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Coefficients for equilibrium partition of a third element between solid and liquid in iron–carbon base ternary alloys and their relation to graphitization during iron–carbon eutectic solidification

AKIO KAGAWA, TAIRA OKAMOTO
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan

During iron–carbon eutectic solidification, the coefficients for partition of a third element between the eutectic liquid and its solid were evaluated thermodynamically. The coefficient $k_M^{A/L}$ for the equilibrium partition of the third element (M) between austenite and liquid iron largely depended on the interaction between carbon and the third element and a simplified method for the evaluation of $k_M^{A/L}$ was introduced. The coefficients, K^S and K^M, for the partition of the element between the eutectic liquid and its solid in the stable and metastable eutectic solidification, respectively, were also calculated from $k_M^{A/L}$ and the coefficient $k_M^{C/A}$ for the equilibrium partition of the element between cementite and austenite. It was indicated by the thermodynamics of the free energy for the co-existing phases that the effect of a third element on graphitization occurring during eutectic solidification was related quantitatively to the value of ΔK which was represented by $K^S - K^M$. The effect of a third element on the difference between the stable and metastable eutectic temperatures and on the carbon activity of liquid iron was closely related to ΔK or the equilibrium partition coefficient, $k_M^{C/A}$.

1. Introduction

Despite of the importance of the coefficients for partition of solute elements between liquid and solid in cast iron and steel in relation to the formation of a solidification structure and the development of segregation, there is limited information on the partition coefficients in the eutectic solidification of cast iron. In previous work [1, 2], we determined the partition coefficients of silicon and chromium on the solidification of iron–carbon–silicon and iron–carbon–chromium eutectic alloys by a zone melting method. In addition, thermodynamic calculation of the partition coefficients was performed to examine the validity of the experimental values. Measurement of the coefficients using the zone melting method was, however, laborious and, furthermore, its application would be restricted because the method is unsuitable for the determination of partition coefficients of volatile and gaseous elements. In this work, the partition coefficients were evaluated by calculation for a third element in the iron–carbon base ternary systems and, for simplicity, a modified calculation method was presented. From the results, the effect of alloying elements on the graphitization of iron–carbon base ternary alloys was appreciated and factors influencing the graphitization were examined on the basis of the thermodynamic stability of the phases concerned.

2. Calculation of the coefficients for partition of alloying elements between the eutectic liquid and its solid

On metastable eutectic solidification, three kinds of equilibrium for an alloying element should be

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established between the phases concerned, that is, between eutectic liquid and austenite, between eutectic liquid and cementite, and between cementite and austenite, and hence the three equilibrium partition coefficients are defined as $k_M^{A/L} = (\%M)^A/(\%M)^L$, $k_M^{C/L} = (\%M)^C/(\%M)^L$, and $k_M^{C/A} = (\%M)^C/(\%M)^A$, respectively, where (%M) is the weight per cent of the alloying element M, and the superscripts L, A, and C denote eutectic liquid, austenite, and cementite, respectively. On stable eutectic solidification, alloying elements equilibrate only between eutectic liquid and austenite because of a negligibly small solubility of the elements in graphite. The coefficients for partition of the alloying elements between the eutectic liquid and its solid on the stable and metastable eutectic solidifications, K^S and K^M, respectively, defined as the ratio of weight per cent of each element in the solid to that in the liquid, are represented using the equilibrium partition coefficients, $k_M^{A/L}$, $k_M^{C/L}$, and $k_M^{C/A}$ as follows:

$$K^S = g^A k_M^{A/L} \tag{1}$$

$$\begin{aligned} K^M &= g^{A'} k_M^{A/L} + (1-g^{A'}) k_M^{C/L} \\ &= [g^{A'} + (1-g^{A'}) k_M^{C/A}] k_M^{A/L} \end{aligned} \tag{2}$$

where g^A and $g^{A'}$ are the weight fraction of austenite in the stable and metastable eutectic solids, respectively. Thus the values of K^S and K^M are evaluated from $k_M^{A/L}$ and $k_M^{C/A}$. Calculation of the equilibrium partition coefficient, $k_M^{C/A}$, was described in detail by Ko *et al.* [3]. Hence only the equilibrium partition coefficient $k_M^{A/L}$ is calculated in this paper.

The equilibrium condition for an alloying element (M) partitioned between austenite and liquid iron is represented by:

$$\mathring{\mu}_M^L + RT \ln \gamma_M^L X_M^L = \mathring{\mu}_M^A + RT \ln \gamma_M^A X_M^A \tag{3}$$

where $\mathring{\mu}_M$ is the chemical potential of the element in a standard state, R the gas constant, T the temperature at which the phases concerned are in equilibrium, γ_M the activity coefficient for the element, and X_M the molar fraction of the element in the phase concerned. From Equation 3, we obtained,

$$k_M^{A/L} = \frac{(\gamma_M^L/\gamma_M^A)}{F} \exp\left(\frac{\mathring{\mu}_M^L - \mathring{\mu}_M^A}{RT}\right) \tag{4}$$

where

$$F = \frac{(\%Fe)^L/W_{Fe} + (\%C)^L/W_C + (\%M)^L/W_M}{(\%Fe)^A/W_{Fe} + (\%C)^A/W_C + (\%M)^A/W_M} \tag{5}$$

and (%i) and W_i denote weight per cent and atomic weight of the element i, respectively. For carbon, graphite is taken as the standard state, and hence $\mathring{\mu}_C^L = \mathring{\mu}_C^A$. We obtained the following equation for carbon:

$$k_C^{A/L} = \frac{(\gamma_C^L/\gamma_C^A)}{F} \tag{6}$$

In the calculation, the activity coefficients for carbon given by Chipman [4] for liquid iron and by Ban-Ya *et al.* [5] for austenite were adopted. The activity coefficient in Equation 4 is expressed in terms of the interaction coefficient:

$$\gamma_M = \mathring{\gamma}_M \exp(\epsilon_M^C X_C + \epsilon_M^M X_M) \tag{7}$$

where $\mathring{\gamma}_M$ is the activity coefficient at infinite dilution of the element M, ϵ_M^C and ϵ_M^M are the interaction coefficient between the element M and carbon and the self-interaction coefficient of the element M, respectively, X_C and X_M are the molar fractions of carbon and the element M, respectively. Equation 4 is then rewritten for dilution of the element M:

$$\begin{aligned} k_M^{A/L} &= \frac{(\mathring{\gamma}_M^L/\mathring{\gamma}_M^A)}{F} \exp\left(\frac{\mathring{\mu}_M^L - \mathring{\mu}_M^A}{RT}\right) \\ &\quad \times \exp(\epsilon_M^{C,L} X_C^L - \epsilon_M^{C,A} X_C^A) \end{aligned} \tag{8}$$

The equilibrium partition coefficients for both carbon and element M were determined by solving the simultaneous Equations 6 and 8. The thermochemical data used for the calculation of $k_M^{A/L}$ are given in Table I and the results are shown in Fig. 1. In the figure, the values obtained experimentally by other workers are also plotted for comparison. In the calculation, it is assumed that the interaction coefficient between carbon and an alloying element is independent of the molar fraction of carbon, because of the small dependence of the coefficient on the molar fraction for the iron–carbon base ternary system [6–8]. In the wide range of molar fraction of carbon up to eutectic composition, the calculated partition coefficients are in good agreement with experimental values.

The equilibrium partition coefficient for the Fe–M binary system, $(k_M^{A/L})^*$ is given as follows.

