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Rate-controlling Processes in the Phosphidation of Copper by Phosphorus Vapor

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The phosphidation kinetics of a copper exposed to a phosphorus atmosphere from 1 to 10 Torr absolute pressure in the temperature range of 150—250°C have been determined with a closed system. The reaction rate in the earlier periods of time was linear and, subsequently, parabolic; therefore, it can be considered that the rate-determining process changes from adsorption to diffusion. The linear rate constants were expressed as a function of the phosphorus pressure on the basis of the Langmuir adsorption isotherm. The P_4 molecule is chemically adsorbed as two $-P=P-$, whereas at higher temperatures and pressures the solubility process appears to be predominant. From the phosphorus distribution in cross sections of scaling films, it has been revealed that, in the adsorptoin-controlled regions, the phosphorus content is maintained at a constant concentration, corresponding to Cu_3P, and that, in the diffusion-controlled regions, solid solutions more rich in phosphorus than Cu_3P are formed at the outer layers. The faceted crystals of Cu_3P have sometimes developed with an orientation of the (300) plane, depending on the reaction conditions.

In the nineteenth century, the existence of copper phosphides with various compositions, namely, Cu_3P, Cu_5P_2, Cu_2P, Cu_3P_2, CuP, and CuP_2, was reported. In 1907, Heyn and Bauer[1)] determined the equilibrium diagram of copper-phosphorus systems up to 15 wt% phosphorus. The rate of the combination of copper and phosphorus was first investigated by Edwards and Murphy.[2)] Haraldsen[3)] pointed out, on the basis of the thermal analysis and the X-ray diffraction, that the CuP_3 and Cu_2P_5 compounds are solid solutions, in which a phosphorus dissolves in any CuP_2-matrix, and concluded that no compounds other than Cu_3P and CuP_2 exist as copper phosphides. The crystal structures of Cu_3P[3)] and CuP_2[4)], the magnetic[3)] and electrical[5)] properties of these two phosphides, and the heats of formation[6)] of the two have been investigated.

The present authors reported previously[7)] the rate of the reaction of copper with gaseous phosphorus, as determined by gravimetric means, using a spring-helix method, in a flow system in the temperature range of 400—650°C and under the partial pressures of 0.8 to 110 Torr. According to those results, the copper was linearly phosphidized in the early stages of reaction, and when the phosphide layers reached a certain thickness, a transition from linear to parabolic behavior took place.

The present paper will deal with the behavior of copper at comparatively lower temperatures (150—250°C) in a gaseous phosphorus at pressures of 1 to 10 Torr, as determined by means of a sealed-tube method.[8)]

Experimental Details

Materials. A copper sheet 0.5 mm thick was cut in the form of rectangles of approximately 7 by 25 mm. The purity was about 99.95 wt%; this sheet contains as much as 0.05 wt% phosphorus as an impurity. The copper coupons were abraded lightly with emery paper, defatted with trichloroethylene, and polished chemically for 120 sec at 70°C in a solution consisting of 200 parts (by volume) of 85% H_3PO_4, 100 parts of 60% HNO_3 and 120 parts of glacial acetic acid. The coupon specimens thus cleaned were then weighed, and their apparent geometric surface areas were determined.

Red phosphorus was treated with a boiling 10% aqueous solution of sodium hydroxide for about 5 hr, and then with dilute hydrochloric acid. After being washed with distilled water, the refined red phosphorus was stored in a desiccator with phosphorus pentoxide.

Methods. A closed reaction system was used for the phosphidation. Figure 1 represents schematically the apparatus employed; it consists of a tube placed over two temperature zones and controlled within variations of less than 3°C, the first zone being used to heat the sample copper sheet in the sealed tube, and the second zone, to control the vapor pressure of phosphorus. The vapor pressure of phosphorus is governed by the minimum temperature in the closed system.

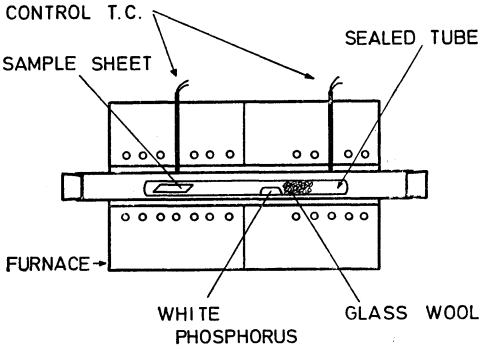

Fig. 1. Schematic drawing of the phosphidation apparatus.

The vapor pressure, P_{Torr}, of white phosphorus is given as a function of the absolute temperature, T, as follows:[9)]

$$\log P_{\mathrm{Torr}} = 7.808 - 2.729 \times 10^3/T,$$

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

This equation was used to obtain the desired pressure.

[1)] E. Heyn and O. Bauer, *Z. Anorg. Allgem. Chem.*, **52**, 129 (1907).

[2)] C. A. Edwards and A. J. Murphy, *J. Inst. Metals* (London), **27**, 183 (1922).

[3)] H. Haraldsen, *Z. Anorg. Allgem. Chem.*, **240**, 337 (1939).

[4)] O. Olofsson, *Acta Chem. Scand.*, **19**, 229 (1965).

