

Effects of Solute-interaction on the Equilibrium Distribution of Solute between Solid and Liquid Phases in Iron Base Ternary System*

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Synopsis

In order to describe the effects of solute-interactions on the equilibrium distributions of solute elements between solid and liquid phases in iron base ternary system, Distribution Interaction Coefficient (DIC), k_i^j , was defined in this work. The coefficient k_i^j is shown as the ratio of the equilibrium distribution coefficient of solute i in Fe- i - j ternary system to that in Fe- i binary one and this is considered to be the parameter indicating the change of the equilibrium distribution coefficient of solute i with the addition of the alloying element j . The influences of solute-interaction on the equilibrium distributions of some solutes in Fe-C, Fe-N, Fe-H, Fe-P and Fe-S base ternary systems could be discussed by the use of the coefficient DIC.

I. Introduction

The equilibrium distribution coefficient of a solute in an iron alloy is known as an important factor in relation to the micro-segregation during the solidification of steels. The equilibrium distribution coefficients of some elements especially in multi-component systems are considered to be different from those in binary systems because of the possible existence of solute-interactions, but the mechanisms are so complicated that a detailed information has not yet been obtained. So, it would be very useful if the effect of an addition of an alloying element on the distribution could be known by the use of a simple parameter which indicates such effects. The purpose of this work is to derive an equation for the change of the equilibrium distribution coefficients with solute-interaction in iron base ternary system and to discuss the influences of the solute-interaction on the equilibrium distribution of some elements in Fe-C, Fe-N, Fe-H, Fe-P and Fe-S base ternary systems.

II. Derivation of an Equation Describing an Effect of Solute Interaction on the Equilibrium Distribution Coefficient

In this work, the equilibrium distribution coefficient is discussed thermodynamically in terms of activity coefficients, interaction parameters as described in the previous work.¹⁾ First of all, the equilibrium distribution coefficients of solute i in Fe- i binary and Fe- i - j ternary system, $k_o^{i,2}$ and $k_o^{i,3}$ are given by Eqs. (1) and (2), respectively.

$$\ln k_o^{i,2} = \frac{\mu_i^l - \mu_i^s}{RT} + \ln \frac{\gamma_i^l}{\gamma_i^s} + (\varepsilon_i^{j,l} - \varepsilon_i^{j,s} \cdot k_o^j) \cdot N_j^i \quad \dots\dots(1)$$

$$\ln k_o^{i,3} = \frac{\mu_i^l - \mu_i^s}{RT} + \ln \frac{\gamma_i^l}{\gamma_i^s} + (\varepsilon_i^{j,l} - \varepsilon_i^{j,s} \cdot k_o^j) \cdot N_j^i + (\varepsilon_i^{l,l} - \varepsilon_i^{l,s} \cdot k_o^l) \cdot N_j^l \quad \dots\dots\dots(2)$$

where, μ_i : the chemical potential of solute i in standard state

γ_i : the activity coefficient of solute i at the infinite dilution

ε_i^j : the self-interaction parameter of solute i

ε_i^j : the interaction parameter of j on i

superscripts l, s : liquid and solid states, respectively.

The fourth term in the right-hand side of Eq. (2) indicates the effect of alloying element j on the equilibrium distribution coefficient of solute i . As the parts from the first term to the third one in the right-hand side of Eq. (2) are equal to $\ln k_o^{i,2}$ of Eq. (1), the following equations (3) and (4) are derived.

$$\ln k_o^{i,3} = \ln k_o^{i,2} + (\varepsilon_i^{j,l} - \varepsilon_i^{j,s} \cdot k_o^j) \cdot N_j^i \quad \dots\dots\dots(3)$$

$$\ln \frac{k_o^{i,3}}{k_o^{i,2}} = (\varepsilon_i^{j,l} - \varepsilon_i^{j,s} \cdot k_o^j) \cdot N_j^i \quad \dots\dots\dots(4)$$

The left-hand side of Eq. (4) shows the ratio of the equilibrium distribution coefficient of solute i in Fe- i - j ternary system to that in Fe- i binary system and this ratio is considered as a parameter indicating the effect of the addition of the alloying element j on the equilibrium distribution coefficient of solute i . Then, the right-hand side of Eq. (4) is discussed furthermore.