TABLE I Thermochemical properties used for the calculation of $k_{\mathrm{M}}^{\mathrm{A/L}}$

	$\ln(\mathring{\gamma}_{\mathrm{Cr}}^{\mathrm{L}}/\mathring{\gamma}_{\mathrm{Cr}}^{\mathrm{A}}) = 3.83 - 1577/T - 0.3305 \ln T$ [9, 10]
	$\dfrac{\mathring{\mu}_{\mathrm{Cr}}^{\mathrm{L}} - \mathring{\mu}_{\mathrm{Cr}}^{\mathrm{A}}}{RT} = 11.73 + 160/T + 5.9 \times 10^{-4}\,T - 1.79 \ln T$ [9, 11]
	$\epsilon_{\mathrm{C}}^{\mathrm{Cr,L}} = 2.58 - 12\,670/T$ [12]
	$\epsilon_{\mathrm{C}}^{\mathrm{Cr,A}} = 22.58 - 38\,750/T$ [13]
Mn	$\ln(\mathring{\gamma}_{\mathrm{Mn}}^{\mathrm{L}}/\mathring{\gamma}_{\mathrm{Mn}}^{\mathrm{A}}) = 0.382 - 670/T$ [10, 14]
	$\dfrac{\mathring{\mu}_{\mathrm{Mn}}^{\mathrm{L}} - \mathring{\mu}_{\mathrm{Mn}}^{\mathrm{A}}}{RT} = 16.8 + 250/T + 8.96 \times 10^{-4}\,T - 1.115 \times 10^{-4}\,T^{-2} - 2.5 \ln T$ [9, 11]
	$\epsilon_{\mathrm{C}}^{\mathrm{Mn,L}} = 4.42 - 11\,980/T$ [15]
	$\epsilon_{\mathrm{C}}^{\mathrm{Mn,A}} = -4930/T$ [16]
Ni	$\ln(\mathring{\gamma}_{\mathrm{Ni}}^{\mathrm{L}}/\mathring{\gamma}_{\mathrm{Ni}}^{\mathrm{A}}) = 0.327 - 1259/T + 4.61 \times 10^{-4}\,T - 1.964 \times 10^{-7}\,T^2$ [17]
	$\dfrac{\mathring{\mu}_{\mathrm{Ni}}^{\mathrm{L}} - \mathring{\mu}_{\mathrm{Ni}}^{\mathrm{A}}}{RT} = 2063/T - 1.194$ [11]
	$\epsilon_{\mathrm{C}}^{\mathrm{Ni,L}} = 8750/T - 1.59$ [12]
	$\epsilon_{\mathrm{C}}^{\mathrm{Ni,A}} = 4640/T + 0.65$ [18]
Co	$\ln(\mathring{\gamma}_{\mathrm{Co}}^{\mathrm{L}}/\mathring{\gamma}_{\mathrm{Co}}^{\mathrm{A}}) = 0.55 - 550/T - 2.51 \times 10^{-4}\,T + 5.2 \times 10^{-8}\,T^2$ [17]
	$\dfrac{\mathring{\mu}_{\mathrm{Co}}^{\mathrm{L}} - \mathring{\mu}_{\mathrm{Co}}^{\mathrm{A}}}{RT} = 1862/T - 1.053$ [11]
	$\epsilon_{\mathrm{C}}^{\mathrm{Co,L}} = 4380/T - 0.58$ [12]
	$\epsilon_{\mathrm{C}}^{\mathrm{Co,A}} = 2.62 - 410/T$ [19, 20]
N†	$(k_{\mathrm{N}}^{\mathrm{A/L}})^* = \exp(1672/T - 1.69)$ [21, 22]
	$\log f_{\mathrm{N}}^{\mathrm{L}} = (280/T - 0.055)(\%\mathrm{C})^{\mathrm{L}} + 0.005\{(\%\mathrm{C})^{\mathrm{L}}\}^2$ [21]
	$\log f_{\mathrm{N}}^{\mathrm{A}} = (395/T - 0.183)(\%\mathrm{C})^{\mathrm{A}}$ [23]
Si	$(k_{\mathrm{Si}}^{\mathrm{A/L}})^* = 0.5$ [24]
	$\epsilon_{\mathrm{C}}^{\mathrm{Si,L}} = 18\,800/T - 0.353$ [10]
	$\epsilon_{\mathrm{C}}^{\mathrm{Si,A}} = 17\,000/T - 0.163$ [15]
Cu	$(k_{\mathrm{Cu}}^{\mathrm{A/L}})^* = 0.88$ [24]
	$\epsilon_{\mathrm{C}}^{\mathrm{Cu,L}} = 12\,900/T - 1.727$ [12]
	$\epsilon_{\mathrm{C}}^{\mathrm{Cu,A}} = 11\,930/T - 1.597^{\ddagger}$
Mo	$(k_{\mathrm{Mo}}^{\mathrm{A/L}})^* = 0.6$ [24]
	$\epsilon_{\mathrm{C}}^{\mathrm{Mo,L}} = 7.88 - 21\,880/T$ [12]
	$\epsilon_{\mathrm{C}}^{\mathrm{Mo,A}} = 5.76 - 21\,880/T$ [26]
W	$(k_{\mathrm{W}}^{\mathrm{A/L}})^* = 0.5$ [24]
	$\epsilon_{\mathrm{C}}^{\mathrm{W,L}} = -11\,988/T$ [27]
	$\epsilon_{\mathrm{C}}^{\mathrm{W,A}} = -7885/T$ [28]

TABLE I (continued)

Ti	$(k_{\mathrm{Ti}}^{\mathrm{A/L}})^* = 0.3$ [25]
	$\epsilon_{\mathrm{C}}^{\mathrm{Ti,L}} = 42.84 - 94\,884/T$ [12]
	$\epsilon_{\mathrm{C}}^{\mathrm{Ti,A}} = 39.63 - 87\,768/T^{\ddagger}$
P	$(k_{\mathrm{P}}^{\mathrm{A/L}})^* = 0.06$ [24]
	$\epsilon_{\mathrm{C}}^{\mathrm{P,L}} = 10\,466/T$ [27]
	$\epsilon_{\mathrm{C}}^{\mathrm{P,A}} = 8305/T^{\ddagger}$
S	$(k_{\mathrm{S}}^{\mathrm{A/L}})^* = 0.02$ [24]
	$\epsilon_{\mathrm{C}}^{\mathrm{S,L}} = 7922/T + 7.554$ [12]
	$\epsilon_{\mathrm{C}}^{\mathrm{S,A}} = 7328/T + 6.987^{\ddagger}$
B	$(k_{\mathrm{B}}^{\mathrm{A/L}})^* = 0.05$ [25]
	$\epsilon_{\mathrm{C}}^{\mathrm{B,L}} = 4680/T$ [29]
	$\epsilon_{\mathrm{C}}^{\mathrm{B,A}} = 4330/T^{\ddagger}$

†$k_{\mathrm{N}}^{\mathrm{A/L}} = (k_{\mathrm{N}}^{\mathrm{A/L}})^* f_{\mathrm{N}}^{\mathrm{L}}/f_{\mathrm{N}}^{\mathrm{A}}$.

‡Estimated from the relation $\epsilon_{\mathrm{C}}^{\mathrm{M,A}} = 0.92\,\epsilon_{\mathrm{C}}^{\mathrm{M,L}}$.

