace, and immediately the end of the tube opposite to the specimen was quenched to avoid the condensation of the phosphorus vapor on the phosphidized specimen. The phosphidized specimen was removed from the sealed tube, and weighed precisely.

3 Experimental Results

3.1 Phosphidation rate

It is impossible to measure continuously the weight change of a sample sheet vs. time by means of the sealed tube method employed in this study. Kinetic measurements have been done at phosphorus pressures

varying from 1 to 760 Torr at 700°C , and at 1 atm in the temperature range of $750\sim 850^\circ\text{C}$. Within this temperature range, the phosphorus vapor is composed of P_4 and P_2 molecules.

Plots of the weight gain per unit area against a square root of the reaction time are shown in Figs. 2 and 3. Each point represented here was obtained by phosphidizing an individual specimen. The phosphidation kinetics followed a parabolic rate law under the experimental conditions used; hence, the rate-determining step seems to be a diffusion or a transport process of iron or phosphorus ion. The rate increases obviously with an increase of the temperature (Fig. 2), and with an increase of the pressure (Fig. 3).

Values of the parabolic rate constants, K_p , are tabulated (Table 1).

Fig. 2 Parabolic plots of the phosphidation of α -iron in phosphorus of 1 atm

Fig. 3 Influence of the phosphorus pressure on the rate of phosphide formation on α -iron at 700°C

Table 1 Parabolic rate constants for phosphidation of α -iron

Temp. (°C)	Absolute pressure (Torr)	Partial pressure ^{a)} (Torr)		$K_p \times 10^8$ ^{b)} (g ² cm ⁻⁴ min ⁻¹)
		P_1	P_2	
700	1	0.81	0.19	2.2 ± 0.2
700	10	9.35	0.65	3.3 ± 0.4
700	100	97.9	2.1	4.8 ± 0.3
700	760	754.2	5.8	6.1 ± 0.6
800	760	740	20	27 ± 3
850	760	726	34	51 ± 2

a) calculated from eq. (2)

b) $\omega^2 = K_p t$; ω , weight gain per unit area; t , time; K_p , parabolic rate constant.

3.2 Reaction products and distribution of phosphorus

Fig. 4 illustrates the x-ray diffraction patterns of the reaction products, employing manganese-filtered iron radiation. In this figure, the patterns of Fe_2P , FeP , and FeP_2 were quoted from the ASTM cards¹²⁾, and that of Fe_3P from the result given by Fasiska, et al.⁴⁾. The resulting x-ray powder diffraction patterns (Fig. 4 A-C) reveal the products to consist mainly of Fe_2P . The powder patterns of the products are identical with each other at all the temperatures.

Powder: A-700°C, 3.6 hr; B-800°C, 3.6 hr; C-850°C, 3.6 hr

Surface: D-700°C, 2 hr; E-700°C, 2 hr (10 Torr); F-800°C, 2.6 hr; G-850°C, 5 hr

Reverse side of phosphide film: H-700°C, 5 hr; I-850°C, 5 hr, θ : Diffraction angle

Fig. 4 X-ray diffractograms of the iron phosphides formed in phosphorus of 1 atm

The surface of the phosphide formed at 850°C under 1 atm of phosphorus for 5 hr (G) consisted mainly of FeP_2 . The others (D-F) were mainly composed of FeP , but the diffraction peaks of FeP_2 also were observed. The peaks of the reverse sides of phosphide films (H, I) were identified as belonging to those of Fe_2P , and under the other experimental conditions also, the formation of Fe_2P took place at the phosphide/metal interface.

The micrographs of the cross sections of the phosphide films are shown in Photo. 1, in which many voids can be observed. Morphologically interesting crystals such as faceted crystals, whiskers and platelets were not found.

A distribution curve of phosphorus in the phosphide scaling film formed at 850°C for 7 hr at 1 atm, obtained with a scanning electron microscope (JSM-U3, Japan Electron Optics Laboratory Co., Ltd.), is given

Photo. 1 Cross sections of specimens phosphidized under 1 atm of phosphorus: (A) 700°C, 7 hr; (B) 850°C, 7 hr

Fig. 5 Distribution of phosphorus in the iron phosphide film formed at 850°C for 7 hr at 1 atm

in Fig. 5, showing that the content of phosphorus in the phosphide film decrease toward the inner layers in the scale.

The three layers having certain constant contents of phosphorus appear in the bulk phosphide, and the compositions of these three layers, namely, the exterior, the second, and the last which is in contact with metallic iron, can be considered to be mainly FeP_2 , FeP , and Fe_2P , respectively, from the x-ray diffraction patterns. In general, a distribution of phosphorus has indicated such a profile regardless of the reaction conditions.