In order to simplify the right-hand side of Eq. (4), the correlation between the interaction parameter of j on i , ε_i^j , in solid phase and that in liquid one is investigated. Figures 1(a) to (c) show the relations between $\varepsilon_i^{j,s}$ ^{2,8)} in solid phase and $\varepsilon_i^{j,l}$ ^{2,7,8)} in liquid one in Fe-C base (where, i : C), Fe-H base (where i : H) and Fe-N base (where, i : N) ternary systems, respectively. It is obvious from these figures that a linear relation holds approximately between $\varepsilon_i^{j,s}$ and $\varepsilon_i^{j,l}$ in each ternary system.

Mori *et al.*^{7,8)} proposed that in Fe-N, Fe-H base ternary systems, the gradients of these linear relations become unity as the temperature of liquid phase approaches that of solid one. They also suggested that these gradients are not strictly equal to unity because of the difference of the structure between solid and liquid phases. Then, these relations are discussed here thermodynamically.

Based on the zeroth approximation of the quasi-chemical model, the activity coefficient at the infinite dilution and ε_i^j are derived as follows⁹⁾:

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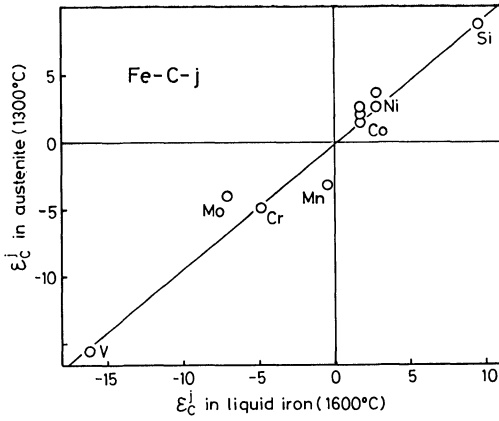


Fig. 1(a). Relation between interaction parameter in liquid iron and that in austenite in Fe-C-j ternary system.

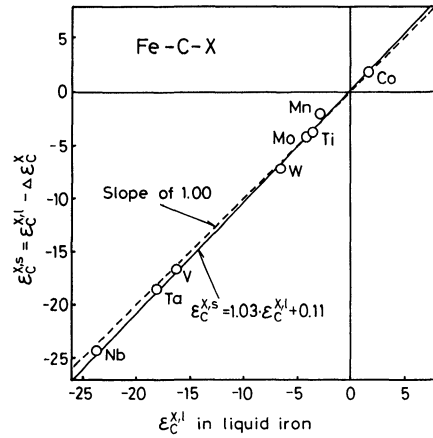


Fig. 2. Relation between interaction parameter in liquid iron and that in solid iron in Fe-C base ternary system.

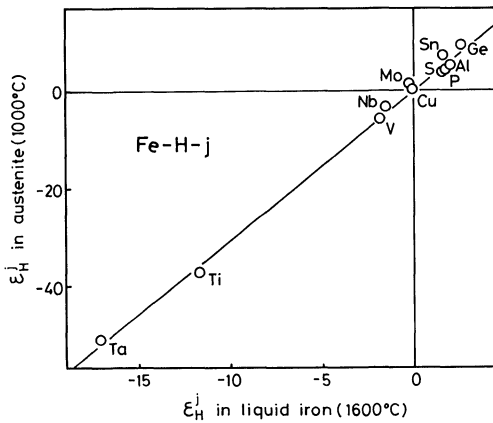


Fig. 1(b). Relation between interaction parameter in liquid iron and that in austenite in Fe-H-j ternary system.