[5)] R. Juza and K. Bär, *Z. Anorg. Allgem. Chem.*, **283**, 230 (1956).

[6)] F. Weibke and G. Schrag, *Z. Elektrochem.*, **47**, 222 (1941).

[7)] S. Ueda, Y. Sasaki, M. Matsuura, and S. Nishimura, *J. Electrochem. Soc.*, **117**, 84 (1970).

[8)] Y. Sasaki, A. Kato, and S. Ueda, *ibid.*, **118**, 101 (1971).

[9)] D. R. Stull, *Ind. Eng. Chem.*, **39**, 540 (1947).

The gaseous phosphorus molecule in the form of symmetrical P_4 tetrahedra dissociates into P_2 molecules according to the following equation[10]:

$$\log K_{atm} = \log (P_d^2/P_t) = 7.5787 - 11489/T^{\circ}\mathrm{K}$$

where P_d and P_t denote the pressures, in atmospheres, of the diatomic and tetratomic molecules respectively. Therefore, for the temperature region of 150—250°C employed in this study, the phosphorus vapor can be regarded as being made up of P_4 molecules.

The sealed tube containing the copper specimen and white phosphorus was prepared as follows. A moderate amount of the refined red phosphorus was introduced into a one-side-closed Pyrex tube (inside diameter: 7 mm). Some clean glass wool was packed in, and then the copper specimen was put in this tube. This tube was evacuated to 10^{-2} Torr, then filled to 1 atm with argon gas purified by having been passed through phosphorus pentoxide and heated active copper, and finally reevacuated. The evacuating and the filling were repeated five times at 200°C in order to remove any moisture, oxygen, and other gaseous impurities adsorbed on the red phosphorus, the glass wool, and the inner wall of the tube. In this case, only the copper specimen placed near the entrance end of the tube was not heated. After these operations, this tube was sealed under a vacuum.

Although red phosphorus is generally amorphous, it can also have various crystal structures; hence, a conversion from red to white phosphorus is necessary to secure stable pressures of phosphorus vapor. In this study, the phosphorus vapor which evolved when the red phosphorus was heated in the sealed tube was condensed into white phosphorus by water cooling in the neighborhood of the packed glass wool.

After selected periods of time of the phosphidation, the tube was taken out of the furnace; the end of the tube opposite the specimen was immediately quenched in order to avoid the condensation of the phosphorus vapor on the phosphidized specimen. Then, this was removed from the sealed tube and weighed. No appreciable attack on the Pyrex tube was detected.

The constituents of the corrosion products were identified by X-ray analyses. Information about the diffusion profiles of the phosphorus across the scale was obtained by means of a scanning electron microscope (JSM-U3, Japan Electron Optics Laboratory Co., Ltd.).

Experimental Results

Kinetics. The results are based on the experimental observations of copper coupons from 150° to 250°C at absolute phosphorus pressures of 1 to 10 Torr. These are plotted in Figs. 2 and 3 as the log of the weight gain per unit area *vs.* the log of the reaction time. The points represented are scattered. It should be noted that each point was obtained by phosphidizing an individual specimen.

The rate of phosphidation obviously increases with an increase in the temperature and with an increase in the phosphorus pressure. Generally, at the temperatures and pressures investigated, copper was found to phosphidize according to the linear mechanism during the first periods of time, showing a phase-boundary-control mechanism. However, when the thickness of the phosphide layers reached a certain

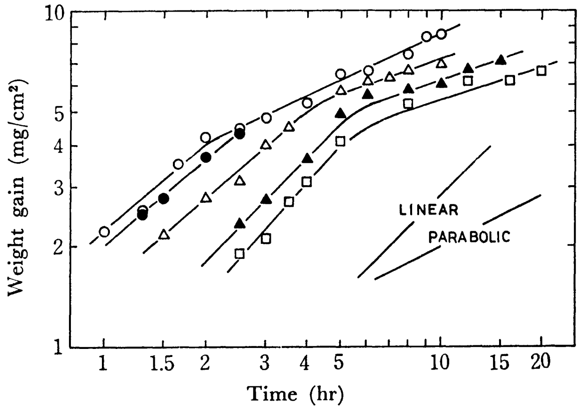

Fig. 2. Phosphidation of copper under various phosphorus pressures at 150°C; ○: 10; ●: 7; △: 4; ▲: 2; □: 1 Torr.

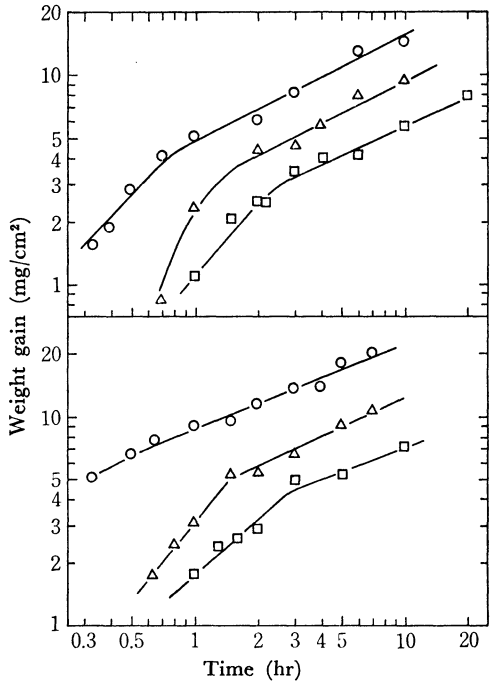

Fig. 3. Phosphidation of copper at 200° (top) and 250°C (bottom): The same symbols as in Fig. 2.

