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Author(s)	Morita, Zen-ichiro; Tanaka, Toshihiro
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Equilibrium Distribution Coefficient of Phosphorus in Iron Alloys*

By Zen-ichiro MORITA** and Toshihiro TANAKA**

Synopsis

In this work, the equilibrium distribution coefficients of phosphorus k_0^p in Fe-P binary and Fe-C-P ternary systems were obtained experimentally and the carbon content dependence of the equilibrium distribution of P was discussed using Distribution Interaction Coefficient. Temperature dependence of k_0^p , α for α phase is given by

$$k_0^{P,\alpha} = \mathcal{N}_P^s/\mathcal{N}_P^l = 0.715 - 3.20 \times 10^{-4} T.$$

From the above equation, $k_0^{p,\alpha}$ at infinite dilution of P, that is to say, at the melting point of iron, is 0.136. $k_0^{p,\gamma}$ for γ phase at high carbon concentration is about 0.09. $k_0^{p,\gamma}$ increases with the concentration of carbon and $k_0^{p,\gamma}$ at infinite dilution is 0.06. Also, the relation between k_0^{χ} of various elements for α phase and that for γ one was derived thermodynamically.

I. Introduction

The micro-segregation of phosphorus in engineering steels is known to affect considerably the physicochemical and mechanical properties of the materials. The information about the equilibrium distribution coefficient of phosphorus is very important to investigate various phenomena during the solidification of steels concerning the micro-segregation. Some investigators have reported the equilibrium distribution coefficients in iron alloys but there seems to be large discrepancies among them. Also, they have not discussed in detail the effects of carbon and the peritectic reaction on the equilibrium distribution of phosphorus between solid and liquid phases in iron-carbon base alloys.

In this work, the equilibrium distribution coefficients of P in Fe-P binary and Fe-P-C ternary alloys were determined experimentally to give values of k_0^P for α and γ phases. Also, the effect of carbon on the equilibrium distribution of P between solid and liquid phases and the segregation of P in Fe-C base steels were discussed. The relation between k_0^X of various elements for α phase and that for γ phase was also studied thermodynamically.

II. Experimental

So as to investigate the equilibrium distribution of P between solid and liquid phases in Fe-P base alloys, solid-liquid phases equilibrated were quenched and the phosphorus concentration in each phase was determined by EPMA; this has been described in more detail in the previous paper.^{1,2)} The apparatus for quenching specimens is shown in Fig. 1. After melting down the sample, it was cooled to a fixed temperature, at which solid and liquid phases co-

existed, and held at that temperature for a given time. When the equilibrium was achieved, by withdrawing the stopper, the sample fell through the hole at the bottom of the crucible and was quenched on the copper plate with argon gas blow.

Area analyses by EPMA were performed in this experiment so that the error in the measurement of the concentration of P in the liquid phase could be as small as possible.

III. Results and Discussion

 The Equilibrium Distribution Coefficient of P between α and liquid Phases in Fe-P Binary Alloys

The concentration of P and the equilibration temperature of the sample used in this experiment to obtain $k_0^{\rm P}$ in Fe–P binary alloys are listed in Table 1. In this work, five samples were used as shown in this table. The temperature range was from 1 733 to 1 405 K and the equilibration temperatures were determined to make the ratio of solid in the samples, which included both solid and liquid phases in the

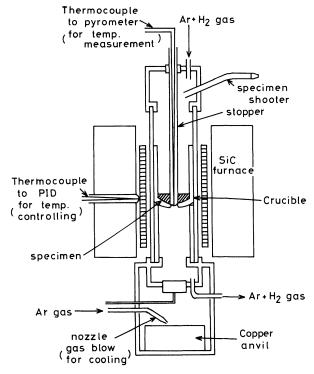


Fig. 1. Apparatus for quenching specimens.

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^{**} Department of Metallurgical Engineering, Faculty of Engineering, Osaka University, Yamadaoka, Suita 565.

Table 1. Chemical composition and equilibration temperature for Fe-P binary alloys.

No.	Mole fraction of phosphorus	Weight percent of phosphorus	Holding temperature (K)
1	0.041	2.31	1 733
2	0.053	3.02	1 695
3	0.089	5.12	1 603
4	0.134	7.88	1 478
5	0.151	8.99	1 405

elevated temperature, about 10 %.