§For the interaction coefficient $\epsilon_{\mathrm{M}}^{\mathrm{C}}$ in the calculation of $k_{\mathrm{M}}^{\mathrm{A/L}}$, Wagner's relation [30], $\epsilon_{\mathrm{M}}^{\mathrm{C}} = \epsilon_{\mathrm{C}}^{\mathrm{M}}$, was used.

$$(k_{\mathrm{M}}^{\mathrm{A/L}})^* = \frac{(\mathring{\gamma}_{\mathrm{M}}^{\mathrm{L}}/\mathring{\gamma}_{\mathrm{M}}^{\mathrm{A}})}{F}\exp\left(\frac{\mathring{\mu}_{\mathrm{M}}^{\mathrm{L}} - \mathring{\mu}_{\mathrm{M}}^{\mathrm{A}}}{RT}\right) \quad (9)$$

Equation 8, therefore, becomes:

$$k_{\mathrm{M}}^{\mathrm{A/L}} = (k_{\mathrm{M}}^{\mathrm{A/L}})^* \times \exp\left(\epsilon_{\mathrm{M}}^{\mathrm{C,L}} X_{\mathrm{C}}^{\mathrm{L}} - \epsilon_{\mathrm{M}}^{\mathrm{C,A}} X_{\mathrm{C}}^{\mathrm{A}}\right) \quad (10)$$

In this equation, the exponential term expresses

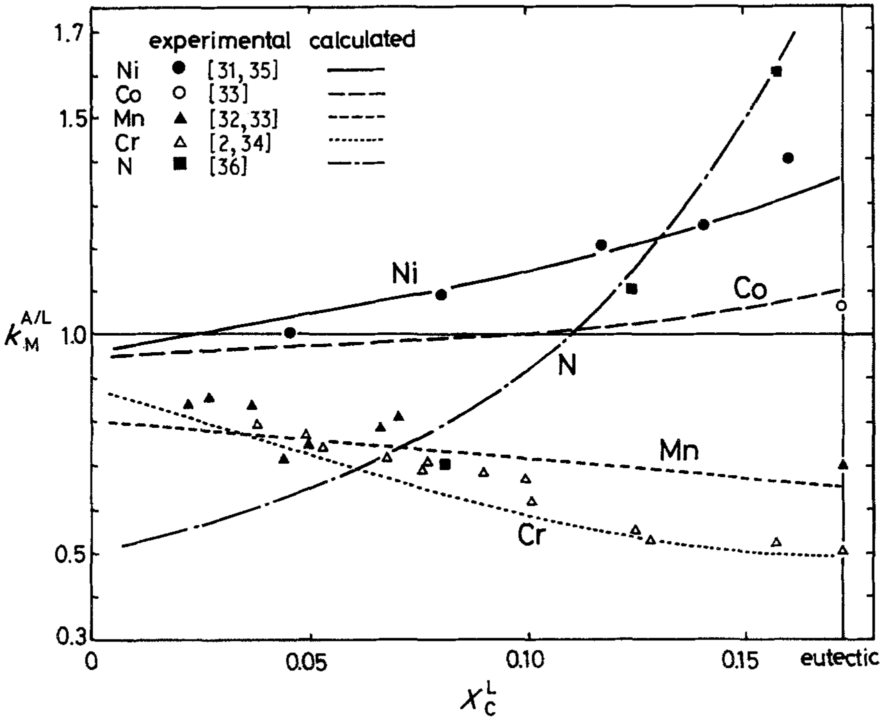

Figure 1 The coefficient $k_{\mathrm{M}}^{\mathrm{A/L}}$ for equilibrium partition of a third element between austenite and liquid iron in Fe–C base ternary alloys containing a small amount of the third element.

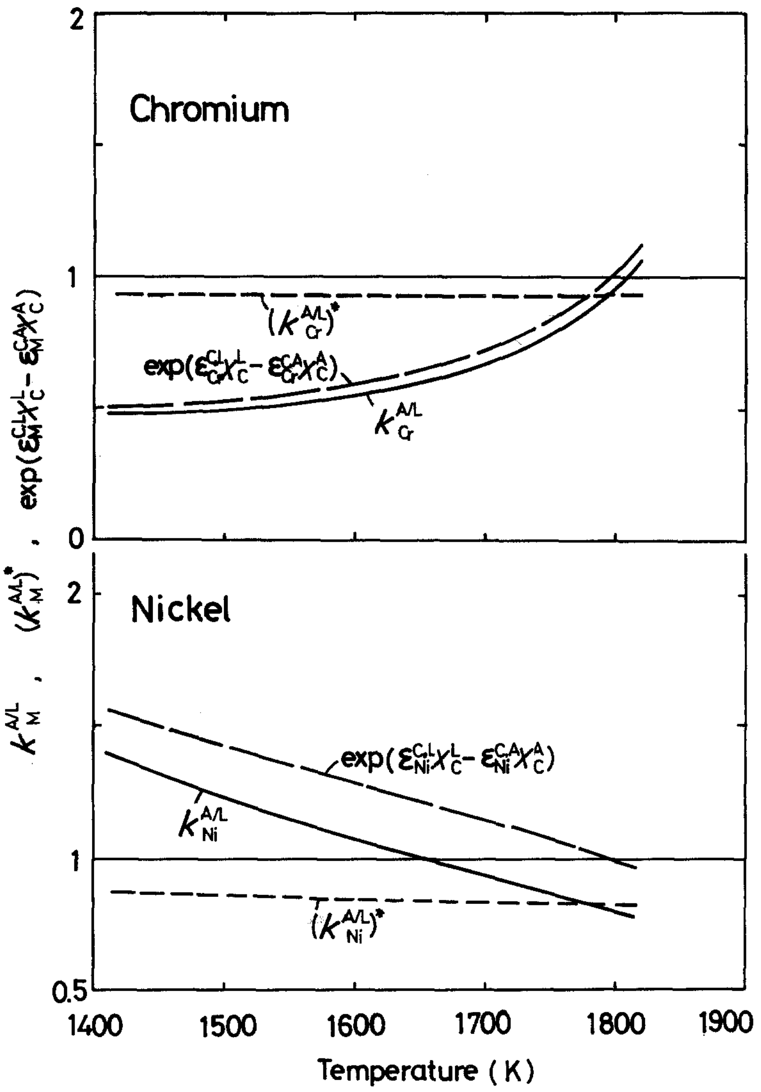

Figure 2 Factors influencing the equilibrium partition coefficient $k_M^{A/L}$.

the interaction between element M and carbon. To examine how the interaction term influences the equilibrium partition coefficient, $k_M^{A/L}$, the values of the two terms in Equation 10 for chromium and nickel are illustrated as a function of the liquidus temperature in Fig. 2. In this case, an increase in the liquidus temperature corresponds to a decrease in the carbon content. The result shows that the interaction term plays an important role in the temperature dependence of the equilibrium partition coefficient in the ternary system and that the term $(k_M^{A/L})^*$ varies little in the temperature range studied. It is assumed that the equilibrium partition coefficient $(k_M^{A/L})^*$ is independent of temperature. Because of limited information on the interaction coefficients for austenite, and for simplification of the calculation, the relation between the interaction coefficients of element M against carbon for liquid iron and for austenite was examined. Fig. 3 shows the relation between both interaction coefficients at 1473, 1573 and 1673 K from the literature [12, 14, 17, 27]. A linear relationship exists and is represented by the same equation after Morita and Tanaka [31], $\epsilon_C^{M,A} = 0.92\,\epsilon_C^{M,L}$, in the temperature range. From Wagner's equation $\epsilon_C^M \simeq \epsilon_M^C$, the relationship is given by $\epsilon_M^{C,A} = 0.92\,\epsilon_M^{C,L}$. The equilibrium partition coefficients for several elements were calculated using this relationship, as shown in Fig. 4, with some experimental data