TABLE 1. LINEAR AND PARABOLIC RATE CONSTANTS FOR THE PHOSPHIDATION OF COPPER

Temp (°C)	Pressure (Torr)	$K_l\times10^5$ (g/cm²-min)	$K_p\times10^8$ (g²/cm⁴-min)
150	1	1.28±0.08	2.58±0.42
	2	1.57±0.07	4.08±0.58
	4	2.20±0.13	4.67±0.67
	7	3.06±0.15	—
	10	3.62±0.12	11.8 ±1.2
200	1	2.01±0.24	5.42±0.41
	4	3.75±0.33	17.0 ±1.7
	10	8.75±0.92	38.7 ±3.6
250	1	2.71±0.29	7.15±0.85
	4	5.17±0.67	26.0 ±1.0
	10	—	95.0 ±7.7

$w=K_l t$, $w^2=K_p t+C$; w: weight gain, t: time, C: constant.

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[10] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, New York, N. Y. (1958).

Table 2. Comparison of interplanar spacings of the phosphides formed on copper metal (*d*-values, Å)

(I) Powder D as typical in A-E	Cu_3P (Ref. 3)	Plane	CuP_2 (Ref. 4)	Plane
2.50 M	2.49 VS	(112)	2.89 VS	(111), (11$\bar{2}$)
2.31 M	2.29 S	(202)	2.68 W	(20$\bar{2}$)
2.18 M	2.16 S	(211)	2.48 W	(21$\bar{1}$)
2.01 VS	2.01 VS	(300)	2.22 M	(11$\bar{3}$)
1.97 S	1.95 VS	(113)	1.85 W	(22$\bar{1}$)
1.93 W	1.92 W	(212)	1.81 M	(20$\bar{4}$), (202)
	1.74 W	(302)	1.79 M	(22$\bar{2}$)
	1.70 M	(104)	1.78 W	(31$\bar{1}$)
	1.62 W	(311)	1.73 W	(122)
	1.56 M	(222)		

A: 250°, 4 Torr, 1 hr (*l*); B: 250°, 4 Torr, 5 hr (*p*); C: 250°, 10 Torr, 3 hr (*p*); D: 150°, 10 Torr, 9 hr (*p*); E: 150°, 1 Torr, 3.5 hr (*l*).
(*l*): Linear rate portion, (*p*): Parabolic rate portion.
VS: Very strong, S, Strong, M: Medium, W: Weak, VW: Very weak.

(II) Surface (s) and Reverse side (r) of films

F		G		H		I		J	
s	r	s	r	s	r	s	r	s (porous, black)	s (flat, silver)
2.52 W	2.52 W			2.51 VW	2.52 W		2.51 M	2.52 W	
2.32 W	2.33 W			2.31 VW	2.33 W		2.32 W	2.32 VW	
2.19 W	2.19 W	2.18 W	2.19 W	2.19 M	2.19 M	2.18 VW	2.18 M	2.18 W	2.18 VW
		2.09 W						2.10 VW	
2.02 VS	2.03 VS	2.02 VS	2.02 VS	2.02 VS	2.02 VS	2.02 VS	2.02 VS	2.02 VS	2.01 VS
1.98 W	1.98 M	1.97 VW		1.97 VW	1.98 M		1.98 M	1.98 M	
1.93 VW	1.93 VW			1.93 VW	1.93 W		1.93 W	1.93 VW	1.89 VW
		1.82 W						1.82 W	
		1.64 VW	1.64 VW	1.63 VW	1.64 VW	1.63 VW	1.63 VW	1.64 VW	1.63 VW
					1.57 VW		1.57 W	1.57 VW	1.60 VW

F: 150°, 1 Torr, 2.5 hr (*l*); G: 200°, 10 Torr, 0.7 hr (*l*); H: 200°, 1 Torr, 6 hr (*p*); I: 250°, 10 Torr, 3 hr (*p*); J: 250°, 1 Torr, 1.6 hr (*l*).

Using a nickel-filtered copper radiation. The employed range of diffraction angle: $15° \leq \theta \leq 30°$.

value, the kinetics undergo a gradual transition from the linear to the parabolic law; the rate-controlling process changes from adsorption to diffusion. This fact is constituent with the previous conclusion reached under the experimental conditions of a 400—650°C temperature range and a pressure range of 0.8—110 Torr in a flow system.[7]

The values of the linear rate constant, K_l, and the parabolic one, K_p, are listed in Table 1.

