JOURNAL OF MATERIALS SCIENCE 17 (1982) 135–144

Partition of solute elements during solidification of iron–carbon–chromium alloys

AKIO KAGAWA, SHIGEO MORIYAMA,* TAIRA OKAMOTO
Institute of Scientific and Industrial Research of Osaka University, Yamadaoka, Suita, Osaka 565, Japan

The partition coefficients of chromium between austenite and liquid iron, $k_{Cr}^{A/L}$, were determined from the experiment of rapid cooling of iron-carbon hypo-eutectic alloys containing a small amount of chromium from coexisting solid–liquid states; the partition coefficients between eutectic and its liquid, $k_{0,Cr}$, and $k'_{0,Cr}$, for the stable and metastable eutectic solidifications were obtained from the zone-melting experiment of iron–carbon eutectic alloys containing a small amount of chromium. Chromium was rejected to liquid iron on the crystallization of primary austenite, $k_{Cr}^{A/L} < 1$. On the eutectic solidification, chromium was enriched in eutectic liquid for the stable system, $k_{0,Cr} < 1$, and was conversely diluted in the liquid for the metastable system, $k'_{0,Cr} > 1$. The relationship between effective and equilibrium partition coefficients given by Burton *et al.* was observed for the results of the zone melting experiment and, from the relationship, the thickness of boundary layer in the liquid ahead of the solid–liquid interface was found to be 0.17 mm for the stable system and 0.11 mm for the metastable system. Thermodynamic calculation of the partition coefficients of chromium and carbon proved to represent the observed partition coefficients well.

1. Introduction

Since the binary system iron–chromium shows a γ-loop, in contrast to the expanded γ-field of the binary system iron–carbon, the austenite liquidus in the ternary system iron–carbon–chromium can be shifted to lower carbon concentration with an increase in chromium concentration. The equilibrium partition coefficient for carbon, as found between a primary γ-phase and liquid for the iron-rich ternary alloy, will be decreased by increasing chromium content. As the carbon content of the alloy is raised, the crystallization of primary austenite is followed by eutectic solidification. In this case, chromium is partitioned at first, between primary austenite and liquid and then between eutectic and liquid.

Rickinson and Kirkwood [1], and Umeda *et al.* [2] have measured the equilibrium partition coefficients for carbon and chromium between the primary phase and liquid for iron–carbon–chromium alloys with less than 2 wt% C and less than 20 wt% Cr, and with less than 1.7 wt% C and less than 2.9 wt% Cr, respectively. The values of the equilibrium partition coefficient for carbon as obtained by them are considerably higher than the values expected from the phase diagram of the iron–carbon–chromium system [3].

Two of the present authors examined the partition of silicon between eutectic and liquid for iron–carbon eutectic alloy with a small amount of silicon and found that the equilibrium partition coefficients for silicon as measured from the stable eutectic solidification and from the metastable eutectic solidification were in good agreement with the values obtained from thermodynamic calculations [4]. The equilibrium partition coefficient for chromium remains unknown in high-carbon iron–carbon–chromium alloys that belong to the family of cast irons.

In the present work, the equilibrium partition

---

*Present address: Toyota Central Research and Development Laboratories Inc., Nagakute-cho, Aichi-gun, Aichi-ken 480-11, Japan.

0022–2461/82/010135–10$03.00/0

coefficients of carbon and chromium between austenite and liquid and of chromium between eutectic and liquid were measured experimentally for iron–carbon–chromium ternary alloys. From the results of the calculation, based on thermodynamic data, the solidus composition in the Fe–C–Cr system was evaluated and the validity of the calculation was discussed.

2. Thermodynamic calculation of equilibrium partition coefficients for solute elements

When austenite is in equilibrium with liquid iron at a temperature within the solidification temperature range of a hypo-eutectic iron–carbon-base alloy containing a small amount of a third element, the following equations are written for carbon and the third element, M, in the two phases

$$\frac{\gamma_C^A X_C^A}{\gamma_C^L X_C^L} = \exp\left(\frac{\dot{\mu}_C^L - \dot{\mu}_C^A}{RT}\right) = W_C^{A\to L} \tag{1}$$

and

$$\frac{\gamma_M^A X_M^A}{\gamma_M^L X_M^L} = \exp\left(\frac{\dot{\mu}_M^L - \dot{\mu}_M^A}{RT}\right) = W_M^{A\to L}, \tag{2}$$

where γ_C and γ_M are the activity coefficients for carbon and the third element, respectively, X_C and X_M are the mole fractions of carbon and the third element, respectively, in the phase concerned, $\dot{\mu}_C$ and $\dot{\mu}_M$ are the chemical potential of carbon and the third element, respectively, in a standard state, R is the gas constant and T is the temperature at which the two phases are in equilibrium. The superscripts A and L denote austenite and liquid iron, respectively. The ratio of the solute concentration in mole fraction in austenite to that in liquid iron is converted as follows: for carbon