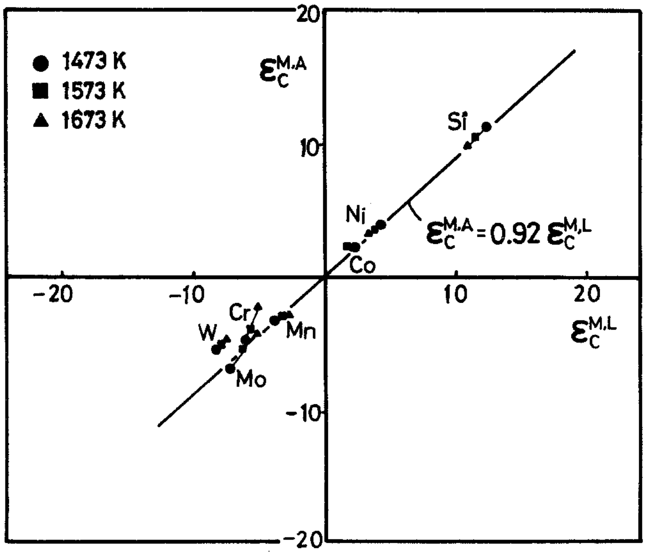

Figure 3 Relationship between the interaction coefficients $\epsilon_C^{M,A}$ and $\epsilon_C^{M,L}$.

from the literature. A good agreement between the calculated partition coefficients and experimental ones was observed even at the eutectic composition, showing that the simplified method is useful for the evaluation of the equilibrium partition coefficients at the eutectic temperature. The calculated values of $k_M^{A/L}$ at the eutectic temperature and those of K^S and K^M evaluated from Equations 1 and 2 are given in Table II with the values of $k_M^{C/A}$ at the eutectic temperature for some alloying elements given by Ko *et al.* [3].

3. Effect of alloying elements on the graphitization of iron–carbon base ternary alloys

The partitioning behaviour of alloying elements between cementite and austenite has been discussed in relation to the graphitization of cast

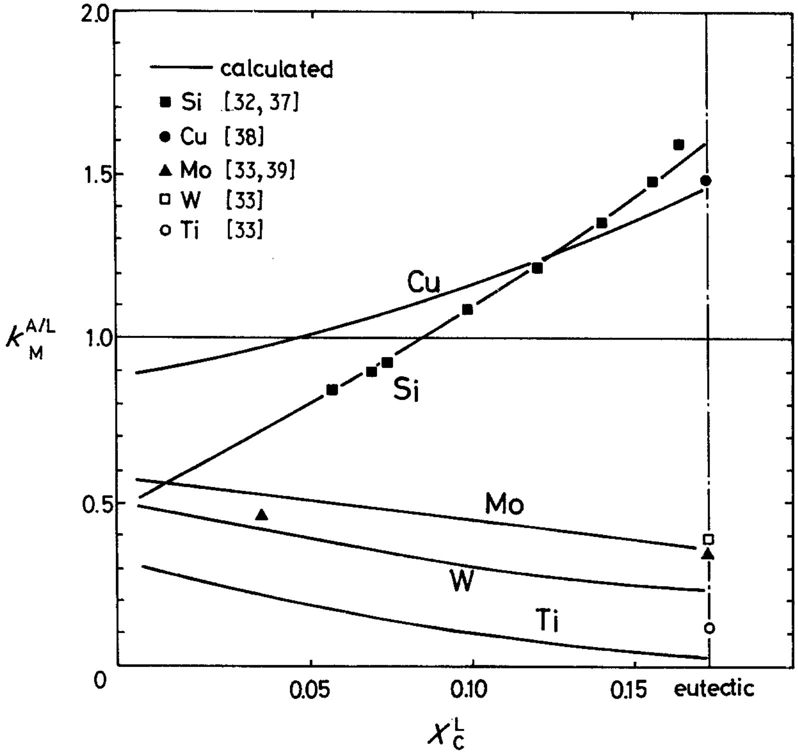

Figure 4 Equilibrium partition coefficient $k_M^{A/L}$ calculated by the simplified method.

TABLE II Equilibrium partition coefficients and factors influencing graphitization

M	$k_M^{A/L}$		$k_M^{C/A}$		K^S	K^M	ΔK $(= K^M - K^S)$	m^S $(K/\text{at}\,\%)$	m^M $(K/\text{at}\,\%)$	Δm $(= m^S - m^M)$	Effect on graphitization	Effect on activity on C
	cal.	obs.	cal.	obs.								
Si	1.59	1.6[1]	–	$\simeq 0$[2]	1.55	0.78	−0.77	10.73	−4.14	14.87	graphitizing (G)	increase (+)
Ni	1.36	1.5[3]	0.34	0.32[4]	1.33	0.90	−0.43	6.44	−1.88	8.32	G	+
Co	1.10	1.05[5]	0.58	0.54[4]	1.07	0.86	−0.21	1.37	−2.63	4.00	G	+
Cu	1.46	1.5[6]	–	0.09[5]	1.43	0.78	−0.65	8.39	−4.14	12.53	G	+
Al	–	1.07[5]	–	0.04[5]	1.05	0.55	−0.50	0.98	−8.46	9.44	G	+
Cr	0.49	0.51[7]	4.3	4[4]	0.48	1.32	0.84	−10.14	6.02	−16.16	carbide stabilizing (C)	decrease (−)
Mn	0.65	0.7[5]	1.7	1.6[5]	0.64	0.90	0.26	−7.02	−1.88	−5.14	C	−
Mo	0.38	0.35[5]	–	1.7[5]	0.37	0.52	0.15	−12.29	−9.02	−3.27	C	−
W	0.24	0.39[5]	–	1.9[5]	0.23	0.35	0.12	−15.02	−12.22	−2.80	C	−
Ti	0.04	–	–	2.42[5]	0.04	0.07	0.03	−18.72	−17.48	−1.24	C	−
N	1.90	1.9[8]	–	1.2[8]	1.86	2.09	0.23	16.77	20.49	−3.72	C	−
P	0.14	–	–	0.63[5]	0.14	0.11	−0.03	−16.77	−16.73	−0.04	C	+
S	0.06	–	–	–	0.06	–	–	–	–	–	–	+
B	0.06	–	–	4[9]	0.06	0.15	0.09	−18.33	−15.98	−2.35	C	+

[1] [37], [2] [1], [3] [31], [4] [3], [5] [33], [6] [38], [7] [2], [8] [36], [9] [40].

iron. Carbide stabilizing elements tend to concentrate more in cementite than in austenite, while graphitizing elements are enriched more in austenite than in cementite. From the viewpoint of free energy of the phases concerned, this appears to be valid. Graphitization of cast iron on eutectic solidification has also been debated in terms of the effect of alloying elements on the iron–carbon binary eutectic temperature [41–43] and on the carbon activity of liquid cast iron [44]. The former has more direct meaning in indicating which of the stable and metastable eutectics is preferably formed, while the meaning of the latter is indistinct. Since graphitization must be explained in terms of free energy of the phases concerned, the theoretical grounds for the points mentioned above will be deduced below.