Phase Identification and Scale Morphology. The phosphidation commenced with the growth of many phosphide crystallites. The coupon specimens have been phosphidized more rapidly at the edges and corners than at the centers of the flat faces. The scaling layers formed on the unchanged copper beneath were examined on a X-ray spectrometer, using nickel-filtered copper radiation. The *d* values, the interplanar spacings, of the phosphides obtained under various reaction conditions are summarized in Table 2. A division was made between the results obtained for pulverized phosphides and those obtained for the phosphide films. The diffraction pattern of the powder reflects the bulk of the scaling layers.

The known *d* values of Cu_3P[3] and CuP_2[4] are given in the same table. The *d* values obtained from the powder patterns revealed that all the scaling films are essentially Cu_3P. No special dependence of the X-ray patterns on the phosphorus pressure was observed.

According to Haraldsen,[3] the Cu_3P compound is silver grey, while CuP_2 is black. In the linear-rate portions, regardless of the reaction conditions, the phosphide surfaces are mostly silver; black products are rare. The silver surfaces are very flat, and the black, apparently porous. The silver products were almost completely Cu_3P. The black products were composed of the Cu_3P phase containing slight amounts of CuP_2 (Table 2-J). Otherwise, in the parabolic-rate portions, the surface products were almost all dark silver grey and were chiefly composed of Cu_3P, X-ray-spectrographically speaking.

The reverse sides of the phosphide films were obviously composed of Cu_3P; it is noteworthy that, at the phosphide/copper interface, the formation of Cu_3P takes place.

As examples, electron micrographs of the silver surfaces of the specimen phosphidized at 150°C for 2 hr in 7 Torr phosphorus are given in Fig. 4. The crystal features are clear; the upper micrograph shows many small pillars; the second, faceted grains which are the largest in faceted crystals grown under the reaction conditions employed and which have the orientation of the (300) plane; and the lower, a chain of mountains composed of numerous crystallites.

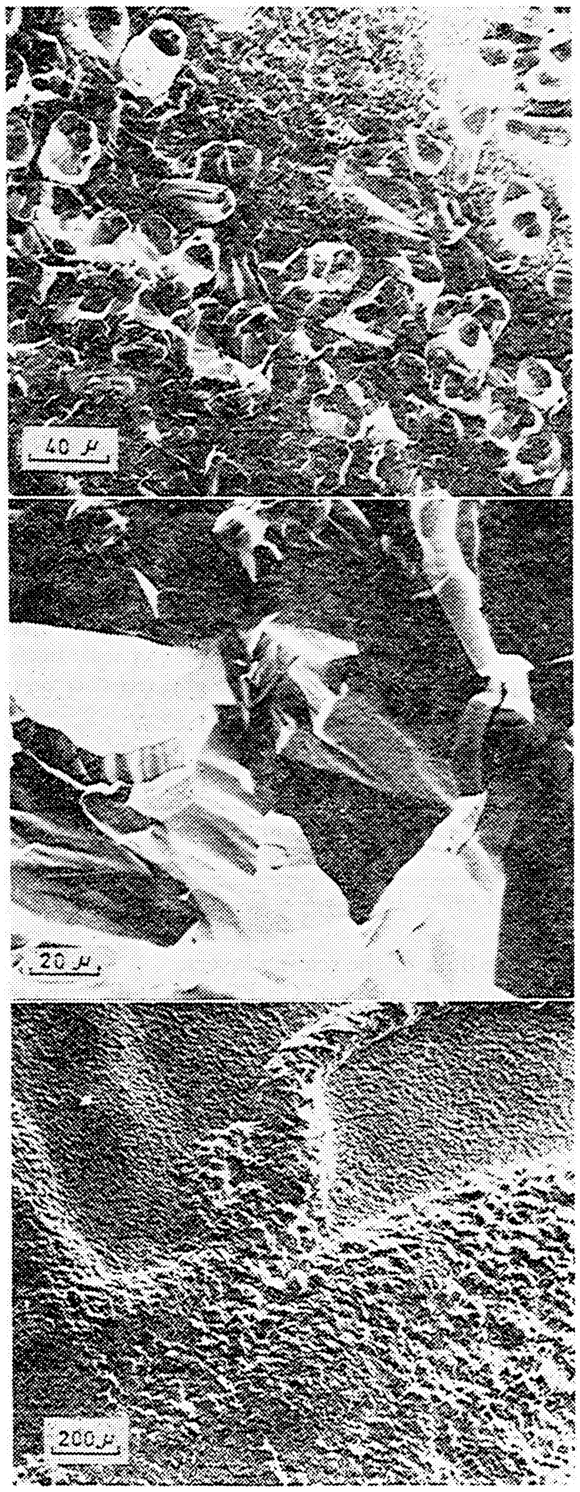

Fig. 4. Electron micrographs of the silver surface of the specimen phosphidized at 150°C for 2 hr in 7 Torr. Upper micrograph, showing many pillars; the second, the faceted crystals; and the lower, a chain of mountains.

These three micrographs were obtained from the different positions of the same phosphidized specimen. As has been indicated just above, all these products are made up of Cu_3P. Localized phosphidation leads to the growth of the porous black products containing CuP_2 as a higher phosphide, such as is exemplified in Fig. 5, in polarized light, showing tablet-like crystals.