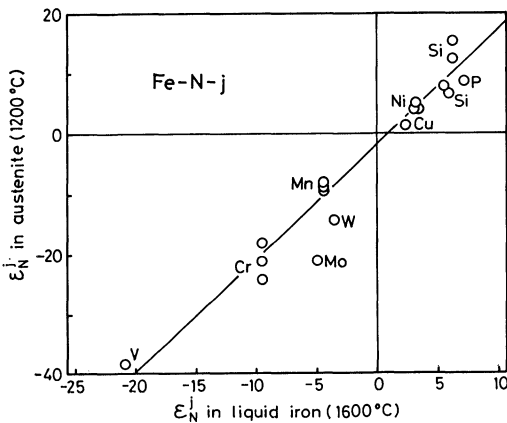


Fig. 1(c). Relation between interaction parameter in liquid iron and that in austenite in Fe-N-j ternary system.

$$(\ln k_o^i)_{Fe-i, Ni \rightarrow 0} = \frac{\mu_i^L - \mu_i^S}{RT} + \ln \frac{\gamma_i^L}{\gamma_i^S} \dots\dots\dots(7)$$

Combining these equations (5) to (7), the difference between the interaction parameter in liquid phase and that in solid one, $\Delta\epsilon$, is given by Eq. (8).¹⁰

$$\begin{aligned} \Delta\epsilon_i^j &= \epsilon_i^{j,L} - \epsilon_i^{j,S} \\ &= (\ln k_o^i)_{Fe-i, Ni \rightarrow 0} - (\ln k_o^i)_{j-i, Ni \rightarrow 0} \dots\dots\dots(8) \end{aligned}$$

As is obvious from Eq. (8), $\Delta\epsilon$ can be obtained from the difference between the equilibrium distribution coefficient of solute i in Fe- i binary system and that in j - i binary one. Then, the relation between $\epsilon_i^{j,L}$ in liquid phase and in solid one which is given by using $\Delta\epsilon$ in Eq. (8), i.e., $\epsilon_i^{j,S} = \epsilon_i^{j,L} - \Delta\epsilon_i^j$ in Fe-C base ternary systems is obtained as shown in Fig. 2. This figure indicates that a linear relation holds approximately between $\epsilon_i^{j,L}$ and $\epsilon_i^{j,S}$. Also, the gradient of this line obtained by the least square method is 1.03 and it is reasonable that the gradient of this line is approximately equal to unity. Thus, the relation of ϵ_i^j between solid and liquid phases is shown by Eq. (9).

$$\epsilon_i^{j,L} \doteq \epsilon_i^{j,S} \dots\dots\dots(9)$$

From Eqs. (4) and (9), the ratio of the equilibrium distribution coefficient of the solute i in Fe- i - j ternary system to that in Fe- i binary system is represented by the simple equation (10).

$$\ln k_i^j \equiv \ln \frac{k_o^{i,3}}{k_o^{i,2}} = (1 - k_o^j) \cdot \epsilon_i^{j,L} \cdot N_j^i \dots\dots\dots(10)$$

$k_i^j \equiv \frac{k_o^{i,3}}{k_o^{i,2}}$: Distribution Interaction Coefficient (DIC)

In Eq. (10), the ratio of $k_o^{i,3}$ to $k_o^{i,2}$, that is to say, the parameter indicating the change of the equilibrium distribution coefficient of solute i with the addition of the alloying element j , is defined as k_i^j , named Distribution Interaction Coefficient (DIC). Furthermore, the equilibrium distribution coefficient of solute i in Fe- i - j ternary system can be obtained from this

$$\ln \gamma_i^j (\text{in Fe}) = \frac{W_{Fe-i}}{RT} \dots\dots\dots(5)$$

$$\epsilon_i^j = \frac{W_{i-j} - W_{Fe-i}}{RT} \dots\dots\dots(6)$$

where, W : the interchange energy. Also, the equilibrium distribution coefficient of solute i at the infinite dilution is represented by¹⁾

coefficient k_i^l when that in Fe- i binary system is known.

III. Results and Discussion

1. Effects of Carbon on the Equilibrium Distribution of Various Alloying Elements between Solid and Liquid Phases in Fe-C Base Ternary Systems

Effects of solute-interaction on the equilibrium distribution coefficients in a few kinds of iron alloys are discussed in this section by using the foregoing coefficient DIC, k_i^l .