$$\frac{X_C^A}{X_C^L} = Fk_C^{A/L}, \tag{3}$$

and for the third element, M,

$$\frac{X_M^A}{X_M^L} = Fk_M^{A/L}, \tag{4}$$

where

$$F = \frac{(\text{wt\% Fe})^L/m_{Fe} + (\text{wt\% C})^L/M_C + (\text{wt\%}M)^L/m_M}{(\text{wt\% Fe})^A/m_{Fe} + (\text{wt\% C})^A/M_C + (\text{wt\%}M)^A/m_M}, \tag{5}$$

where symbols, (wt%i) and m_i, denote, respectively, the concentration and the atomic weight of the element, i, and $k_C^{A/L}$ and $k_M^{A/L}$ are the equilibrium partition coefficients for carbon and for the third element, M, respectively, defined as follows:

$$k_C^{A/L} = (\text{wt\% C})^A/(\text{wt\% C})^L, \tag{6}$$

and

$$k_M^{A/L} = (\text{wt\%}M)^A/(\text{wt\%}M)^L. \tag{7}$$

For the activity coefficients for carbon in Equation 1, the following equations were adopted: from [5]

$$\ln \gamma_C^A = \frac{8680}{T} - 24.24 + 2.72 \ln T + \left(0.99 + \frac{8980}{T}\right)\frac{X_C^A}{X_{Fe}^A} - \ln X_{Fe}^A \tag{8}$$

and from [6]

$$\ln \gamma_C^L = \frac{2720}{T} - 2.00 + \left(1.66 + \frac{7830}{T}\right) \times \frac{X_C^L}{X_{Fe}^L} - \ln(X_{Fe}^L - X_C^L). \tag{9}$$

For the Fe–C–M ternary system, these equations were rewritten as

$$\ln \gamma_C^A = \frac{8680}{T} - 24.24 + 2.72 \ln T + \left(0.99 + \frac{8980}{T}\right)\frac{X_C^A}{1 - X_C^A} - \ln(1 - X_C^A) + \epsilon_C^{M,A} X_M^A \tag{10}$$

and

$$\ln \gamma_C^L = \frac{2720}{T} - 2.00 + \left(1.66 + \frac{7830}{T}\right)\frac{X_C^L}{1 - X_C^L} - \ln(1 - 2X_C^L) + \epsilon_C^{M,L} X_M^L. \tag{11}$$

The activity coefficients for M in Equation 2 are expressed in terms of interaction parameters

$$\ln \gamma_M^A = \ln \dot{\gamma}_M^A + \epsilon_M^{C,A} X_C^A + \epsilon_M^{M,A} X_M^A \tag{12}$$

and

$$\ln \gamma_M^L = \ln \dot{\gamma}_M^L + \epsilon_M^{C,L} X_C^L + \epsilon_M^{M,L} X_M^L. \tag{13}$$

From Equations 3 to 13, Equations 1 and 2 can be rewritten. For carbon

$$Fk_C^{A/L} = \left(\frac{1 - X_C^A}{1 - 2X_C^L}\right) \exp\left\{22.24 - \frac{5960}{T} - 2.72 \ln T + \left(1.66 + \frac{7830}{T}\right)\right.$$

$$\times \frac{X_{\mathrm{C}}^{\mathrm{L}}}{1-X_{\mathrm{C}}^{\mathrm{L}}} - \left(0.99 + \frac{8980}{T}\right)\frac{X_{\mathrm{C}}^{\mathrm{A}}}{1-X_{\mathrm{C}}^{\mathrm{A}}}$$

$$\left. + \epsilon_{\mathrm{C}}^{M,\mathrm{L}} X_M^{\mathrm{L}} - \epsilon_{\mathrm{C}}^{M,\mathrm{A}} X_M^{\mathrm{A}} \right\} \qquad (14)$$

For M

$$k_M^{\mathrm{A/L}} \exp\left(F\epsilon_M^{M,\mathrm{A}} X_M^{\mathrm{L}} k_M^{\mathrm{A/L}}\right) = \frac{W_M^{\mathrm{A}\to\mathrm{L}}}{F}\left(\frac{\dot{\gamma}_M^{\mathrm{L}}}{\dot{\gamma}_M^{\mathrm{A}}}\right)$$

$$\exp\left\{\epsilon_M^{M,\mathrm{L}} X_M^{\mathrm{L}} + \left(\epsilon_M^{\mathrm{C,L}} - F\epsilon_M^{\mathrm{C,A}} k_{\mathrm{C}}^{\mathrm{A/L}}\right) X_{\mathrm{C}}^{\mathrm{L}}\right\}. \qquad (15)$$