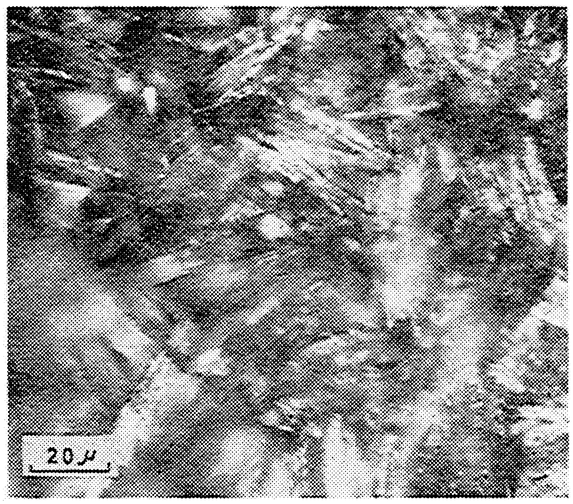

Fig. 5. Optical micrograph showing tablet-like crystals formed for 1.5 hr at 200°C in phosphorus vapor at 1 Torr, in polarized light.

Figure 6 represents a typical cross section of the scale, showing approximatly the formation of two scaling layers. Almost all the scaling films formed in the present study were similar to that shown in Fig. 6. In general, the scales are laminar; the generation of fissures was also faintly observed. This is apparently due to the tensile stresses produced in the outer layers of the scale by the outward pressure of the newly-forming phosphide.

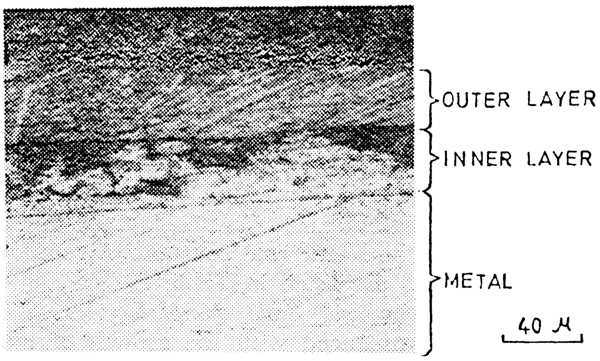

Fig. 6. The cross section of the specimen phosphidized at 150°C for 2.5 hr in 7 Torr, showing the scale to consist of two phosphide layers.

The distributions of phosphorus in phosphide films, obtained with the electron microprobe, suggest that, in the linear-rate portion (Fig. 7A), the phosphorus concentration is held constant, corresponding to Cu_3P, while in the parabolic-rate portion (Fig. 7C) the solid solutions that phosphorus dissolves in the Cu_3P-matrix are formed; the outer layers of the scale are more phos-

phosphorus-rich than the inner. It is reasonable that some phosphorus-activity gradient exists across the adherent layer, thus providing the driving force for the phosphorus flux required by the reactions at the inner interface. However, at the linear rate, since an adsorption process is slower than a diffusion process, it can be concluded that the content of phosphorus was maintained at the constant concentration. The reaction conditions of Fig. 7B exactly correspond to that of the neighborhood of a transition point from a linear to a parabolic rate (Fig. 2); this pattern may be due to the rate-determining diffusion.

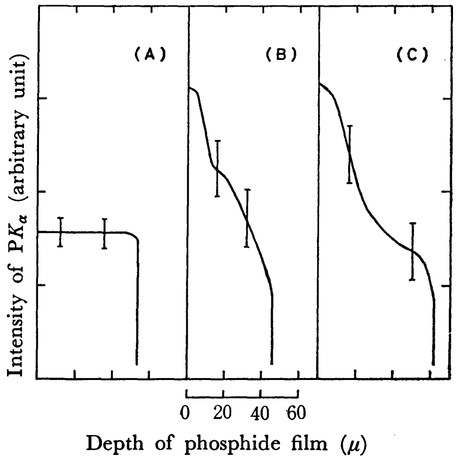

Fig. 7. The profiles of distribution of phosphorus in the phosphide films, obtained with electron microprobe facilities: (A) 250°C, 4 Torr, 1 hr; (B): 150°C, 7 Torr, 2.5 hr; (C): 150°C, 4 Torr, 5 hr.

Discussion

During the earlier stages of the reaction, the observed rates of phosphidation are linear; hence, the rate-determining step is presumably a surface reaction, that is, a phase-boundary reaction or an adsorption process. The generalized mechanism for such a heterogeneous surface reaction involves the following consecutive steps: (a) the diffusion of gas molecules to the surface, (b) the adsorption of gas on the surface, (c) a reaction on the surface, (d) the desorption of the products, and (e) the diffusion of the products away from the reacting surface.

The general form of the linear equation in terms of the weight gained, $w=K_l t$, is not suitable to account for the effect of the pressure at a constant temperature. It is possible to explain the pressure dependence of the reaction by assuming that (I) the phosphorus concentration at some interface is determined by an equilibrium adsorption process, and (II) the rate of the rate-determining process is a function of the phosphorus concentration at this interface. On this model, the interface concentration is given by a Langmuir isotherm. If an adsorbed molecule dissociates into n phosphorus atoms, the fractional coverage of the adsorption interface, θ, is given by:

$$\theta = \alpha P^{1/n}/(1+\alpha P^{1/n}) \qquad (1)$$

where P is the pressure of the vapor composed of P_4 molecules and where α is the chemisorption equilibrium constant, and where an interaction between the adsorbed matters is neglected completely. At low pressures, $\alpha P^{1/n} \ll 1$ and $\theta = \alpha P^{1/n}$.