First, the change of the coefficient DIC of solute i with carbon concentration is discussed when the concentration of solute i is dilute in Fe-C- i ternary system. Then, the equilibrium distribution coefficient of solute i in Fe-C base ternary system is calculated from the DIC for the carbon concentration range up to the eutectic point on the equilibrium between austenite and liquid phases and also compared with the experimental results.

The change of the coefficient DIC of solute i with carbon concentration is given by

$$\ln k_i^c = \ln \frac{k_o^{i,3}}{k_o^{i,2}} = (1 - k_o^c) \cdot \epsilon_i^{c,i} \cdot N_c^l \dots \dots \dots (11)$$

Since the concentration of solute i is considered to be dilute in this work, the values of the equilibrium distribution coefficient of carbon in Fe-C binary system can be used as k_o^c in Eq. (11). Besides, the data of $\epsilon_i^{c,i}$, which is valid for the range up to high concentration and at any temperature, must be used, but nothing has been reported. Then, such values are obtained in the following way.

Using the interaction parameter ϵ_o^c at the infinite dilution reported by Sigworth and Elliott²⁾ and that at the carbon-saturated state obtained by Neumann and Schenck,¹¹⁾ and also assuming that ϵ_o^c is proportional to carbon concentration and the reciprocal of the absolute temperature, the value of ϵ_i^c at arbitrary carbon concentration and temperature can be obtained. In this case, as the interaction parameter reported at the carbon-saturated state is the interaction parameter at constant carbon activity ω_o^c , this parameter has to be converted into the interaction parameter at constant concentration, ϵ_o^c , which can be expanded at arbitrary concentration. When the concentration of solute i is dilute in Fe-C base ternary system, the equation for the conversion of the interaction parameter at constant activity to that at constant concentration is shown by Eq. (12).¹²⁾

$$\begin{aligned} (\epsilon_o^c)_{N_C=N_C^o, N_i=0} &= \left(\frac{\partial \ln \gamma_C}{\partial N_i} \right)_{N_C=N_C^o, N_i=0} \\ &= \left\{ 1 + \left(\frac{\partial \ln \gamma_C}{\partial N_C} \right)_{N_i=0, N_C=N_C^o} \cdot N_C^o \right\} \\ &\quad \cdot \left(\frac{\partial \ln \gamma_C}{\partial N_i} \right)_{a_C=a_C^o, N_i=0} \dots \dots \dots (12) \end{aligned}$$

In this equation, the left-hand side is the interaction parameter at constant concentration and the last term in the right-hand side is the interaction param-

eter at constant activity. The second term in the parentheses of the right-hand side corresponds to the self-interaction parameter of carbon and this term can be obtained from the change of the activity of carbon with its concentration in Fe-C binary system reported by Ban-ya *et al.*¹³⁾

Finally, ϵ_i^c obtained above has to be converted into ϵ_i^o . The equation for this conversion is given by Eq. (13).¹⁴⁾

$$(\epsilon_i^o)_{N_i} = (\epsilon_i^c)_{N_C} + (\epsilon_{Fe}^c)_{N_{Fe}} \dots \dots \dots (13)$$

In the infinite dilution, ϵ_i^o is equal to ϵ_o^c . However, the last term in the right-hand side of the equation is needed when this conversion is applied at the arbitrary concentration. The last term shows the change of the activity of Fe with carbon concentration and can be obtained from the data by Chipman.¹⁵⁾

Thus, the interaction parameters ϵ_i^o at any temperature and carbon concentration can be obtained. Figure 3 indicates the changes of ϵ_i^o of various elements i with the temperature and carbon concentration corresponding to the liquidus in Fe-C binary system.