Since graphite is taken for the standard state in Equations 8 and 9, $\dot{\mu}_{\mathrm{C}}^{\mathrm{L}} = \dot{\mu}_{\mathrm{C}}^{\mathrm{A}}$, i.e., $W_{\mathrm{C}}^{\mathrm{A}\to\mathrm{L}} = 1$ in Equation 1. In the case of chromium as the third element the value of $W_M^{\mathrm{A}\to\mathrm{L}}$ in Equation 15 can be calculated from the following:

$$\mathrm{W}\; W_{\mathrm{Cr}}^{\mathrm{A}\to\mathrm{L}} = \exp\left(\frac{\dot{\mu}_{\mathrm{Cr}}^{\mathrm{L}} - \dot{\mu}_{\mathrm{Cr}}^{\mathrm{A}}}{RT}\right)$$

$$= \exp\left\{\left(\frac{\dot{\mu}_{\mathrm{Cr}}^{\mathrm{L}} - \dot{\mu}_{\mathrm{Cr}}^{\mathrm{F}}}{RT}\right) + \left(\frac{\dot{\mu}_{\mathrm{Cr}}^{\mathrm{F}} - \dot{\mu}_{\mathrm{Cr}}^{\mathrm{A}}}{RT}\right)\right\}$$

$$= \exp\left(\frac{\dot{\mu}_{\mathrm{Cr}}^{\mathrm{F}} - \dot{\mu}_{\mathrm{Cr}}^{\mathrm{A}}}{RT}\right)$$

$$\times \exp\left\{\frac{\Delta H_{\mathrm{f,Cr}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{F,Cr}}}\right) + \frac{1}{RT}\left(\int_{T_{\mathrm{f,Cr}}}^{T} \Delta C_{\mathrm{p}}\,\mathrm{d}T - T\int_{T_{\mathrm{f,Cr}}}^{T} \frac{\Delta C_{\mathrm{p}}}{T}\,\mathrm{d}T\right)\right\}$$

$$\simeq \exp\left(\frac{\dot{\mu}_{\mathrm{Cr}}^{\mathrm{F}} - \dot{\mu}_{\mathrm{Cr}}^{\mathrm{A}}}{RT}\right)$$

$$\times \exp\left\{\frac{\Delta H_{\mathrm{f,Cr}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{f,Cr}}}\right)\right\}, \qquad (16)$$

where

$$\Delta C_{\mathrm{p}} = C_{\mathrm{p}}^{\mathrm{L}} - C_{\mathrm{p}}^{\mathrm{F}}, \qquad (17)$$

where $\Delta H_{\mathrm{f,Cr}}$ is the heat-of-fusion of chromium, $T_{\mathrm{f,Cr}}$ is the melting point of chromium, and the superscript F indicates ferrite. The value of $(\dot{\mu}_{\mathrm{Cr}}^{\mathrm{F}} - \dot{\mu}_{\mathrm{Cr}}^{\mathrm{A}})$ in Equation 16 is given by $-(2500 + 0.15T)$ [7]. Substituting values, $\Delta H_{\mathrm{f,Cr}} = 5000$ cal mol^{-1} and $T_{\mathrm{f,Cr}} = 2130$ K, given by Kubaschewski *et al.* [8], for thermochemical properties in Equation 16 gives

$$W_{\mathrm{Cr}}^{\mathrm{A}\to\mathrm{L}} \simeq \exp(11.73 + 160/T$$

$$+ 0.00059T - 1.79 \ln T). \qquad (18)$$

The equilibrium partition coefficient of a solute element, M, in the Fe–M binary system, $(k_M^{\mathrm{A/L}})'$, is related to the value of $W_M^{\mathrm{A}\to\mathrm{L}}$ through a similar equation to Equation 2,

$$\frac{\dot{\gamma}_M^{\mathrm{A}}}{\dot{\gamma}_M^{\mathrm{L}}}\left(k_M^{\mathrm{A/L}}\right)' = W_M^{\mathrm{A}\to\mathrm{L}}. \qquad (19)$$

The activity coefficient at infinite dilution, $\dot{\gamma}_M^{\mathrm{L}}/\dot{\gamma}_M^{\mathrm{A}}$, is evaluated from Equation 19 using the equilibrium partition coefficient $k_{\mathrm{Cr}}^{\mathrm{A/L}}$ for the Fe–Cr binary system, $(k_{\mathrm{Cr}}^{\mathrm{A/L}})' = 0.85$ [9]. Although the value of $(k_{\mathrm{Cr}}^{\mathrm{A/L}})'$ was determined for high temperatures, it was assumed to vary little in the temperature range consulted in the present work. The values of $\dot{\gamma}_M^{\mathrm{L}}/\dot{\gamma}_M^{\mathrm{A}}$ for chromium is given by

$$\dot{\gamma}_{\mathrm{Cr}}^{\mathrm{L}}/\dot{\gamma}_{\mathrm{Cr}}^{\mathrm{A}} = \exp(1.79 \ln T - 11.59$$