Assuming that the chemical adsorption of the phosphidation obeys a Langmuir isotherm and that the rate of nucleation and the growth of phosphide nuclei are proportional to the number of chemisorbed phosphorus atoms, the linear rate may be rewritten as:

$$\begin{aligned} rate &= \mathrm{d}w/\mathrm{d}t = k'\theta \\ &= k'\alpha P^{1/n}/(1+\alpha P^{1/n}) \qquad (2) \end{aligned}$$

where k' is a specific rate constant.

As Fig. 8 demonstrates, plots of K_l against the pressure on a log-log scale give about 0.5 as a slope, namely, $n=2$ under the experimental conditions of "150°C, 1—10 Torr," "200°C, 1—4 Torr," and "250°C, 1—4 Torr." It should be emphasized that the adsorption takes place with the dissociation of the P_4 molecule into two –P=P– or P≡P. This can be explained in terms of the facility of the dissociation of P_4 into two P_2 molecules at high temperatures in the gas phase. For the pressure range of 1—2 Torr at 150°C, however, the slope appears to become somewhat smaller (the broken line in Fig. 8), showing $n=ca.$ 4; this suggests that the P_4 molecule probably adsorbs as four phosphorus atoms.

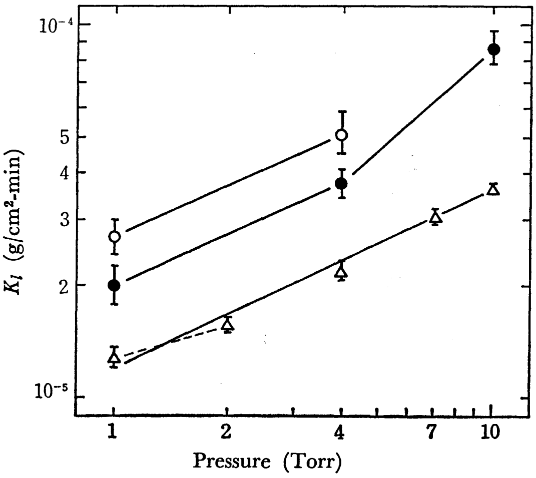

Fig. 8. Influence of the phosphorus pressure on the rate of phosphide formation on copper: ○ 250°; ● 200°; △ 150°C.

On the other hand, for 4—10 Torr at 200°C, the solubility process seems to govern the reaction, because n is approximately equal to unity. This process appears to be predominant at higher temperatures and pressures.

From the above, the processes of the phosphidation can be described as:

$$1/2\ P_4(g) + 2\ \text{Site(Cu or Phosphide)} \rightleftarrows \begin{matrix}\text{P-Site} \\ \| \\ \text{P-Site}\end{matrix}\ \text{(Chemisorbed)}$$

$$\text{or; } 1/4\ P_4(g) + \text{Site} \rightleftarrows \text{P-Site}$$

$$\text{Site-P=P-Site or P-Site} + \text{Cu} \xrightarrow[\text{dissolution}]{\text{diffusion}} \text{Cu-P solid solution} \xrightarrow[\text{growth}]{\text{nucleation}} Cu_3P \text{ and } CuP_2$$

In Table 3, the values of n, k', and α in Eq. (2), calculated from the observed values of K_l, are summarized.

The empirical equations obtained from Table 3 are based on a reaction mechanism in which the rate-controlling process is linearly dependent on the concentration of the phosphorus adsorbed as P_2 or P_4. Figure 9 indicates the curves of these equations. Since the original kinetic data are scattered, these calculated curves are of a low precision. The fractional coverages were found to be, for instance, 0.18 at 150°C–10 Torr, 0.12 at 200°C–10 Torr, and 0.05 at 250°C–1 Torr, on calculation.

Table 3. Values of n, k', and α

Temp (°C)	Pressure range (Torr)	n	$k'\times10^4$ (g/cm²-min)	α
150	1—10	2	1.9	0.068
200	1—4	2	2.9	0.075
250	1—4	2	5.2	0.055
200	4—10	1	7.7	0.013

$K_l=k'\alpha P^{1/n}/(1+\alpha P^{1/n})$

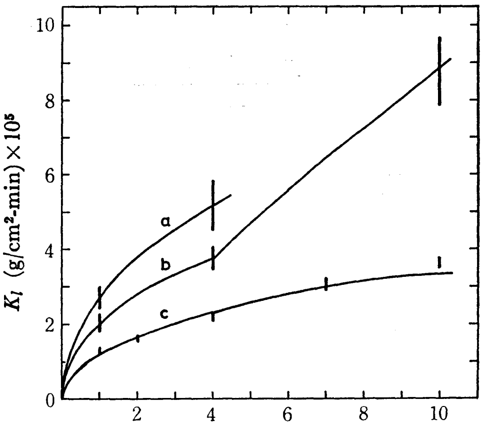

Fig. 9. The relations between K_l and the pressure of phosphorus vapor composed of P_4 molecule: a, 250°; b, 200°; c, 150°C. Curve: calculated, Rod: observed.