Using Eq. (11) and ϵ_i^o obtained above, the change of the coefficient DIC of various elements with the temperature and carbon concentration corresponding to the liquidus in Fe-C binary system can be calcu-

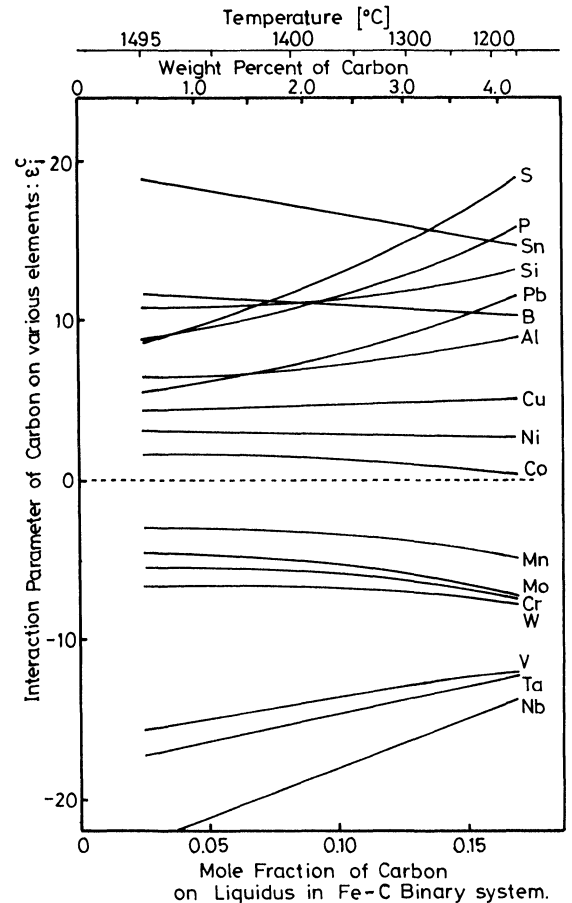


Fig. 3. Change of interaction parameter of various elements with carbon concentration in Fe-C base ternary system.

lated. The results are shown in Fig. 4. As illustrated in this figure, the coefficients DIC of Si, Al, Ni and so on having the repulsive effects against carbon increase with increasing carbon concentration. On the other hand, the DIC of Cr, V, and so on having the attractive effect against carbon decrease with increasing carbon concentration.

Moreover, the equilibrium distribution coefficients of various elements in Fe-C base ternary system are calculated from the coefficient DIC and the equilibrium distribution coefficient in iron base binary system, and the calculated results are compared with the measured values by various investigators,^{1,16-24} as

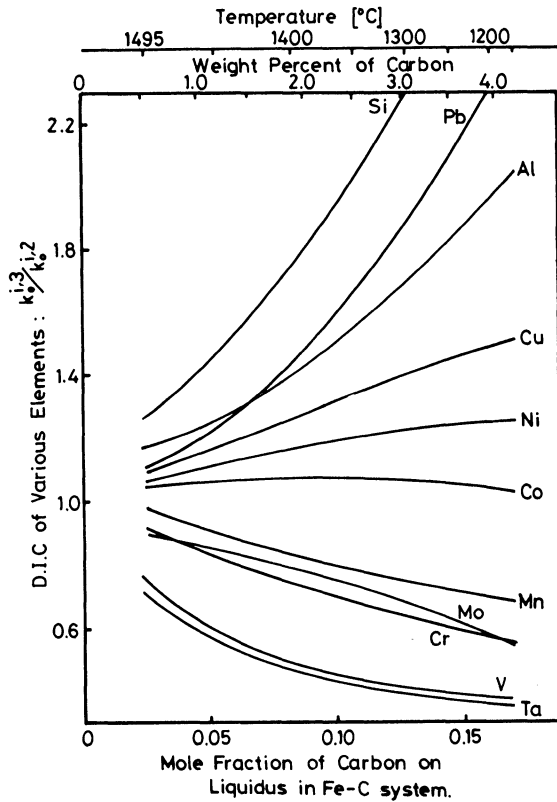


Fig. 4. Change of DIC of various elements with carbon concentration in Fe-C base ternary system.

shown in Fig. 5. Here, regarding the data of the equilibrium distribution coefficients of various elements in iron base binary system, the values in the report by Takahashi *et al.*²⁵ about the equilibrium distribution coefficient are assumed to be approximately equal to the values in binary system and then adopted. In Fig. 5, the solid and dashed lines denote the calculated and experimental results, respectively. This figure indicates that the calculated results obtained from the coefficient DIC are in good agreement with the experimental ones in each system.