$$- 160/T - 0.00059T). \qquad (20)$$

The interaction parameters ϵ_i^j adopted for the calculation of $k_{\mathrm{Cr}}^{\mathrm{A/L}}$ for the ternary system in Equation 15 were, from [10],

from [11],

$$\epsilon_{\mathrm{Cr}}^{\mathrm{C,L}} = 2.58 - 12670/T, \qquad (21)$$

$$\epsilon_{\mathrm{Cr}}^{\mathrm{C,A}} = 22.58 - 38750/T, \qquad (22)$$

and from [12]

and

$$\epsilon_{\mathrm{Cr}}^{\mathrm{Cr,L}} = 2.52 - 5000/T \qquad (23)$$

$$\epsilon_{\mathrm{Cr}}^{\mathrm{Cr,A}} = 1.51 - 1780/T. \qquad (24)$$

The equilibrium partition coefficients of chromium and carbon for the iron–carbon–chromium ternary system were determined by solving simultaneous equations of Equations 14 and 15. The theoretical dependence of the partition coefficients for chromium and carbon on temperature and on chromium content are shown in Fig. 1. For this, the liquidus composition, $(\mathrm{wt\%\,C})^{\mathrm{L}}$ and $(\mathrm{wt\%\,Cr})^{\mathrm{L}}$ for the iron–carbon–chromium ternary system at a temperature, T, was expressed as follows:

$$(\mathrm{wt\%\,C})^{\mathrm{L}} + \alpha(\mathrm{wt\%\,Cr})^{\mathrm{L}} = (\mathrm{wt\%\,C})^{\mathrm{L}'}, \qquad (25)$$

where [3]

$$\alpha = 0.07 - 3.30 \times 10^{-5}\,T \qquad (26)$$

and where $(\mathrm{wt\%\,C})^{\mathrm{L}'}$ is the carbon concentration of liquidus for the iron–carbon binary system. The results indicate that the equilibrium partition coefficients of chromium and carbon are smaller than unity, the former increasing and the latter decreasing with elevating temperature, and that the coefficients display a small dependence on chromium content.

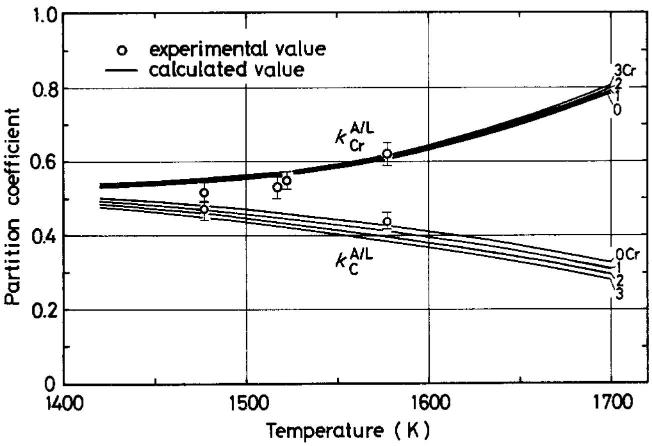


Figure 1 Dependence of partition coefficients of chromium and carbon on temperature and chromium content.

3. Experimental procedure

Iron–carbon eutectic alloy containing a small amount of chromium as the third element was prepared from electrolytic iron, electrode graphite and electrolytic chromium of 99.99% purity by being melted in alumina crucibles in vacuum at 1773 K in a high-frequency induction furnace and then by being cast into steel moulds of inside diameter 10 mm. Four hypo-eutectic alloys with different carbon contents were also prepared by adding electrolytic iron to the eutectic alloy. The chemical compositions of the alloys are shown in Table I.

3.1. Partition of chromium between austenite and liquid

For measurements of the equilibrium partition coefficients for chromium between austenite and liquid iron, the hypo-eutectic alloys were rapidly cooled from a coexisting solid–liquid state. The apparatus for the rapid cooling experiment is illustrated in Fig. 2. An alloy of about 10 g was melted above the liquidus temperature and was then cooled to a given temperature within the solidification temperature range. The alloy consisting of liquid and solid was held at the temperature for 1 h and was then dropped in oil by pulling up the stopper in Fig. 2. In the preliminary work, it was recognized that the concentrations of chromium and carbon in liquid and solid were constant in the holding time of longer than 50 min at 1473 K. The quenched specimen was cut in two and the section was polished and lightly etched in a 3% nital solution. The area in which chromium was analysed by an electron microprobe analyser was marked with a Vickers microhardness indenter and then the surface was repolished to remove etch features. The back-diffusion distance for carbon to

TABLE I The chemical composition of Fe–C–Cr hypo-eutectic alloys used for the rapid-cooling experiment

Holding temperature	C (wt%)	Cr (wt%)
1478	3.7	0.51
1518	3.0	0.42
1523	3.0	0.42
1578	2.8	0.38

