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.

1 Introduction

Studies in regard to the phase diagram^{1),2)}, X-ray diffractions^{2),3)}, and heats of formation⁴⁾ of iron-phosphorus system have been made by many workers. Recently the crystal structures of $\text{Fe}_3\text{P}^{5),6)}$, $\text{Fe}_2\text{P}^{7)}$, $\text{FeP}^{8)}$, and $\text{FeP}_2^{9)}$ have been studied in detail, and their magnetic properties also have been extensively investigated.

However, kinetics of the reaction between an iron and phosphorus has not been reported up to the present. This paper is concerned with the rate of phosphidation of iron sheets exposed to phosphorus vapor in a flow system.

2 Experimental

2.1 Materials

A commercial α -iron sheet 0.5 mm thick was cut in the form of rectangles approximately 10×20 mm. The analysis of the material as supplied by the manufacturer is shown in Table 1.

Table 1 Analysis of the sample iron sheet

Element	Amounts, w/o
C	0.016
Si	0.19
Mn	0.11
P	0.008
S	0.007
Cu	0.006
Al	0.036

The sample iron sheets were polished through 0/5—0/9 emery papers, and then degreased with trichloroethylene vapor. They were weighed and their geometric surface areas were determined.

Purification of red phosphorus is much the same as in the previous paper¹⁰⁾.

2.2 Apparatus and Procedure

A schematic drawing of the phosphidation apparatus employed is shown in Fig. 1, which is similar to that described in the earlier paper¹⁰⁾.

The sample α -iron sheet was suspended from a quartz rod hanging from a glass hook inside the top of a quartz reactor. A quartz cell filled with the refined red phosphorus was placed at the bottom of the reactor. This reactor was evacuated to 10^{-2} Torr at room temperature, then was filled to 1 atm with argon gas purified by a method described below, and finally was reevacuated. The evacuating and the filling were repeated three times in order to remove moisture, oxygen and other gaseous impurities adsorbed on the specimen, the red phosphorus and the inner wall of the reactor.

A : Sample α -iron sheet F : Cock
B : Quartz rod G : Needle valve cock
C : Red phosphorus H : Flow meter
D : Furnace I : Manometer
E : Control T.C. J : Vacuum pump

Fig. 1 Schematic drawing of apparatus

The temperatures of the specimen and of the red phosphorus were controlled individually with two automatic regulators: The upper furnace gives desired temperatures of phosphidation within $\pm 6^\circ\text{C}$, whereas the other is used to adjust phosphorus partial pressures.

An argon carrier gas was dried by passing through phosphorus pentoxide and deoxygenated by passing through heated active copper, and then introduced into the bottom of the reactor from the heated side tube at a flow rate of 100 ml/min and at 1 atm. Partial pressures of phosphorus vapor were calculated from the rate of sublimation to P_4 vapor and the flow rate of this carrier gas.

3 Experimental Results

By means of this experimental method, it is impossible that the weight change, caused by phosphidation, of a sample sheet vs. time is measured continuously. Kinetic findings are shown in Fig. 2 on phosphidation of the α -iron sheets exposed to phosphorus vapor at temperatures from 715° to 860°C . It should be noted that each data point was obtained by phosphidizing a distinct specimen. The deviation in the square of the weight gain for each time was not greater than $0.8 \text{ mg}^2/\text{cm}^4$ for temperatures of 860° and 815°C , and than $0.3 \text{ mg}^2/\text{cm}^4$ for those of 765° and 715°C .

Fig. 2 shows that the weight gain increases with time, and with an increase of temperature, and that the phosphidations obey the parabolic rate law based on a diffusion process.

Values of the parabolic rate constants, K_p , obtained as slopes from each straight line are summarized in Table 2. Pressure dependence of K_p is not recognizable over the entire temperature range employed.

From the above, it can be concluded that a diffusion process is distinctly slower than an interface or adsorption reaction; hence, diffusion control predominates throughout the reaction time.

Fig. 3 illustrates X-ray diffraction patterns on the surfaces of the phosphide films formed for 100 min at 5.5 Torr and at various temperatures, and on their reverse sides. In Fig. 3, the X-ray patterns of Fe_2P , FeP , and FeP_2 were cited from the ASTM cards⁽¹⁾, and that of Fe_3P from the result given by Fasiska and Zwell⁽⁶⁾.