Figure 2 indicates the experimental results of the concentration of P in both solid and liquid phases at various temperatures in Fe-P binary alloys with the liquidus and solidus published by other investigators.^{3–8)} As obvious from this figure, the present results are in good agreement with the results by Schürmann and Keizer.8) In this experiment, the solid phase equilibrated with liquid one is α phase. Then, using the mole fraction of P in both α and liquid phases, the equilibrium distribution coefficients of P for α phase, $k_0^{P,\alpha}$ were obtained. The temperature dependence of the equilibrium distribution coefficient of P is shown in Fig. 3. The error bars in this figure indicate both the maximum and the minimum of the measured values. As obvious from this figure, the value of $k_0^{p,\alpha}$ changes from 0.153 to 0.256 in the range of temperature and concentration of P measured in this work. Also, $k_0^{P,\alpha}$ increases as the temperature decreases, in other words, the concentration of P increases. Furthermore, the linear relation holds between the equilibrium distribution coefficient of P, $k_0^{P,\alpha}$, and temperature, T within the experimental error as shown in Fig. 3. If the temperature dependence of $k_0^{\rm p,\alpha}$ is regressed approximately by an order of temperature T, the following equation can be derived.

$$k_0^{P,\alpha} = \mathcal{N}_P^s / \mathcal{N}_P^t = 0.715 - 3.20 \times 10^{-4} T$$
(1)

When the equilibrium distribution coefficient of P at the melting point of pure iron, that is to say, 1 809 K, is calculated using the above equation, $k_0^{p,\alpha}$ can be obtained as 0.136. $k_0^{p,\alpha}$ at that temperature corresponds practically to $k_0^{p,\alpha}$ at infinite dilution of P in engineering steels which contain quite small amount of phosphorus. By the way, $k_0^{p,\alpha}$ in Eq. (1) is the equilibrium distribution coefficient when the mole fraction is used so as to identify the concentration of phosphorus in iron alloys. The equilibrium distribution coefficient described using weight percent for the concentration of phosphorus as follows:

$$k_0^{P,\alpha} = [\text{wt \% P}]^s / [\text{wt \% P}]^t$$

= 0.643-2.80×10⁻⁴T(2)

In this case, the value 0.136 can also be obtained for the $k_0^{P,\alpha}$ at the melting point of pure iron and the value of $k_0^{P,\alpha}$ changes from 0.153 to 0.242 in the range of temperature and concentration of P measured in this work.

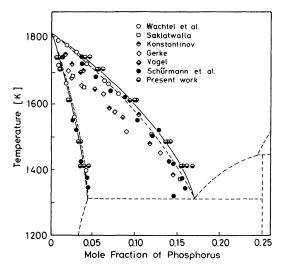


Fig. 2. Experimental results of phosphorus concentrations in solid and liquid phases in Fe-P binary alloys.

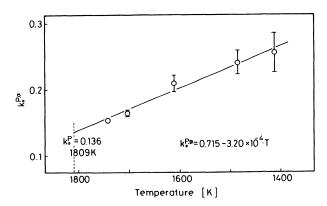


Fig. 3. Temperature dependence of $k_0^{\rm P,\alpha}$ of P in Fe–P binary alloys.

Table 2 gives the equilibrium distribution coefficient of P for both α and γ phases equilibrated with liquid one published by other workers^{9–19)} together with the present results. In this table, the present experimental result of $k_0^{\rm P,\alpha}$ shows 0.136 at infinite dilution for α phase and it coincides with the results by Hays and Chipman⁹⁾ and Wada and Wada.¹⁰⁾

2. The Equilibrium Distribution Coefficient of P for γ Phase and the Effect of Carbon on $k_0^{\alpha,\gamma}$

As can be seen in Table 2, the equilibrium distribution coefficient of P for γ phase was reported as 0.06 by Chipman,¹⁷⁾ 0.08 by Wada and Wada¹⁰⁾ and 0.13 by Nakamura and Esaka.¹⁸⁾ Generally these values are smaller than those for α phase. In order to obtain the equilibrium distribution coefficient of P for γ phase, the equilibrium distribution coefficients of P between liquid and γ phases in Fe–C–P ternary alloys, which contain about 0.5 wt% of P, were measured at the concentration of carbon between 2.08 and 3.93 wt%.