Photo. 2 is a micrograph of an iron substrate surface after removal of the phosphide film. The three layers (FeP_2 , FeP and Fe_2P) of the phosphide film were so strongly adherent to each other. The dapple aspect shown here results perhaps from the various crystal grains of the metallic iron, viz., from the difference in the crystal plane. The x-ray pattern showed this substrate surface to consist of iron alone (only two peaks, viz., $2\theta_{\text{FeK}\alpha}=57.1$, $I/I_1=100$; $2\theta_{\text{FeK}\alpha}=51.4$, $I/I_1=24$). This dapple feature is not due to the surface constituents, but to the reflection of a light of the microscope.

Photo. 2 Surface of iron substrate after removal of the phosphide scale. Sample phosphidized at 800°C in 1 atm phosphorus for 2.6 hr

4 Discussion

A semilogarithmic plot of K_p under 1 atm of phosphorus against the reciprocal of the absolute temperature yielded the activation energy of 31 ± 2 kcal/mole (Fig. 6).

A graph of the dependence of K_p on the P_4 -vapor pressure at 700°C is shown in Fig. 7, which yields a straight line, whose slope corresponds to $0.14 \sim 0.18$. On the other hand, the relationship between K_p and the P_2 -vapor pressure at the same temperature gives a slope of $0.27 \sim 0.36$ (Fig. 8).

The K_p was given as functions of temperature, T in $^\circ\text{K}$, and of the absolute pressure, P in Torr, by the following expression:

$$K_p = 0.2 P^{1/6} \exp(-31,000/RT), \text{ g}^2 \text{ cm}^{-4} \text{ min}^{-1}$$

The mole fractions of P_2 molecule in phosphorus vapor at 700°C and 850°C are 0.0076 and 0.045, respectively, when calculated from eq. (2). Although

the mole fractions of P_2 molecule are very small, these small amounts of P_2 seem to affect the reaction. From the experimental fact that the compound FeP_2 was formed at phosphide surfaces, if FeP_2 is a p-type scale, lattice defect equations can be written as follows

and

where $\text{Fe}\square''$ and $\oplus$ denote a divalent cation vacancy and an electron hole, respectively. The mass action law on the assumption of ideal conditions in very

Fig. 6 Temperature dependence of the parabolic rate constant for the α -iron phosphidation between 700° and 850°C in 1 atm phosphorus

Fig. 7 The dependence for K_p of the α -iron phosphidation on P_4 -vapor pressure at 700°C

Fig. 8 The dependence for K_p of the α -iron phosphidation on P_2 -vapor pressure at 700°C

dilute electrolytes can be expressed as

$$C_{\text{Fe}\square} \cdot C_{\text{P}} = K' (\text{Pressure of } P_4)^{1/2} \quad (5)$$

$$C_{\text{Fe}\square} \cdot C_{\text{P}} = K'' (\text{Pressure of } P_2) \quad (6)$$

where C denotes the concentration. The dependence of the lattice defect concentration on the phosphorus pressure can be expressed with an electrical neutrality condition as follows:

$$2C_{\text{Fe}\square} = C_{\text{P}} \propto (\text{Pressure of } P_4)^{1/6} \quad \text{from eq. (5),}$$

$$2C_{\text{Fe}\square} = C_{\text{P}} \propto (\text{Pressure of } P_2)^{1/3} \quad \text{from eq. (6).}$$

A parabolic rate constant seems to be proportional to $C_{\text{Fe}\square}$ or C_{P} . This discussion is consistent with the experimental results shown in Figs. 7 and 8.

From the data of the decomposition pressures in the iron-phosphorus system, given by Franke, et al.²³, the pressures, in atmospheres, were obtained as a function of the absolute temperature as follows:

$$(a) \quad 4\text{FeP}_2 \rightleftharpoons 4\text{FeP} + P_4; \quad \log P = -14930/T + 11.83 \quad (7)$$

$$(b) \quad 2\text{FeP}_2 \rightleftharpoons 2\text{FeP} + P_2; \quad \log P = -13510/T + 9.93 \quad (8)$$

$$(c) \quad 4\text{FeP} \rightleftharpoons 2\text{Fe}_2\text{P} + P_2; \quad \log P = -15870/T + 9.18 \quad (9)$$

The chemical potential diagram of the iron-phosphorus system is shown in Fig. 9.

When eq. (7) is substituted in eq. (2), we obtain $\log P_4 = 9.705 - 13210/T$ (10)

Fig. 9 Chemical potential diagram of the iron-phosphorus system

which is represented with a broken line in Fig. 9. An inequality $\log P$ of eq. (10) $>$ that of eq. (8) holds for the temperature range used in this study. Eventually, Fig. 9 shows that the phosphidation with P_2 rather than with P_4 takes place preferentially, namely, eq. (4), and that the phosphide-layer structure of (phosphorus vapor)/ $\text{FeP}_2/\text{FeP}/\text{Fe}_2\text{P}/(\text{Fe})$ is formed under the present experimental conditions.

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