From Eq. (2) and the Clausius-Clapeyron equation, $q=\boldsymbol{R}T^2(\mathrm{d}\ln P/\mathrm{d}T)$, the following relation can be derived;

$$q=-\boldsymbol{R}T^2n(\partial\ln\alpha/\partial T)_\theta \tag{3}$$

Accordingly, $\alpha=\alpha_0\exp(q/\boldsymbol{R}Tn)$, where α_0 is a constant and where q is the heat of adsorption. From the $\log\alpha$ —$1/T$ plots at $n=2$, it has become apparent that q falls into the category of approximately 2—6 kcal/mol.

Table 4. Activation energies of phosphidation of copper

Pressure (Torr)	Temp range (°C)	E_l (kcal/mol)	E_p (kcal/mol)
1	150—250	3.3±0.7	—
	150—200	—	6.2±1.9
	200—250	—	2.6±1.7
4	150—250	3.9±0.7	—
	150—200	—	10.7±1.8
	200—250	—	3.9±1.2
10	150—200	7.3±1.1	—
	150—250	—	9.3±0.8

E_l: derived from K_l, E_p: derived from K_p.

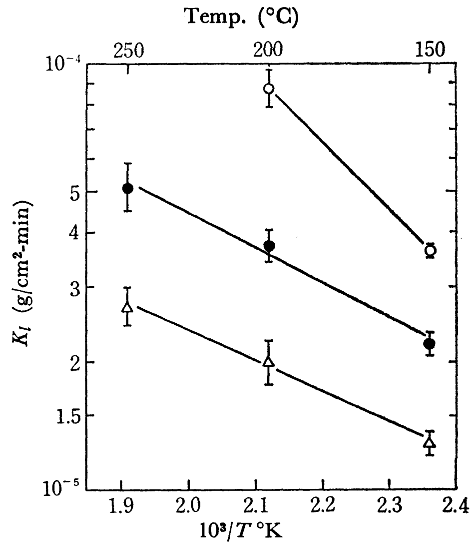

Fig. 10. Arrhenius plot for the linear phosphidation rate of copper: ○: 10; ●: 4; △: 1 Torr.

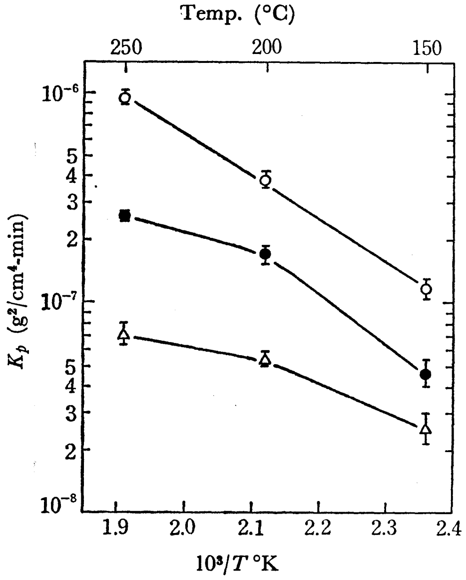

Fig. 11. Temperature dependence of the parabolic rate of phosphidation of copper: The same symbols as in Fig. 10.

The temperature dependence of K_l and K_p is plotted in Figs. 10 and 11. The apparent activation energies, E, evaluated from them are represented in Table 4.

The Eyring absolute-rate theory[11] was used here for a further discussion of the linear behavior. From the θ and the specific rate constant expressed as $\kappa(\boldsymbol{k}T/\boldsymbol{h})\exp(-\Delta G^{\ddagger}/\boldsymbol{R}T)$, the linear rate constant may be written as follows:

$$\begin{aligned}K_l&=k_0\theta\kappa(\boldsymbol{k}T/\boldsymbol{h})\exp(-\Delta G^{\ddagger}/\boldsymbol{R}T)\\&=k_0\{\alpha P^{1/n}/(1+\alpha P^{1/n})\}\kappa(\boldsymbol{k}T/\boldsymbol{h})\exp(\Delta S^{\ddagger}/\boldsymbol{R}-\Delta H^{\ddagger}/\boldsymbol{R}T)\end{aligned} \tag{4}$$

where k_0 is a proportionality constant; κ, the transmission coefficient; $\boldsymbol{k}$, Boltzmann's constant; $\boldsymbol{h}$, Planck's constant, and T and $\boldsymbol{R}$, the usual significance.

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[11] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y. (1941).