The resulted diffraction patterns reveal that the surface products may consist of mixtures of Fe_2P and FeP from identification with the known patterns, and that the phosphides in contact with metallic iron phase

Table 2 Parabolic rate constants for phosphidation of α -iron

Temp. (°C)	$K_p \times 10^8$ (g ² /cm ⁴ -min)				
	Pressure : (Torr)	1.3	2.6	5.5	25
715		4.5	4.3	5.0	5.3
765		7.3	7.7	7.5	7.3
815		15.1	14.5	14.5	14.9
860		40.0	35.4	35.1	36.8

Fig. 2 Phosphidation of iron between 715° and 860°C at phosphorus partial pressures of (a) 1.3, (b) 2.6, (c) 5.5, and (d) 25 Torr

are Fe_2P . These X-ray diffraction patterns were hardly altered throughout phosphidation time. It is of interest that iron phosphides richer in iron than Fe_2P have not been formed.

No dependence of X-ray patterns on the phosphorus partial pressure was entirely recognized: The compositions of the reaction products are independent of the phosphorus partial pressure.

Microscopic observations showed that the phosphidations involve the growth of mounds of iron phosphides under all conditions studied. Phosphide scales were generally very adherent to the metallic iron substrates even at room

temperature. Photo. 1 illustrates a micrograph of the peculiar surface of the specimen phosphidized at 715°C

Photo. 1 Surface of specimen phosphidized for 100 min at 715°C and a partial pressure of 5.5 Torr

Photo. 2 Surface of specimen phosphidized for 100 min at 860°C and a partial pressure of 5.5 Torr

Surface : A; 715°C, B; 765°C, C; 815°C, D; 860°C
Reverse side of phosphide film : E; 715°C, F; 765°C, G; 815°C, H; 860°C

θ : Diffraction angle

Fig. 3 X-ray diffraction patterns of the phosphides formed for 100 min under a partial pressure of 5.5 Torr, employing Ni-filtered copper radiation

at a partial pressure of 5.5 Torr for 100 min, showing a large number of phosphide mounds. In general, surfaces at 715°C were more flat than that shown in Photo. 1 throughout the reaction time. At 765°C also, more-flat surface aspects were observed.

In Photo. 2 is shown the surface of the specimen phosphidized at 860°C for 100 min under a partial pressure of 5.5 Torr. Surface features formed at 815°C were almost the same as in Photo. 2. Only a few of small whisker-like crystals also were seen at 715°, 765°, and 815°C.

4 Discussion

According to the phase diagram of the iron-phosphorus system¹¹, the solubility of phosphorus in metallic α -iron is about 1.0 w/o viz. 1.8 a/o at 715°C and about 1.4 w/o viz. 2.5 a/o at 860°C. Phosphidation may comprise phosphorus chemisorption on the metallic iron, penetration of the chemisorbed phosphorus, formation of solid solutions, and formation of iron phosphides.

A plot of the logarithm of K_p obtained in each partial pressure against the reciprocal of the absolute temperature is shown in Fig. 4. The appearance of a curve might be explained as being results of the differences in the solubility and in diffusion processes of iron and phosphorus ions.

Fig. 4 Arrhenius plot of the parabolic rate constant for the α -iron phosphidation between 715° and 860°C under phosphorus partial pressures 1.3 to 25 Torr

Activation energies were derived to be about 20 and 50 kcal/mol for the low and for the high temperature regions, respectively.

The gaseous phosphorus molecule in the form of symmetrical P_4 tetrahedra dissociates into P_2 molecules according to the following equation¹².

$$\log K_{atm} = \log(P_2^2/P_4) = 7.5787 - 11489/T^{\circ}K$$

where P_2 and P_4 stand for the pressures, in atmospheres, of the diatomic and tetratomic molecules, respectively. According to this equation, P_2^2/P_4 is equal to 0.002744 atm at 860°C. Although it seems that this dissociation may affect more or less the phosphidation rate, kinetic rates may probably be unaffected by an existence of P_2 molecules, because a diffusion process became a rate-determining step.

The results in this study is not enough to explain the mechanism of the α -iron phosphidation. Details and further developments will appear elsewhere.

5 Conclusions

Results of phosphidation of α -iron between 715° and 860°C under phosphorus partial pressures of 1.3 to 25 Torr in a flow system are as follows:

1. The phosphidations obey the parabolic rate law, and these rate constants, K_p , were summarized in Table 2.
2. No dependence of K_p on the phosphorus partial pressure was entirely recognized.
3. The relationship between the logarithm of K_p and the reciprocal of the absolute temperature gave a curve, so that constant values of activation energy could not be obtained.
4. X-ray diffraction peaks of the surfaces of the specimens which were phosphidized under the experimental conditions employed were identified as belonging to those of Fe_2P and FeP , and also at the phosphide/metal interface the formation of Fe_2P takes place.
5. Microscopic observations showed that the phosphorus/phosphide interfaces were covered all over with small phosphide mounds.

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