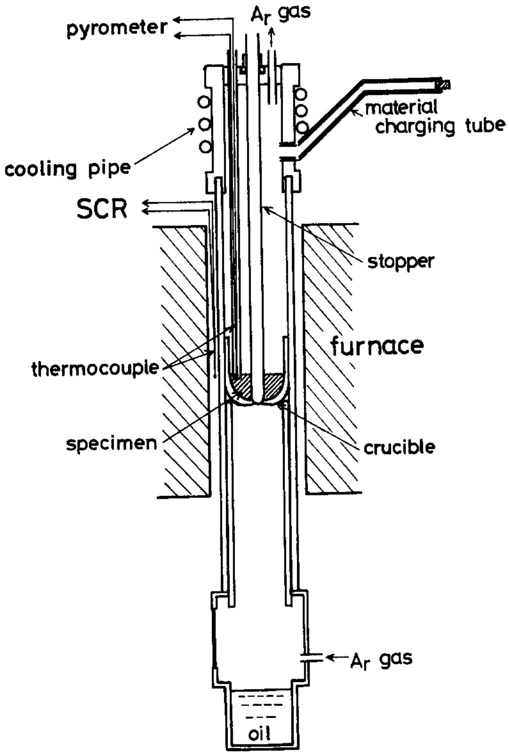


Figure 2 Scheme of the apparatus for the rapid-cooling experiment.

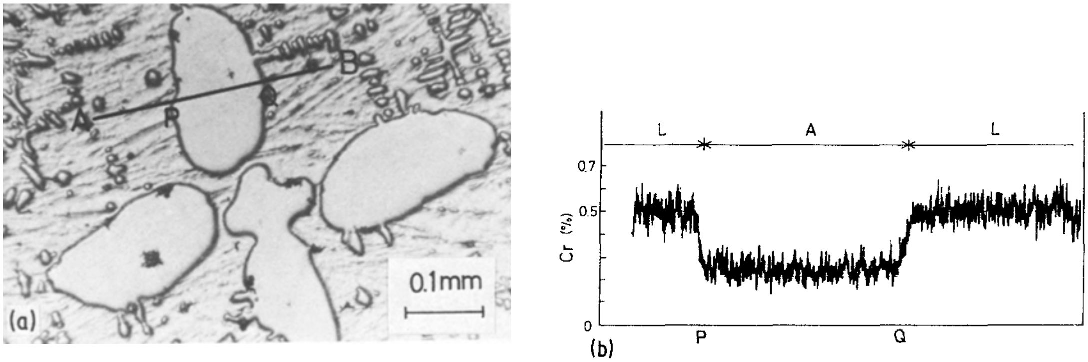


Figure 3 (a) Microstructure and (b) chromium distribution on the line AB in a specimen quenched from a coexisting solid–liquid state.

austenite during quenching was at most 50 μm in the present work. Accordingly, grains of quenched austenite larger than 150 μm were used for the analysis of carbon in austenite. The accuracy of analysis was ± 3% and ± 4% for chromium in quenched austenite and liquid, respectively, and ± 8% and ± 5% for carbon in quenched austenite and liquid, respectively.

3.2. Partition of chromium during eutectic solidification

Round bars of iron–carbon eutectic alloys containing a small amount of chromium were used for the zone-melting experiment by which the partition coefficient for chromium during eutectic solidification was determined. The bars were examined metallographically and also by X-ray non-destructive inspection to determine whether they had enough sound regions. The dimensions of the bars were 10 mm in diameter and 200 mm in length. The chromium-content of the alloys was about 0.1 and 0.6 wt% for eutectic solidification producing the stable and metastable systems, respectively, and such different chromium levels were necessary to obtain both types of eutectic. Zone melting operation and the subsequent treatment for obtaining chromium distribution in the zone-passed region were carried out in the same way as that described in the previous work [4].

4. Results

The microstructure of a rapidly-cooled specimen is shown in Fig. 3. In the photograph, the regions of primary austenite and liquid before rapid cooling are of coarse dendrites and of fine ledeburitic structure in which fine dendrites are imbedded, respectively. The distribution of chromium is given along the line AB which is across a primary austenite, being uniform in the austenite region where chromium concentration is lower than that in the quenched liquid. The equilibrium partition coefficient $k_{\mathrm{Cr}}^{\mathrm{A/L}}$, defined by Equation 7, for chromium between austenite and liquid is shown as a function of the holding temperature in Fig. 1. The values are smaller than unity and approach unity with increasing temperature.