In the case of the present phosphidation, the enthalpy of activation is expressed as $\Delta H^{0\ne} = E - \boldsymbol{R}T$. Therefore,

$$K_l = k_0 \theta \kappa e(\boldsymbol{k}T/\boldsymbol{h}) \exp(\Delta S^{0\ne}/\boldsymbol{R}) exp(-E/\boldsymbol{R}T) \qquad (5)$$

In Eq. (5), the usual assumption is made that the κ is unity. By the division of the experimental values of K_l on the Arrhenius plot in Fig. 10 by θ, the relation can be obtained as independent of the change in the surface concentration of phosphorus. Figure 12 shows the $\log(K_l\boldsymbol{h}/\theta\boldsymbol{k}T) - 1/T$ relationship, which gives about 3.6 kcal/mol as the free energy of activation, $\Delta G^{0\ne}$, for the 150—250°C range. Hence, since E_l is, for example, at 4 Torr and 200°C, 3.9 kcal/mol, the value of $\Delta H^{0\ne}$ is approximately 3 kcal/mol, and the entropy of activation, $\Delta S^{0\ne}$, is about −1.3 e. u. The negative value in $\Delta S^{0\ne}$ is thus reasonable.

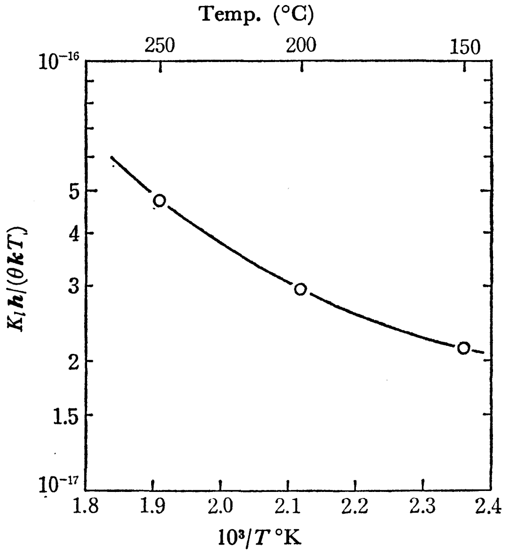

Fig. 12. Absolute rate of reaction of copper in phosphorus vapor *vs.* reciprocal temperature.

The decomposition of CuP_2 has been found to be as follows[3,10]:

$$12/5\,CuP_2(s) \rightleftarrows 4/5\,Cu_3P(s) + P_4(g)$$

$$\log P_{atm} = -11370/T°K + 10.946$$

where P_{atm} stands for the pressure of the P_4 vapor. In Fig. 13, the chemical potential diagram of the copper-phosphorus system reveals that the phase structure becames (P_4 vapor)/CuP_2/Cu_3P/Cu under the present experimental conditions, because the CuP_2 and Cu_3P compounds alone exist in the phosphorus-copper system. The formation of CuP_2 mentioned before can be explained on these thermodynamic grounds.

The pressure dependence of K_p is shown in Fig. 14, which yields following relations: $K_p \propto P^{0.6}$ at 150°, $K_p \propto P^{0.9}$ at 200°, and $K_p \propto P^{1.1}$ at 250°C. The Cu_3P compound was formed at the scale/metal interface. Even if the mass action law is applied as a *p*-type scale to the lattice-defect equation:

$$1/4\,P_4(g) \rightleftarrows Cu_3P + 3\,Cu\square' + 3\,\oplus,$$

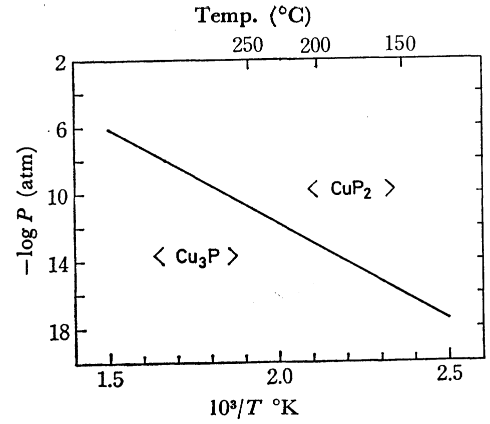

Fig. 13. Chemical potential diagram of the copper-phosphorus system.

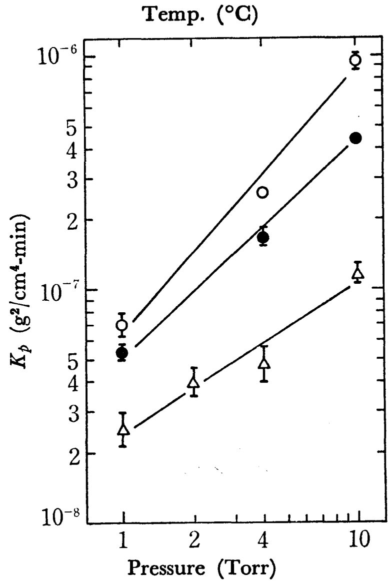

Fig. 14. Phosphorus-pressure dependence for the parabolic rate of phosphidation of copper: The same symbols as in Fig. 8.

the pressure dependence of the parabolic rate is only 1/24 power of the pressure. According to the phase diagram,[1,10] the solubility of phosphorus in metallic copper is about 0.5 wt% *viz.* 1 at% around 200°C. The higher pressure-dependence of K_p, shown above, can probably be attributed to the phosphorus-solubility process. The temperature dependence of K_p at 1 and 4 Torr (Fig. 11) gives two apparent activation energies; this fact may result from differences in the nucleation and growth of copper phosphides and in the solubility of phosphorus in metallic copper.

Although several explanations have been proposed, the fundamental mechanism underlying the phosphidation phenomena has hardly been clarified yet.

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