The experimental method is the same as described in previous section. The results are presented in Fig. 4. It is obvious from this figure that the equilibrium distribution coefficient of P indicates about 0.09 and the effects of carbon on $k_0^{\rm P, T}$ can not be seen

Table 2.	Equilibrium distribution coefficient of P for
	both α phase and γ phase in iron alloys.

		_	, -	
Solid	Com- position (wt%)	k ₀	Investigators	Ref.
		0.13	Hays & Chipman (1938)	9)
		0.14	Wada & Wada (1967)	10)
		0.15~ 0.18	Oeters, Ruttiger, Diener & Zahn (1969)	11)
	0.015~ 0.092	0.16± 0.04	Fischer & Frye (1970)	12)
	0.204~ 0.211	0.17	Fischer, Spilzer & Hishinuma (1960)	13)
		0.2	Tiller (1959)	14)
α		0.2~ 0.5	Smith & Rutherford (1957)	15)
phase	0.07~ 0.28	0.23	Takahashi, Kudo & Ichikawa (1977)	16)
	-	0.27	Smith & Rutherford (1957)	15)
		0.28	Fischer & Frye (1970)	12)
		0.23	Nakamura & Esaka (1981)	18)
		0.29	Suzuki, Umeda & Kimura (1981)	19)
	Infinite	0.136		
	dilution 2.31~ 8.99	0.153~ 0.242	Present work (1986)	
		0.06	Chipman (1951)	17)
		0.08	Wada & Wada (1967)	10)
γ phase		0.13	Nakamura & Esaka (1981)	18)
P	Infinite dilution	0.06	Present work (1986)	

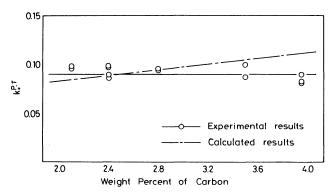


Fig. 4. Change of $k_0^{\mathbf{P},\mathbf{r}}$ of P with the concentration of C in Fe-C base ternary alloys.

remarkably in the concentration of carbon measured in the experiment. Then, the equilibrium distribution coefficients of phosphorus for γ phase at infinite dilution were determined by means of Distribution Interaction Coefficient defined in the previous work.²⁰⁾ The equilibrium distribution coefficient of phosphorus in Fe–C–P alloys, $k_0^{p,\gamma}$ is given in the following equation when Distribution Interaction Coefficient is used so as to represent the effect of carbon on the equilibrium distribution of phosphorus.

Table 3. Data for the calculation of the equilibrium distribution coefficients of phosphorus in Fe-C-P alloys.

Temperature (K)	1 673	1 623	1 573	1 523	1 473	1 423
$[\%\mathbf{C}]^{t}$	1.88	2.47	3.12	3.50	3.93	4.26
k_0^{C}	0.378	0.409	0.430	0.454	0.470	0.488
$e_{\mathrm{P}}^{\mathrm{C}}$, t	0.113	0,119	0.124	0.128	0.132	0.135
k_0^{P} , r	0.082	0.089	0.098	0.106	0.113	0.118

$$\ln k_0^{P,\gamma}/k_0^{P,\gamma,2} = (1 - k_0^{C}) \cdot e_P^{C,l} \cdot [\%C]^{l} \dots (3)$$

where, $k_0^{\mathrm{p},\gamma,2}$: equilibrium distribution coefficient of phosphorus at infinite dilution in Fe-P binary alloy

 k_0^c : equilibrium distribution coefficient of carbon in Fe-C-P alloy

 $e_{
m F}^{{
m C},t}$: interaction parameter of carbon on phosphorus in liquid Fe-C-P alloy

[%C]¹: carbon concentration by means of weight percent in iron alloy.