Thus, the coefficient DIC defined in this work is considered to be useful as the parameter indicating the effects of solute-interaction on the equilibrium distribution coefficient.

2. Effects of Various Alloying Elements on the Equilibrium Distribution between Solid and Liquid Phases of Nitrogen and Hydrogen in Fe-N, H Base Ternary Systems

It is important to know the equilibrium distribution behaviours of gaseous elements in relation to various phenomena during solidification of steels, but little information has not been obtained so far concerning this problem. Then, the purpose of this section is to discuss the effects of various alloying elements on the equilibrium distributions between solid and liquid phases of nitrogen and hydrogen in iron base ternary system by using the foregoing DIC.

The variation of the DIC of nitrogen and hydrogen with the concentration of various alloying elements in Fe-i-X ternary stem (i: N or H) is represented by Eq. (14).

$$\ln k_i^X = \ln \frac{k_0^{i,3}}{k_0^{i,2}} = (1 - k_0^X) \cdot \epsilon_i^{X,i} \cdot N_X^i \dots\dots\dots(14)$$

Since the solubility of nitrogen and hydrogen in solid and liquid alloys is considerably small, the effects of these gaseous elements on the distribution of the alloying element X between solid and liquid phases can be neglected. Then, in this work, the value of k_0^X in Fe-X binary system was used as k_0^X in Fe-X-i ternary system in Eq. (14). Also the data of Sigworth and Elliott,²⁾ Ban-ya *et al.*^{26,27} and Morita *et al.*²⁸⁾

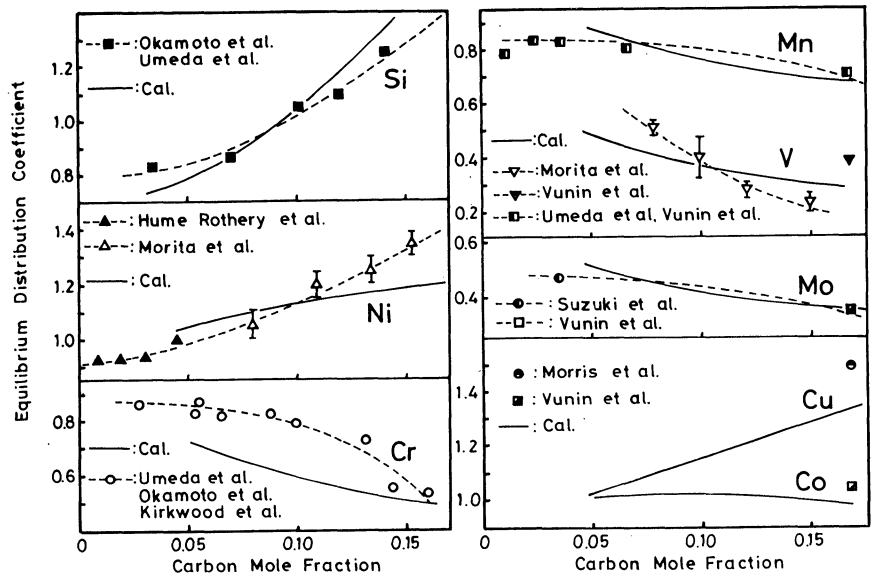


Fig. 5. Change of the equilibrium distribution coefficient of some elements with carbon concentration in Fe-C base ternary system.

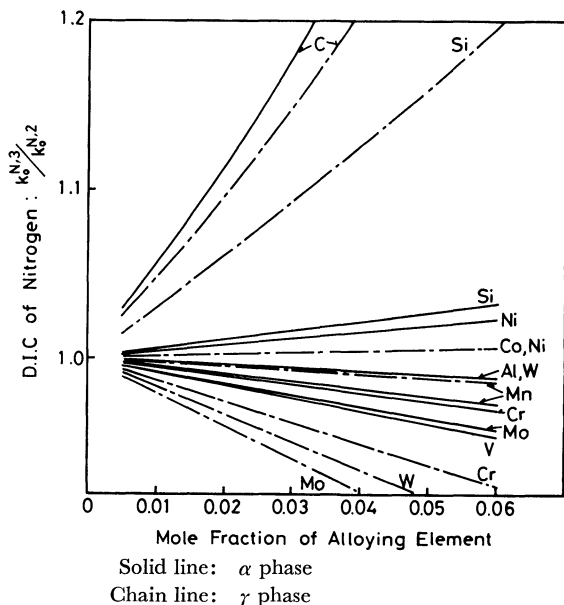


Fig. 6(a). Change of DIC of nitrogen with the concentration of alloying elements.