The free energy of mixing for both austenite (A) and cementite (C) is given by:

$$\begin{aligned} G_{\mathrm{m}}^{\mathrm{A}} &= \Delta\mu_{\mathrm{Fe}}^{\mathrm{A}} X_{\mathrm{Fe}}^{\mathrm{A}} + \Delta\mu_{\mathrm{C}}^{\mathrm{A}} X_{\mathrm{C}}^{\mathrm{A}} + \Delta\mu_{\mathrm{M}}^{\mathrm{A}} X_{\mathrm{M}}^{\mathrm{A}} \\ &= RT(X_{\mathrm{Fe}}^{\mathrm{A}} \ln a_{\mathrm{Fe}}^{\mathrm{A}} + X_{\mathrm{C}}^{\mathrm{A}} \ln a_{\mathrm{C}}^{\mathrm{A}} + X_{\mathrm{M}}^{\mathrm{A}} \ln a_{\mathrm{M}}^{\mathrm{A}}) \end{aligned} \tag{11}$$

$$G_{\mathrm{m}}^{\mathrm{C}} = \Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}} Y_{\mathrm{Fe}}^{\mathrm{C}} + \Delta\mu_{\mathrm{M_3C}}^{\mathrm{C}} Y_{\mathrm{M}}^{\mathrm{C}} \tag{12}$$

where $\Delta\mu_{\mathrm{i}}$ is the partial molar free energy of mixing for the element i; $\Delta\mu_{\mathrm{Fe}}^{\mathrm{A}} = RT \ln a_{\mathrm{Fe}}^{\mathrm{A}}$, $\Delta\mu_{\mathrm{C}}^{\mathrm{A}} = RT \ln a_{\mathrm{C}}^{\mathrm{A}}$, and $\Delta\mu_{\mathrm{M}}^{\mathrm{A}} = RT \ln a_{\mathrm{M}}^{\mathrm{A}}$; X_{i} the molar fraction of the element i, a_{i} the activity of the element i, $\Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}}$ and $\Delta\mu_{\mathrm{M_3C}}^{\mathrm{C}}$ the free energy of formation of Fe_3C and M_3C, respectively, and $Y_{\mathrm{Fe}}^{\mathrm{C}}$ and $Y_{\mathrm{M}}^{\mathrm{C}}$ are given by the equations; $Y_{\mathrm{Fe}}^{\mathrm{C}} = X_{\mathrm{Fe}}^{\mathrm{C}}/(X_{\mathrm{Fe}}^{\mathrm{C}} + X_{\mathrm{M}}^{\mathrm{C}})$, $Y_{\mathrm{M}}^{\mathrm{C}} = X_{\mathrm{M}}^{\mathrm{C}}/(X_{\mathrm{Fe}}^{\mathrm{C}} + X_{\mathrm{M}}^{\mathrm{C}})$.

The free energy of mixing, G^{S} and G^{M}, of the eutectic liquids which equilibrate with austenite and graphite, and with cementite and austenite, respectively, are expressed as follows:

$$\begin{aligned} G^{\mathrm{S}} &= G_{\mathrm{m}}^{\mathrm{A}} n^{\mathrm{A}} + G_{\mathrm{m}}^{\mathrm{gr}}(1 - n^{\mathrm{A}}) \\ &= RTn^{\mathrm{A}}(X_{\mathrm{Fe}}^{\mathrm{A}} \ln a_{\mathrm{Fe}}^{\mathrm{A}} + X_{\mathrm{C}}^{\mathrm{A}} \ln a_{\mathrm{C}}^{\mathrm{A}} + X_{\mathrm{M}}^{\mathrm{A}} \ln a_{\mathrm{M}}^{\mathrm{A}}) \end{aligned} \tag{13}$$

$$\begin{aligned} G^{\mathrm{M}} &= G_{\mathrm{m}}^{\mathrm{A}} n^{\mathrm{A'}} + G_{\mathrm{m}}^{\mathrm{C}}(1 - n^{\mathrm{A'}}) \\ &= RTn^{\mathrm{A'}}(X_{\mathrm{Fe}}^{\mathrm{A}} \ln a_{\mathrm{Fe}}^{\mathrm{A}} + X_{\mathrm{C}}^{\mathrm{A}} \ln a_{\mathrm{C}}^{\mathrm{A}} + X_{\mathrm{M}}^{\mathrm{A}} \ln a_{\mathrm{M}}^{\mathrm{A}}) \\ &\quad + (1 - n^{\mathrm{A'}})(\Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}} Y_{\mathrm{Fe}}^{\mathrm{C}} + \Delta\mu_{\mathrm{M_3C}}^{\mathrm{C}} Y_{\mathrm{M}}^{\mathrm{C}}) \end{aligned} \tag{14}$$

where n^{A} and $n^{\mathrm{A'}}$ are the molar fractions of austenite in the graphitic and ledeburitic eutectics, respectively. Pure elements are taken as standard states, i.e. free energy of mixing for graphite, $G_{\mathrm{m}}^{\mathrm{gr}} = 0$, in Equation 13. From the condition for equilibrium between cementite and austenite,

$$\begin{aligned} \Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}} &= \tfrac{3}{4}\Delta\mu_{\mathrm{Fe}}^{\mathrm{A}} + \tfrac{1}{4}\Delta\mu_{\mathrm{C}}^{\mathrm{A}} \\ &= RT(\tfrac{3}{4} \ln a_{\mathrm{Fe}}^{\mathrm{A}} + \tfrac{1}{4} \ln a_{\mathrm{C}}^{\mathrm{A}}) \end{aligned} \tag{15}$$

and

$$\begin{aligned} \Delta\mu_{\mathrm{M_3C}}^{\mathrm{C}} &= \tfrac{3}{4}\Delta\mu_{\mathrm{M}}^{\mathrm{A}} + \tfrac{1}{4}\Delta\mu_{\mathrm{C}}^{\mathrm{A}} \\ &= RT(\tfrac{3}{4} \ln a_{\mathrm{M}}^{\mathrm{A}} + \tfrac{1}{4} \ln a_{\mathrm{C}}^{\mathrm{A}}) \end{aligned} \tag{16}$$

Substituting Equations 15 and 16 into Equation

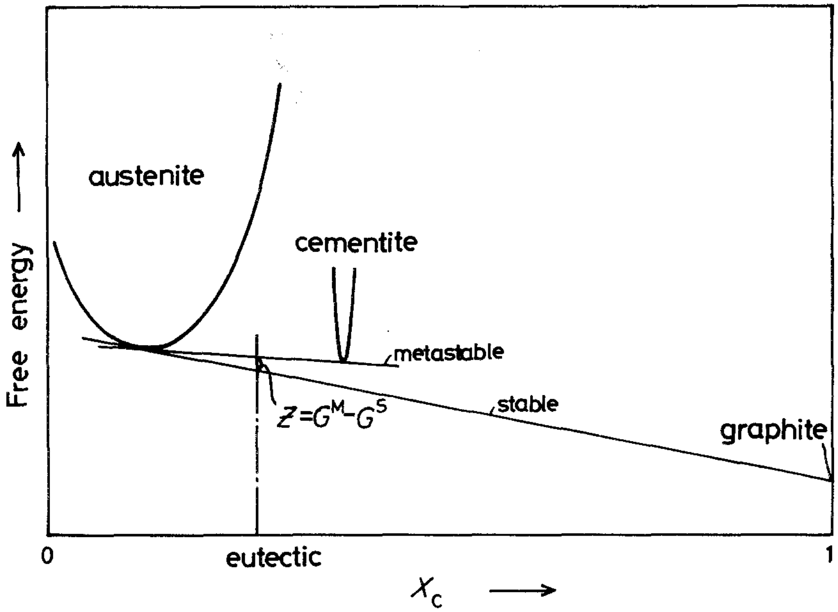

Figure 5 Schematic illustration of the free energy curves for the co-existing phases in the stable or metastable eutectic solidification in the equilibrium condition.