The values of k_0^c , $e_r^{c,t}$ and $[\%C]^t$ at various temperatures on the liquidus of iron alloys are shown in Table 3. In this table, the values of k_0^c and $[\%C]^t$ on the liquidus of Fe–C binary alloys given by Chipman²¹⁾ are used because the contents of phosphorus in the samples of Fe–C–P alloys in the present experiment were very dilute. Also, as for $e_r^{c,t}$, the values were determined by using both $e_r^{c,t}$ in dilute liquid alloys and $e_r^{c,t}$ in carbon-saturated liquid iron alloys obtained by Ban-ya *et al.*²²⁾ and by considering their temperature and carbon concentration dependence, that is to say, $e_r^{c,t}$ is presumed to be proportional to reciprocal of the absolute temperature and carbon concentration.

If these values in Table 3 are substituted into Eq. (3) and also the values of $k_0^{p,\tau}$ at infinite dilution are assumed to be 0.06, the calculated results of $k_0^{p,\tau}$ shown by the chain line in Fig. 4 are in good agreement with the experimental ones. Consequently, it is supposed that the equilibrium distribution coefficient of P for γ phase at infinite dilution is about 0.06 and it increases to about 0.09 at the concentration of carbon between 2.08 and 3.93 wt%.

By the way, the value 0.06 assumed as the equilibrium distribution coefficient of P for γ phase is consistent with the results by Chipman.²¹⁾

3. Change of the Equilibrium Distribution Coefficient and the Segregation Coefficient of P with the Concentration of Carbon

In this section, the effect of carbon on the segregation of P in steels is discussed using the results obtained above. Figure 5 shows the change of the equilibrium distribution coefficient of P, k_0^p , (Fig. 5(B)) and the segregation coefficient of P, $1-k_0^p$, (Fig. 5(C)) for both α and γ phases with the concentration of carbon in the range which includes the peritectic reaction of Fe-C binary system. In these figures, the equilibrium distribution coefficient of P can be estimated to be

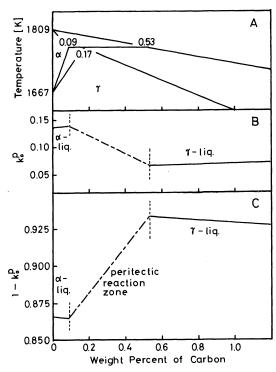


Fig. 5. Change of the equilibrium distribution coefficient and the segregation coefficient of phosphorus with the concentration of carbon in Fe-C base alloys.

0.136 for α phase at the melting point of pure iron and 0.06 for γ phase at the infinite dilution, respectively. The effect of carbon on the phosphorus distribution can be also evaluated using the Distribution Interaction Coefficient. Since the equilibrium distribution coefficient of P in the peritectic reaction region may possibly change between k_0^p for α phase and that for γ phase, then the variation of k_0^p for that region is hypothetically indicated as a straight line in Fig. 5. As exhibited in Fig. 5(B), the equilibrium distribution coefficient of P gives about 0.136 for α phase and about 0.06 for γ phase and it increases slightly with the increasing of the concentration of carbon for both α and γ phases. Figure 5(C) shows that the segregation coefficient of P increases as the solid phase equilibrated with liquid one changes from α phase to γ one, and it decreases with the increasing of the concentration of carbon in each phase.

The change of the segregation coefficient of P with carbon content is compared with the experimental results of the segregation of P in steels previously published by other investigators. Figure 6(A) represents the variation of the segregation coefficient of P shown in Fig. 5(C) with the concentration of carbon up to 0.2 wt%. Figure 6(B) denotes the change of the concentration of P in liquid phase with that of carbon when the solidification ratio of unidirectional solidified steels is regarded as 0.9983, reported by Matsumiya et al.²³⁾ Misumi and Kitamura²⁴⁾ reported the effect of carbon contents on the area where the segregation ratio of P at the center of the continuously cast slab is larger than 10 %, as illustrated in Fig. 6(C). Figure 6(D) gives the experimental results by Ichikawa et al.25) about the influence of carbon on

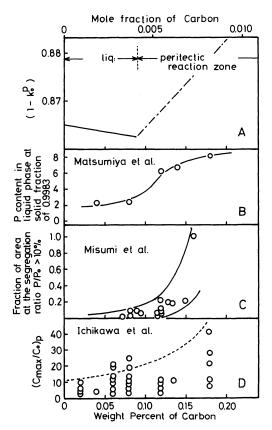


Fig. 6. Change of the segregation coefficient of phosphorus with the concentration of carbon in Fe-C base alloys.

the maximum segregation ratio of P in the continuously cast slab. All of these figures indicate that the segregation ratio of P increases with the concentration of carbon. Compared with the results of this work in Fig. 6(A), it is suggested that the effect of carbon on the segregation of P in steels depends strongly on the variation of the segregation coefficient of P accompanied with the change of the solid phase equilibrated with liquid one from α phase to γ one due to the peritectic reaction.