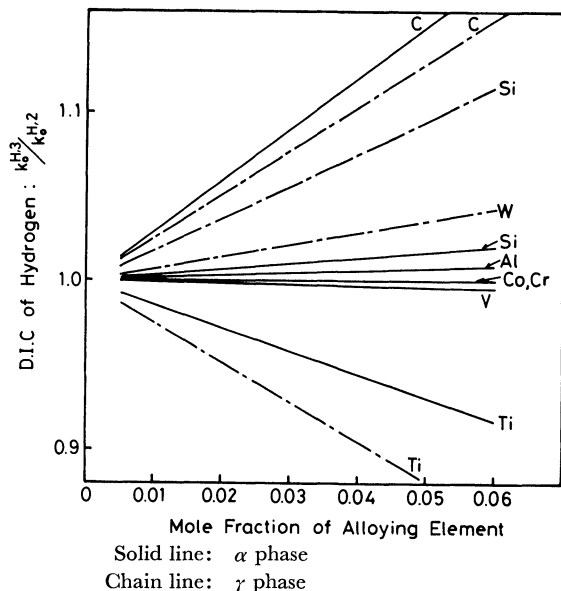


Fig. 6(b). Change of DIC of hydrogen with the concentration of alloying elements.

were used as ϵ_i^x . Figures 6(a) and (b) show the variations of the coefficient DIC of nitrogen and hydrogen with the concentrations of various alloying elements in Fe-N and Fe-H base ternary system, respectively. In these figures, solid lines are the calculated results when α phase is assumed to crystallize out of liquid solution and the values of k_0^x for α phase are used in Eq. (14). Similarly, chain lines show the calculated results when the primary crystals are presumed to be γ phase. It is obvious from these figures that C, Si and so on indicating the repulsive effects against N and H increase the DIC of these gaseous elements, and on the other hand Cr, Ti and so on showing the attractive effects against N and H decrease the DIC of these gaseous elements. When the equilibrium distribution coefficients of nitrogen and hydrogen are

calculated from the coefficient DIC, the values of the equilibrium distribution coefficient of these gaseous elements in iron base binary system can be obtained from the solubility curves of these elements in pure iron, as discussed in the previous work.¹⁾

3. Application of the Coefficient DIC to the Equilibrium Distribution of P and S between Solid and Liquid Phases in Iron Base Ternary System

Although the concentrations of P and S are dilute in steels generally, these elements are known to play an important role in relation to the micro-segregation. So, many studies have been carried out in order to make clear the mechanisms of their segregations and also to improve them. However, the influences of various alloying elements on the equilibrium distributions of P and S have not yet been known quite well. In this section, these kinds of effects are discussed by using the foregoing coefficient DIC when the concentrations of P and S are dilute in Fe- i -X (i : P or S) ternary system. The change of DIC of P and S with the concentration of the alloying elements in Fe- i -X ternary system (i : P or S) is given by Eq. (15).

$$\ln k_i^x = \ln \frac{k_0^{i,3}}{k_0^{i,2}} = (1 - k_0^x) \cdot \epsilon_i^{x,i} \cdot N_x^i \dots\dots\dots(15)$$

As the concentrations of P and S are considered to be dilute in this work, the equilibrium distribution coefficient of the alloying element in iron base binary system can be used as k_0^x in Eq. (15), as described in the last section. Also, the data of Sigworth and Elliott²⁾ and Ban-ya *et al.*²⁹⁾ were adopted as $\epsilon_i^{x,i}$. The changes of the coefficients DIC of P and S with various alloying elements are shown in Figs. 7(a) and (b) in Fe-P and Fe-S base ternary system, respectively. In these figures, solid lines and chain ones indicate the calculated results for α phase and γ one, respectively. As can be seen from these figures, the elements denoting the repulsive effects against P and S, *e.g.*, C, Si, and so on, increase the DIC of P and S, while the elements indicating the attractive effects against P and S, *e.g.*, Cr, V, and so on, decrease those of P and S.