Zone-melted eutectic alloys have microstructures as shown in Fig. 4, on the longitudinal section. The specimens solidified following the stable system have flake graphite and pearlite matrix in the zone-melted region and directionally-aligned ledeburite in the final zone. The specimens solidified following the metastable system have ledeburitic lamellae aligned in parallel to the zone-travelling direction in the zone-melted region and fine ledeburite in the final zone. Chromium distribution profiles in alloys solidified to form the stable and metastable structures after single zone-pass are shown in Fig. 5. The profiles after both manners of eutectic solidification apparently differ from each other. The effective partition coefficient of chromium was determined as the ratio of chromium concentration in the region ranging to the back distance 200 μm from the solid–liquid interface at the final zone to that in the final zone, similar to that found in the previous work [4]. The value is smaller than unity for the stable eutectic solidification and larger than unity for the metastable eutectic solidification, approaching unity with increasing zone-travelling velocity, as shown in Table II. If solid–liquid interfaces are flat during the zone-melting, the relationship between effective and equilibrium partition coefficients, which

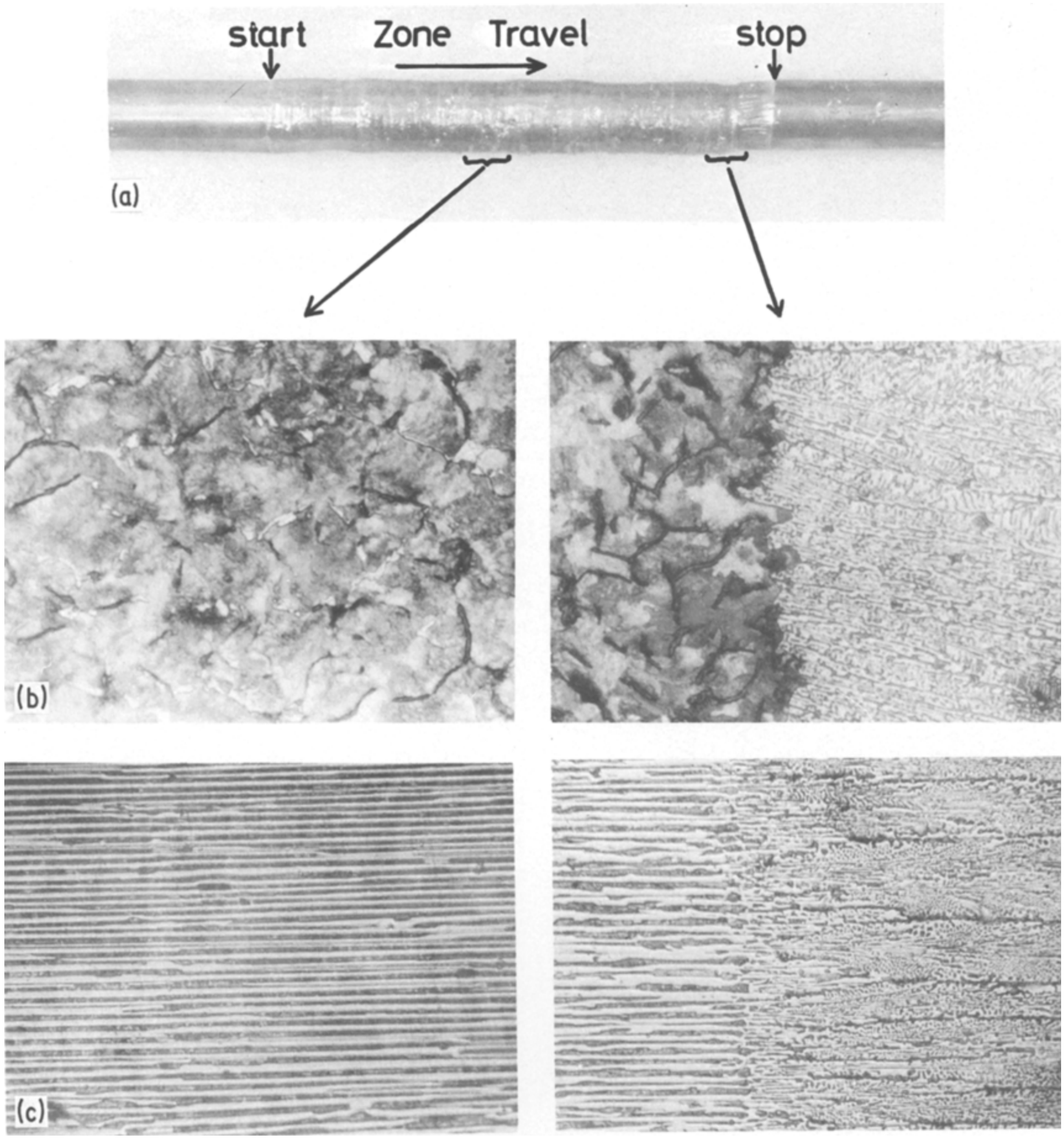


Figure 4 Microstructures on the longitudinal section of zone-melted Fe–C–Cr alloys solidified following the stable and metastable systems. (a) zone-melted alloy, (b) austenite–graphite eutectic solidification, (c) austenite–cementite eutectic solidification.