4. Thermodynamical Relation between Equilibrium Distribution Coefficients of Various Solute Elements for α Phase and those for γ Phase

As is seen in the previous section, in order to discuss the segregation of solute elements in Fe–C base steels, it is very important to know the equilibrium distribution coefficients of these elements for both α phase and γ one.

The purpose of this section is to derive the relation between the equilibrium distribution coefficients of various elements for α phase and those for γ one thermodynamically and to discuss the validity of this relation compared with the experimental results. Also, the changes of the equilibrium distribution coefficients and the segregation coefficients of various elements with the concentration of carbon are studied in Fe–G base steels.

At the infinite dilution of solute element X in iron alloys, the equilibrium distribution coefficients of the

solute elements for the equilibrium of liquid- α phases and liquid- γ phases, $k_0^{\chi,\alpha}$ and $k_0^{\chi,\gamma}$, are given in the following equations (4) and (5), respectively.

$$RT \ln k_0^{x,\alpha} = (\dot{\mu}_x^l - \dot{\mu}_x^\alpha) + RT \ln \dot{\gamma}_x^l / \dot{\gamma}_x^\alpha \quad(4)$$

$$RT \ln k_0^{x,\gamma} = (\dot{\mu}_x^l - \dot{\mu}_x^\gamma) + RT \ln \dot{\gamma}_x^l / \dot{\gamma}_x^\gamma \quad(5)$$

where, $\dot{\mu}_X$: chemical potential of element X in standard state

 \dot{r}_X : activity coefficient of element X at infinite dilution

R: gas constant

T: absolute temperature.

Superscripts l, α , γ : liquid, α and γ phases, respectively.

The following equation (6) is obtained from Eqs. (4) and (5).

$$RT \ln k_0^{X,\alpha}/k_0^{X,\gamma} = (\dot{\mu}_X^{\gamma} - \dot{\mu}_X^{\alpha}) + RT \ln \dot{\gamma}_X^{\gamma}/\dot{\gamma}_X^{\alpha}$$
.....(6)

In Eq. (6), the right hand side is equal to Ferrite/Austenite Stabilizing Parameter $\Delta G_X^{a,r}$ defined as the free energy change accompanied by transfer of one mole of each alloying element from ferrite to austenite.²⁶⁾ That is to say,

$$\ln k_0^{X,\alpha}/k_0^{X,\gamma} = \Delta G_X^{\alpha-\gamma}/RT \qquad(7)$$

It is clear from Eq. (7) that $\Delta G_X^{r,\tau}$ gives the thermodynamical relation between $k_0^{\gamma,\tau}$ for the equilibrium of liquid- α phases and $k_0^{\gamma,\tau}$ for that of liquid- γ phases. Values of $\Delta G_X^{r,\tau}$ of various elements have been reported by many investigators. Particularly, Ishida and Nishizawa²⁶ reported the temperature dependence of $\Delta G_X^{r,\tau}$ of various elements as shown in Fig. 7. The ratio of $k_0^{\gamma,\alpha}/k_0^{\gamma,\tau}$ can be calculated in Eq. (7) by using $\Delta G_X^{r,\tau}$ obtained from the results of Ishida and Nishizawa at 1 768 K, the temperature of the peritectic reaction in Fe-C binary alloy. The results are shown in Table 4. As is obvious from this table, for ferrite stabilizing elements:

$$k_0^{X,\alpha} > k_0^{X,\gamma}$$
(8)

for austenite stabilizing elements:

$$k_0^{X,\alpha} < k_0^{X,\gamma}$$
(9)

The relations in Eqs. (7), (8) and (9) are compared to the experimental results of some elements¹⁶⁾ in Figs. 8 and 9. In these figures, the relations for Mo, Ni, Cr, Cu obtained from Eq. (7) are in good agreement with the experimental ones. For Mn, the relation in Eq. (7) is almost satisfied except the result by Fischer *et al.*¹³⁾ for α phase.