14, the free energy difference $Z(=G^{\mathrm{M}}-G^{\mathrm{S}})$, illustrated in Fig. 5, is obtained:

$$\begin{aligned} Z = {} & [(1-X^{\mathrm{A}}_{\mathrm{C}})(n^{\mathrm{A}'}-n^{\mathrm{A}})+\tfrac{3}{4}(1-n^{\mathrm{A}'})]\,RT\ln a^{\mathrm{A}}_{\mathrm{Fe}} \\ & +[X^{\mathrm{A}}_{\mathrm{C}}(n^{\mathrm{A}'}-n^{\mathrm{A}})+\tfrac{1}{4}(1-n^{\mathrm{A}'})]\,RT\ln a^{\mathrm{A}}_{\mathrm{C}} \\ & +[X^{\mathrm{A}}_{\mathrm{M}}(n^{\mathrm{A}'}-n^{\mathrm{A}})+(1-n^{\mathrm{A}'})\,X^{\mathrm{A}}_{\mathrm{M}}k^{\mathrm{C/A}}_{\mathrm{M}}] \\ & \times(RT\ln a^{\mathrm{A}}_{\mathrm{M}}-RT\ln a^{\mathrm{A}}_{\mathrm{Fe}}) \end{aligned} \tag{17}$$

For dilution of the element M, the third term in this equation, which represents a contribution of the element M to Z, ΔZ_{M}, becomes:

$$\begin{aligned} \Delta Z_{\mathrm{M}} = {} & [X^{\mathrm{A}}_{\mathrm{M}}(n^{\mathrm{A}'}-n^{\mathrm{A}})+(1-n^{\mathrm{A}'})\,X^{\mathrm{A}}_{\mathrm{M}}k^{\mathrm{C/A}}_{\mathrm{M}}] \\ & \times RT\ln(a^{\mathrm{A}}_{\mathrm{M}}/a^{\mathrm{A}}_{\mathrm{Fe}}) \end{aligned} \tag{18}$$

Employing the coefficients for partition between eutectic liquid and its solid for both the stable and metastable systems, P^{S} and P^{M}, respectively, which are defined as the ratio of molar fraction of the element M in eutectic solid to that in eutectic liquid, the following equations similar to Equations 1 and 2 are obtained.

$$P^{\mathrm{S}} = n^{\mathrm{A}}p^{\mathrm{A/L}}_{\mathrm{M}} \tag{19}$$

$$P^{\mathrm{M}} = [n^{\mathrm{A}'}+(1-n^{\mathrm{A}'})p^{\mathrm{C/A}}_{\mathrm{M}}]\,p^{\mathrm{A/L}}_{\mathrm{M}} \tag{20}$$

where $p^{\mathrm{A/L}}_{\mathrm{M}}$ and $p^{\mathrm{C/A}}_{\mathrm{M}}$ are the equilibrium partition coefficients represented in molar fraction. These partition coefficients are approximately equal to those represented in weight per cent for dilution of the element M; $p^{\mathrm{A/L}}_{\mathrm{M}} \simeq k^{\mathrm{A/L}}_{\mathrm{M}}$, $p^{\mathrm{C/A}}_{\mathrm{M}} \simeq k^{\mathrm{C/A}}_{\mathrm{M}}$ and since $n^{\mathrm{A}} \simeq g^{\mathrm{A}}$ and $n^{\mathrm{A}'} \simeq g^{\mathrm{A}'}$, $P^{\mathrm{S}} \simeq K^{\mathrm{S}}$ and $P^{\mathrm{M}} \simeq K^{\mathrm{M}}$. Hence, from Equations 19 and 20, Equation 18 is rewritten:

$$\begin{aligned} \Delta Z_{\mathrm{M}} & \simeq RT(K^{\mathrm{M}}-K^{\mathrm{S}})X^{\mathrm{L}}_{\mathrm{M}}\ln(a^{\mathrm{A}}_{\mathrm{M}}/a^{\mathrm{A}}_{\mathrm{Fe}}) \\ & = (K^{\mathrm{M}}-K^{\mathrm{S}})\beta \end{aligned} \tag{21}$$

where

$$\beta = RT\,X^{\mathrm{L}}_{\mathrm{M}}\ln(a^{\mathrm{A}}_{\mathrm{M}}/a^{\mathrm{A}}_{\mathrm{Fe}})$$

In Equation 21, $(a^{\mathrm{A}}_{\mathrm{M}}/a^{\mathrm{A}}_{\mathrm{Fe}}) \ll 1$ for dilution of the element M, and thus, $\beta < 0$, which means that the sign of ΔZ_{M} depends on the term $(K^{\mathrm{M}}-K^{\mathrm{S}})$. The values of ΔK $(=K^{\mathrm{M}}-K^{\mathrm{S}})$ are shown in Table II. A positive value of ΔK for an element corresponds to a negative value of ΔZ_{M}, resulting in a decrease in the free energy difference Z, which means that the element tends to stabilize the eutectic melt in equilibrium with austenite and cementite. On the other hand, the negative value of ΔK for an element causes an increase in the free energy difference Z and the element acts as a graphitizer.

From Equations 1 and 2, the value of ΔK is given as follows:

$$\Delta K = [(g^{\mathrm{A}'}-g^{\mathrm{A}})+(1-g^{\mathrm{A}'})\,k^{\mathrm{C/A}}_{\mathrm{M}}]\,k^{\mathrm{A/L}}_{\mathrm{M}} \tag{22}$$

The values of g^{A} and $g^{\mathrm{A}'}$ are approximately given from the equilibrium phase diagram.

From the iron–carbon phase diagram, $g^{\mathrm{A}'} \simeq 0.5$ and $g^{\mathrm{A}} \simeq 1$ and thus, Equation 22 becomes:

$$\Delta K \simeq 0.5\,k^{\mathrm{A/L}}_{\mathrm{M}}(k^{\mathrm{C/A}}_{\mathrm{M}}-1) \tag{23}$$

Since $k^{\mathrm{A/L}}_{\mathrm{M}} > 0$, a positive value of $(k^{\mathrm{C/A}}_{\mathrm{M}}-1)$, that is, $k^{\mathrm{C/A}}_{\mathrm{M}} > 1$, has the same meaning as a positive value of ΔK and vice versa.