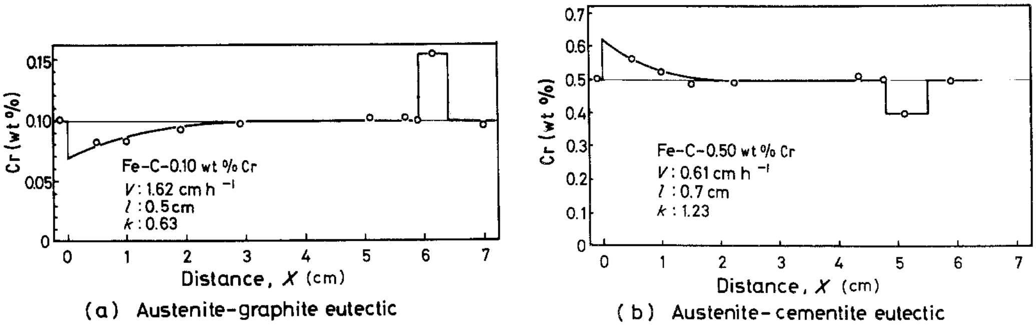
was derived by Burton *et al.* [13], can be applied to this case. The relationship is expressed by

$$\ln\left|1-\frac{1}{k_e}\right| = \ln\left|1-\frac{1}{k_0}\right| - \frac{R\delta}{D}, \qquad (27)$$

where k_e is the effective partition coefficient at the zone-travelling velocity, R, which equals the growth rate of solid, k_0 is the equilibrium partition coefficient, δ is the thickness of the boundary layer, and D is the diffusion coefficient of chromium in the eutectic liquid. In Fig. 6 the values of $\ln|1-(1/k_e)|$ are plotted against zone-travelling velocity, R, and linear relationships are observed. From the intercepts on the vertical axis, the equilibrium partition coefficients for chromium were determined as follows:

$k_{0,\mathrm{Cr}} = 0.48$, for the stable eutectic solidification, and

$k'_{0,\mathrm{Cr}} = 1.28$, for the metastable eutectic solidification.



(a) Austenite-graphite eutectic

(b) Austenite-cementite eutectic

Figure 5 Redistribution of chromium in the Fe–C–Cr alloys solidified following the stable and metastable systems. (a) Austenite–graphite eutectic, (b) austenite–cementite eutectic.

From the slopes of the lines in Fig. 6, the values of δ/D for the stable and metastable eutectic solidifications were 1690 and 1070 sec cm^{-1}, respectively. The accepted value of the diffusion coefficient for chromium at the eutectic temperature is 1×10^{-5} cm^2 sec^{-1} [14] and thus the thickness of the boundary layer becomes 0.17 mm for the stable eutectic solidification and 0.11 mm for the metastable one.

5. Discussion

In the present work, the chromium content of the specimens used for the rapid-cooling experiment was 0.4 to 0.5 wt%. From the results of the calculation shown in Fig. 1, the equilibrium partition coefficient of chromium between austenite and liquid displays a small chromium-content dependence in the temperature range where the experiments were carried out. The equilibrium partition coefficients obtained in the present work are also plotted in Fig. 1. It is seen that the experimental values are in good agreement with the calculated ones, within experimental error. From Equations 14 and 15, the equilibrium partition coefficients of chromium and carbon were also calculated as functions of chromium and carbon content of alloys with up to 3 wt% Cr and 4 wt% C. The results, and also contour lines of equilibrium partition coefficient, are shown in Figs 7 and 8. In Fig. 7, the calculated partition coefficients of chromium agree well with the experimental values obtained both in the present work and in work by Rickinson and Kirkwood [1] and Umeda *et al.* [2]. On the other hand, the calculated values for carbon are quite different from the values reported by these authors. Rickinson and Kirkwood [1] who measured the equilibrium partition coefficients for carbon and chromium, using a splat-cooling method, pointed out that the equilibrium partition coefficient of carbon for an alloy containing 1.5 wt% Cr was much larger than that obtained from the Fe–C binary equilibrium diagram, implying that the alloy had a dramatically narrow freezing range. Umeda *et al.* [2] also showed that the equilibrium partition coefficients of carbon were much larger than those expected from the Fe–C binary system. However, the values given by Umeda *et al.* [2] were smaller than those by Rickinson and Kirkwood [1] and were not strikingly different from one another within the composition range from 1 to 3 wt% Cr. To examine the possibility of large partition coefficients of carbon in the presence of chromium, as shown by [1], the specimens used for the determination of chromium partition coefficient in the present work were also employed for the determination of the partition coefficient of

TABLE II The effective partition coefficients for chromium at different zone-travelling velocities