For P, some reported that the equilibrium distribution coefficient k_0^p is $0.13 \sim 0.15$ for α phase and about 0.06 for γ one, and others showed k_0^p as $0.2 \sim 0.23$ for α phase and about 0.13 for γ one. However, the values reported by each group are satisfied with the relation in Eq. (7) as shown in Fig. 9. So, it seems questionable, for instance, to use the equilibrium distribution coefficient of P as about 0.2 for α phase and about 0.06 for γ phase.

The equilibrium distribution coefficients of V and A1 for γ phase have not been reported, but they can be estimated from those for α phase by using Eq. (7). The results are indicated in Fig. 10. It is obvious from this figure that $k_0^{\gamma,\tau}$ is $0.7 \sim 0.75$ for V and $k_0^{\lambda 1,\tau}$ is $0.48 \sim 0.75$ for Al. By the way, it has been already described in the previous work²⁰⁾ that the calculated result of the equilibrium distribution coefficient of V for γ phase in Fe–C–V system agreed well with the experimental one when the value 0.76 was used as $k_0^{\gamma,\tau}$.

Figure 11 shows the variation of the segregation coefficients of various alloying elements with the change of solid phase equilibrated with liquid one from α phase to γ one due to the peritectic reaction in Fe–C base steels. In this figure, the abscissa indicates the concentration of carbon up to 0.8 wt% where the

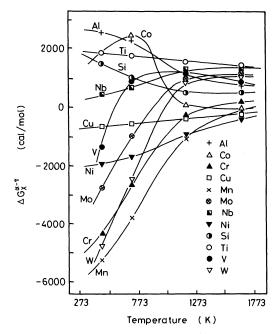


Fig. 7. Temperature dependence of Ferrite/Austenite Stabilizing Parameter $\Delta G_X^{e\tau}$ of various elements in iron alloys.

Table 4. $\Delta G_{\alpha}^{x,\tau}$ and $k_0^{x,\alpha}/k_0^{x,\tau}$ of various elements at 1 768 K in iron alloys.

	Elements	${\it \Delta G_X^{lpha-r}}$ (cal)	$k_0^{X,\alpha}/k_0^{X,\alpha}$
	Ti	1 450	1.51
	Nb	1 350	1.47
	Mo	1 170	1.40
Ferrite	W	1 070	1.36
stabilizing	V	900	1.29
elements	Al	760	1.24
	Si	550	1.17
	Cr	220	1.06
	P	2 200	1.87
	Co	- 50	0.99
Austenite stabilizing elements	Mn	—70	0.98
	Cu	—170	0.95
	Ni	-360	0.90

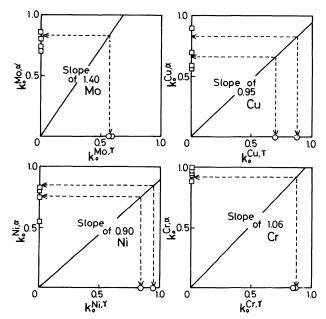


Fig. 8. Comparison of calculated $k_0^{\eta,\eta}/k_0^{\eta,\eta}$ of Mo, Cr, Mn and Cu with the experimental results.

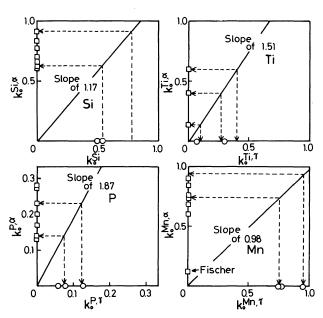


Fig. 9. Comparison of calculated $k_0^{X,\alpha}/k_0^{X,\tau}$ of Si, Ti, Ni and P with the experimental results.

peritectic reaction is included. As is seen from Fig. 11, the segregation coefficients of the ferrite stabilizing elements increase with the increasing of the concentration of carbon, on the other hand, those of the austenite stabilizing elements decrease.