According to Lupis [45], when an element is added to a binary eutectic, the derivative of the binary eutectic temperature with respect to the concentration of the element, m, is formulated as a function of the partition coefficient, K, of the element to be taken between eutectic liquid and its solid as follows:

$$m = -RT^2_{\mathrm{E}}(1-K)/H_{\mathrm{f}} \tag{24}$$

where R is the gas constant, T_{E} the eutectic temperature of the binary eutectic, and H_{f} the heat-of-fusion of the eutectic. Equation 24 is rewritten, using the values, $H^{\mathrm{S}}_{\mathrm{f}} = 8677\ \mathrm{J\,mol^{-1}}$ [46] and $T^{\mathrm{S}}_{\mathrm{E}} = 1426\ \mathrm{K}$ [47] for the stable system, and $H^{\mathrm{M}}_{\mathrm{f}} = 8936\ \mathrm{J\,mol^{-1}}$ [46] and $T^{\mathrm{M}}_{\mathrm{E}} = 1420\ \mathrm{K}$ [47] for the metastable system.

$$m^{\mathrm{S}} = -1949(1-K^{\mathrm{S}}) \quad \text{for the stable system} \tag{25}$$

$$m^{\mathrm{M}} = -1877(1-K^{\mathrm{M}}) \quad \text{for the metastable system} \tag{26}$$

The calculated values of m^{S} and m^{M} from Equations 25 and 26, using the equilibrium partition coefficients in Table II, are listed in the same table. A positive value of Δm $(=m^{\mathrm{S}}-m^{\mathrm{M}})$ for an element means that the element increases the difference between the stable and metastable eutectic temperatures and elements with negative values of Δm decrease it. From Equations 25 and 26, $\Delta m \propto \Delta K$. Thus, the effect of alloying elements on the difference of two eutectic temperatures of the iron–carbon binary system has the same meaning as that of the partition coefficient $k^{\mathrm{C/A}}_{\mathrm{M}}$ and the ΔK value from the view point of the thermodynamical stability of the phases concerned.

On eutectic solidification, the equilibrium partition coefficients $k_{\mathrm{M}}^{\mathrm{A/L}}$ and $k_{\mathrm{M}}^{\mathrm{C/A}}$ are expressed by the interaction in Equation 10 and by the following equation [3], respectively.

$$k_{\mathrm{M}}^{\mathrm{C/A}} = \exp\left(\frac{A_{\mathrm{M}}^{\mathrm{C/A}}}{RT} + \epsilon_{\mathrm{M}}^{\mathrm{C,A}} X_{\mathrm{C}}^{\mathrm{A}}\right) \qquad (27)$$

$$A_{\mathrm{M}}^{\mathrm{C/A}} = \Delta G_{\mathrm{M}}^{\mathrm{A-C}} + \Omega_{\mathrm{FeM}}^{\mathrm{A}} - \Omega_{\mathrm{FeM}}^{\mathrm{C}} \qquad (28)$$

where $\Delta G_{\mathrm{M}}^{\mathrm{A-C}}$ is the free energy difference between the free energy of formation for $\mathrm{Fe_3C}$ and that for $\mathrm{M_3C}$, $\Omega_{\mathrm{FeM}}^{\mathrm{A}}$ and $\Omega_{\mathrm{FeM}}^{\mathrm{C}}$ are the interaction energies between iron and the element M in austenite and in $\mathrm{(Fe,M)_3C}$, respectively. As already mentioned, the equilibrium partition coefficient, $k_{\mathrm{M}}^{\mathrm{A/L}}$, strongly depends on the interaction between carbon and the element M in liquid iron and in austenite. The equilibrium partition coefficient, $k_{\mathrm{M}}^{\mathrm{C/A}}$, given by Equation 27 is also considered to be influenced by the interaction between carbon and element M in austenite and in cementite, because the standard free energy of the reaction to transfer element M from cementite to austenite, denoted by $A_{\mathrm{M}}^{\mathrm{C/A}}$, is related to the interaction between carbon and element M through the first term $\Delta G_{\mathrm{M}}^{\mathrm{A-C}}$ in Equation 28. This term is expressed as:

$$\Delta G_{\mathrm{M}}^{\mathrm{A-C}} = \tfrac{4}{3}(\Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}} - \Delta\mu_{\mathrm{M_3C}}^{\mathrm{C}}) \qquad (29)$$

The free energy of formation for $\mathrm{Fe_3C}$ and $\mathrm{M_3C}$, $\Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}}$ and $\Delta\mu_{\mathrm{M_3C}}^{\mathrm{C}}$, arises from the interaction between carbon and iron and between carbon and element M, respectively. These values at 1423 K are given in the literature [48] for manganese and nickel as follows:

$$\Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}} = 4.1\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta\mu_{\mathrm{Mn_3C}}^{\mathrm{C}} = -12.1\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta\mu_{\mathrm{Ni_3C}}^{\mathrm{C}} = 23.8\ \mathrm{kJ\ mol^{-1}}$$

Thus, the $\Delta G_{\mathrm{M}}^{\mathrm{A-C}}$ value reflects the free energy of formation for $\mathrm{M_3C}$, that is, the interaction between carbon and element M, predominantly because of the small value of $\Delta\mu_{\mathrm{Fe_3C}}^{\mathrm{C}}$. The value of $(\Omega_{\mathrm{FeM}}^{\mathrm{A}} - \Omega_{\mathrm{FeM}}^{\mathrm{C}})$ may be small relative to $\Delta G_{\mathrm{M}}^{\mathrm{A-C}}$. Hence, a correlation between $A_{\mathrm{M}}^{\mathrm{C/A}}$ and the interaction coefficient $\epsilon_{\mathrm{C}}^{\mathrm{M,L}}$ is observed, as shown in Fig. 6. The relations between $k_{\mathrm{M}}^{\mathrm{A/L}}$ and $\epsilon_{\mathrm{C}}^{\mathrm{M,L}}$ and between $k_{\mathrm{M}}^{\mathrm{C/A}}$ and $\epsilon_{\mathrm{C}}^{\mathrm{M,L}}$ are shown in Fig. 7. From the relations in Fig. 7, the partition coefficient $k_{\mathrm{M}}^{\mathrm{A/L}}$ is shown to be inversely proportional to the partition coefficient $k_{\mathrm{M}}^{\mathrm{C/A}}$, although exceptions are included for some elements with small solubilities in the phases concerned, such as phosphorus, sulphur, boron and nitrogen. Therefore, it is concluded that the effect of alloying elements

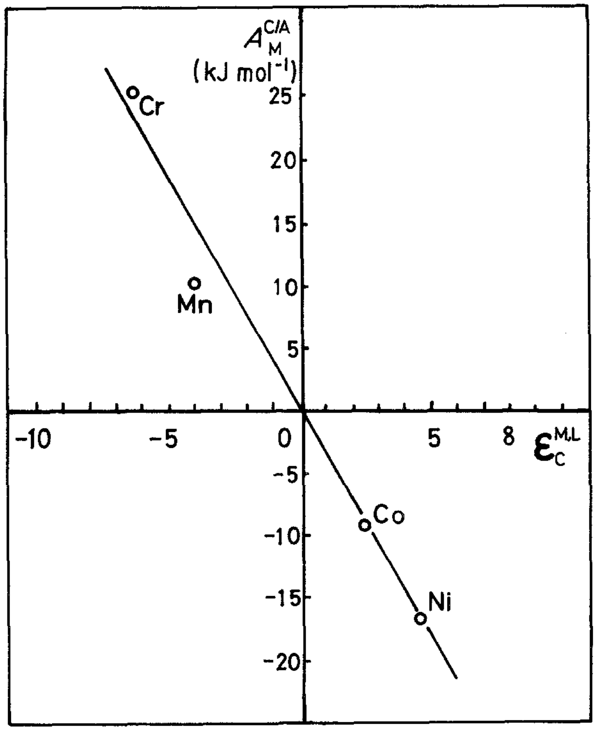

Figure 6 Relationship between the standard free energy of the reaction to transfer the element M from cementite to austenite, $A_{\mathrm{M}}^{\mathrm{C/A}}$ and the interaction coefficient $\epsilon_{\mathrm{C}}^{\mathrm{M,L}}$.