Thus, it is obvious that effects of solute-interaction on the equilibrium distributions of N, H, P and S, which are intimately concerned with the micro-segregation of steels, can be discussed by using the coefficient DIC.

IV. Summary

In order to describe the effects of solute-interaction on the equilibrium distribution of solute elements between solid and liquid phases in iron base ternary system, the coefficient DIC, k_i^j , which is defined as the ratio of the equilibrium distribution coefficient of solute i in Fe- i - j ternary system to that in Fe- i binary one, was derived. This coefficient DIC is considered to be the parameter indicating the change of the equilibrium distribution coefficient of solute i with the addition of j .

The effects of solute-interaction on the equilibrium

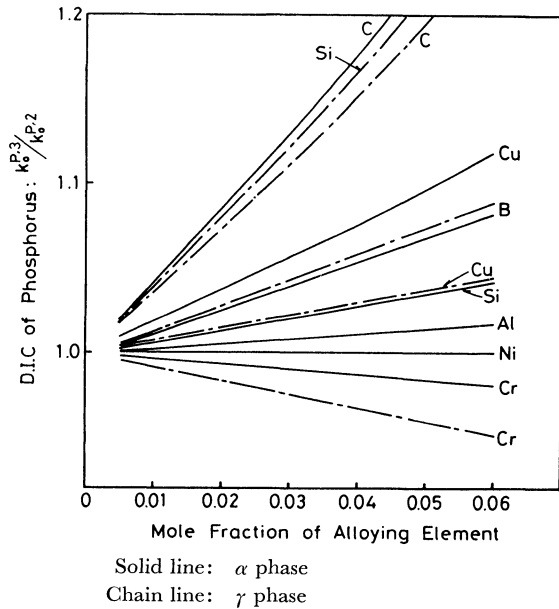


Fig. 7(a). Change of DIC of phosphorus with the concentration of alloying elements.

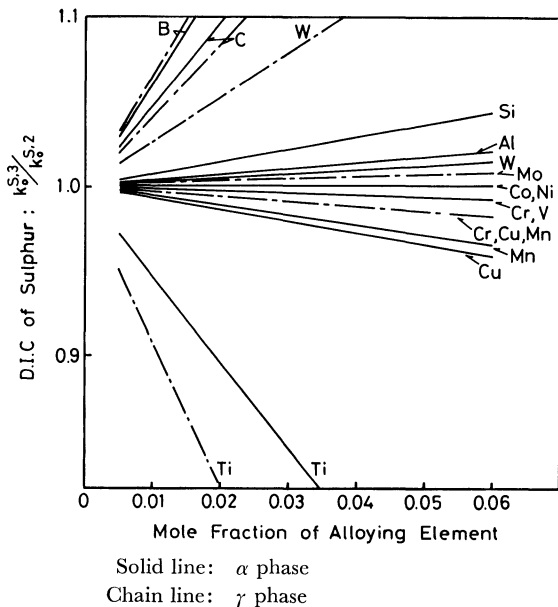


Fig. 7(b). Change of DIC of sulphur with the concentration of alloying elements.

distribution coefficient in Fe-C, Fe-N, Fe-H, Fe-P and Fe-S base ternary systems could be estimated by the use of the DIC. Consequently, the coefficient DIC of Si, Al, Ni and so on having the repulsive effects against carbon in iron alloys increase with increasing carbon concentration. On the other hand, the DIC of Cr, V, and so on having the attractive effect against carbon in the alloys decrease with increasing carbon concentration. Also, the elements denoting the repulsive effects against N, H, P and S in iron alloys, e.g., C, Si, and so on, increase the DIC of N, H, P

and S, while the elements indicating the attractive effects against N, H, P and S in the alloys, e.g. Cr, V, and so on, decrease those of N, H, P and S.

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