Figure 12 represents the experimental results of the variations of the segregation ratios for Cr and Ni with carbon contents.^{27–30)} In Figs. 7 and 12, P and Cr are ferrite stabilizing elements and their segregation ratios increase with carbon content, while Ni is austenite stabilizing element and the segregation ratio of Ni decreases. Consequently, the calculated results from Eqs. (7) to (9) are in good agreement with the experimental ones.

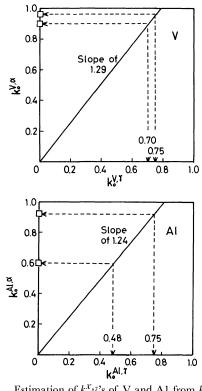


Fig. 10. Estimation of $k_0^{X,\gamma}$'s of V and A1 from $k_0^{X,\alpha}/k_0^{X,\gamma}$.

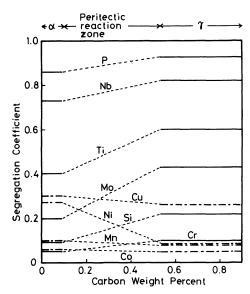


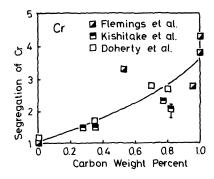
Fig. 11. Variation of the segregation coefficients of various elements with carbon content in Fe-C base alloys.

IV. Summary

In this work, the equilibrium distribution coefficients of P in Fe-P binary and Fe-P-C ternary systems were obtained experimentally and the carbon content dependence of the equilibrium distribution coefficient of P was discussed using Distribution Interaction Coefficient. Also, the relation between k_0^{α} of various elements for α phase and that for γ one was derived thermodynamically.

The results obtained are summarized as follows:

(1) Temperature dependence of $k_0^{\mathrm{P},\alpha}$ for α phase in Fe–P binary alloy is given by



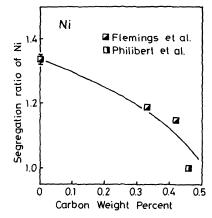


Fig. 12. Variation of the segregation ratios of Cr and Ni with carbon content in iron alloys,

$$k_b^{P,\alpha} = 0.715 - 3.20 \times 10^{-4} T$$
(Mole fraction is used.)
$$k_b^{P,\alpha} = 0.643 - 2.80 \times 10^{-4} T$$

(Weight percent is used.) For the above equation, $k_0^{\mathbf{p},\alpha}$ at infinite dilution of P

- (2) $k_0^{\rm P, \tau}$ for γ phase is about 0.09 at the concentration of carbon between 2.08 and 3.93 wt%. $k_0^{\rm P, \tau}$ increases with the concentration of carbon and $k_0^{\rm P, \tau}$ at infinite dilution is 0.06.
- (3) The increase of the segregation of P with carbon content in steels is dependent on the change of the equilibrium distribution coefficient of P accompanied with the transformation of the solid phase equilibrated with liquid one due to the peritectic reaction.
- (4) The equilibrium distribution coefficients of solute element X, $k_0^{\chi,\alpha}$ for α phase and $k_0^{\chi,\gamma}$ for γ phase are related to Ferrite/Austenite Stabilizing Parameter $\Delta G_{\chi}^{\alpha,\gamma}$ as shown in the following equation.

$$\ln k_0^{X,\alpha}/k_0^{X,\gamma} = \Delta G_X^{\alpha-\gamma}/RT$$

The ratio of $k_0^{x,a}/k_0^{x,\tau}$ can be calculated from $\Delta G_X^{a-\tau}$.

- (5) For ferrite stabilizing elements: $k_0^{X,\alpha} > k_0^{X,\tau}$ and for austenite stabilizing elements: $k_0^{X,\alpha} < k_0^{X,\tau}$.
 - (6) In Fe-C base steels, as the solid phase equilib-

rated with liquid one changes from α phase to γ phase with the increasing of the concentration of carbon due to the peritectic reaction, the segregation coefficients of ferrite stabilizing elements increase while those of austenite stabilizing elements decrease.

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