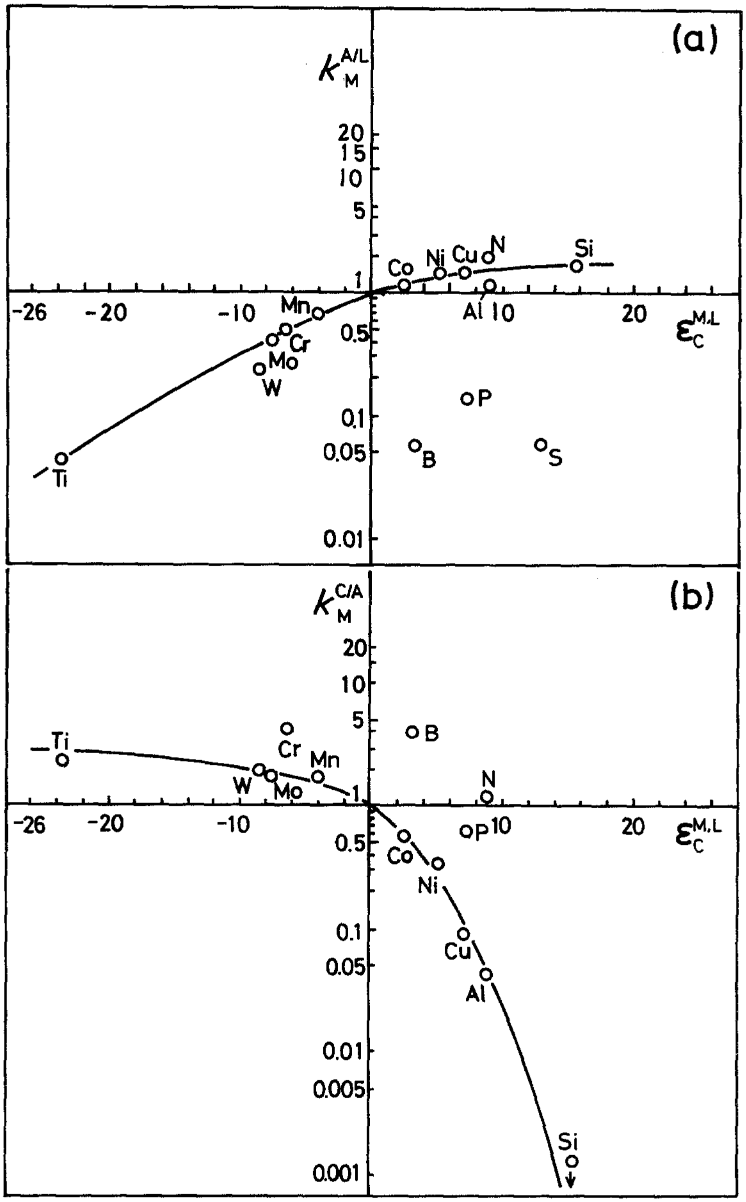

Figure 7 Changes in the equilibrium partition coefficients $k_M^{A/L}$ and $k_M^{C/A}$ with the interaction coefficient $\epsilon_C^{M,L}$.

on the carbon activity in liquid iron, as well as the equilibrium partition coefficient, $k_M^{C/A}$, and the values of ΔK and Δm, is one of the parameters indicating which mode of stable or metastable eutectic solidification preferentially occurs. Fig. 8 illustrates the relationship between the value of Δm and the graphitization ability for alloying elements in cast iron [49]. The graphitizing ability of alloying elements was measured by a chill test, given by the normalized addition of each element required for increasing or decreasing by a given chill depth. A linear relationship exists between those quantities, although some elements (silicon, aluminium and titanium) which have strong affinity for nitrogen, deviate significantly from the line. It is noted that strong graphitizing tendency of these elements might superpose, for example, the behaviour as a scavenger of nitrogen on the intrinsic nature of the elements.

4. Conclusion

In iron–carbon base ternary alloys, the validity of the thermodynamic evaluation of the equilibrium partition coefficient of the third element

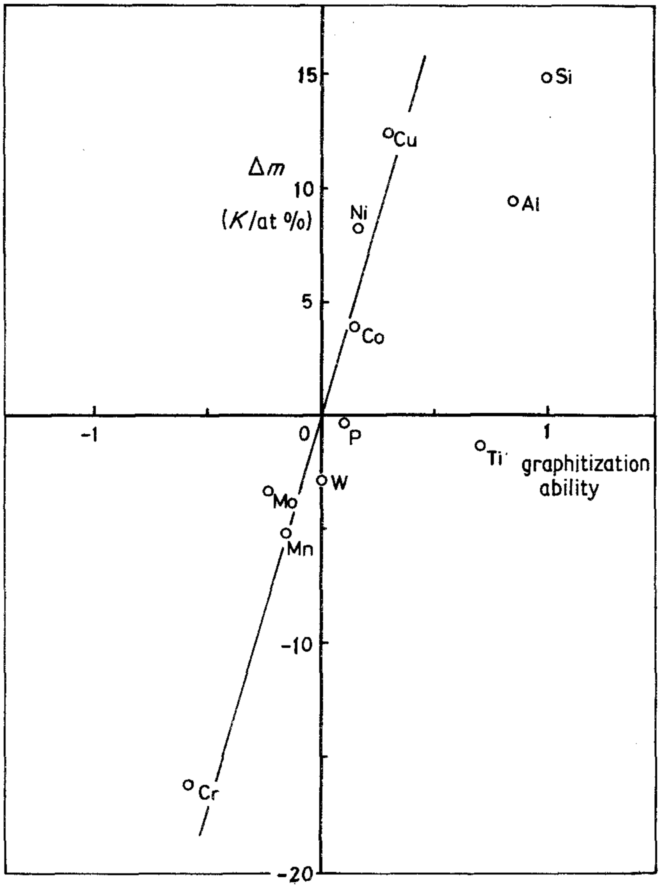

Figure 8 Relationship between graphitization ability and the quantity Δm.

between eutectic liquid and austenite, $k_M^{A/L}$, and between eutectic liquid and its solid, K^S and K^M, for the stable and metastable eutectic solidifications, respectively, was examined and compared with the experimental data given in the literature. From analysis of the parameters influencing $k_M^{A/L}$, it was indicated that the interaction between carbon and the third element had a predominant effect on $k_M^{A/L}$ and a simplified method for the evaluation of $k_M^{A/L}$ was introduced for those elements for which knowledge was lacking of thermochemical properties. It was concluded that the thermodynamic calculation was useful for the evaluation of those equilibrium partition coefficients. On the other hand, parameters influencing graphitization during eutectic solidification of iron–carbon base ternary alloys were deduced from the thermodynamic stability of the phases concerned. It was verified that the difference ΔK $(= K^S - K^M)$ in the equilibrium partition coefficients of an alloying element, the coefficient $k_M^{C/A}$ for equilibrium partition of the element between cementite and austenite, the effect of the element on the difference between the stable and metastable eutectic temperatures, and that on the carbon activity of liquid iron, relate to one another and have similar effects on graphitization during eutectic solidification. Comparing these parameters with the graphitizing tendency of alloying elements measured by a chill test of the elements, a fair agreement was observed except for the nitride-forming elements such as silicon, aluminium and titanium, which had larger graphitizing tendencies than expected.

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