Austenite–graphite eutectic solidification			Austenite–cementite eutectic solidification		
Cr (wt %)	Zone-travelling velocity (cm h^{-1})	k_E	Cr (wt %)	Zone-travelling velocity (cm h^{-1})	k_E
0.12	0.61	0.53	0.50	0.61	1.23
0.10	1.14	0.60	0.59	1.80	1.15
0.10	0.62	0.63	0.59	3.00	1.10
0.10	3.06	0.78			

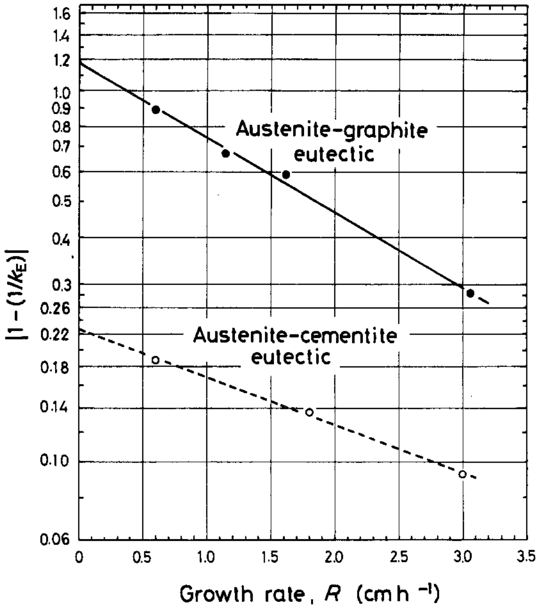


Figure 6 Relationship between ln $|1 - (1/k_e)|$ and growth rate, R.

carbon. Electron microprobe analysis was carried out at an accelerating voltage of 20 kV and a probe current of 0.02 μA and the carbon K_α radiation was detected using a lead stearate crystal. The results are plotted in Fig. 8, representing an excellent accordance with the calculated values. According to Bungardt *et al.* [3], the liquidus of the ternary system Fe—C—Cr shifts to lower carbon concentration with increasing chromium content. From the calculation in the present work, the solidus of Fe—C—Cr alloy shifts more than does the liquidus, with increasing chromium content, to the low-carbon side, which may result from the behaviour of chromium as a ferrite stabiliser. Such a shift in the solidus has been found in the work done by Tofaute *et al.* [15], although the solidus surface given by them is of doubtful accuracy in the carbon concentration.

The equilibrium partition coefficient for a solute element, M, between eutectic and liquid is represented by the following:

for the stable eutectic system

$$k_{0,M} = f_A k_M^{A/L} \qquad (28)$$

and for the metastable eutectic system

$$k'_{0,M} = [f'_A + k_M^{C/A}(1 - f'_A)]k_M'^{A/L}, \qquad (29)$$

where f_A is the weight fraction of austenite in eutectic, $k_M^{C/A}$ is the equilibrium partition coefficient for the element, M, between cementite and austenite at the metastable eutectic temperature (for chromium $k_{Cr}^{C/A}$ equals 4 [16]) and the symbols with and without a prime concern metastable and stable systems, respectively. The values of $k_{Cr}^{A/L}$ are evaluated in the preceding calculation and, hence, the dependence of $k_{0,Cr}$ and $k'_{0,Cr}$ on chromium content at 1426 K can be calculated using Equations 28 and 29. The results are presented in Fig. 9, together with the values obtained in the zone-melting experiment. The calculated values of the equilibrium partition coefficients for both the eutectic systems cause little change with chromium content and agree well with the experimental values.

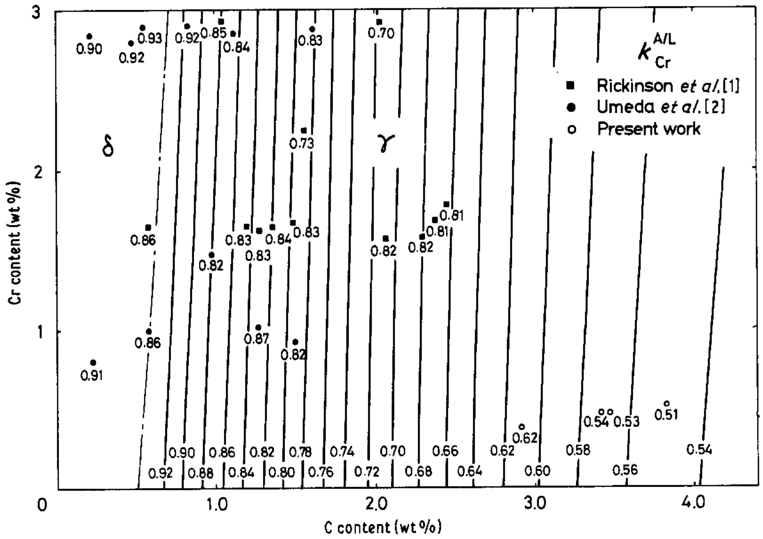


Figure 7 Partition coefficient diagram for chromium in the Fe—C—Cr system.

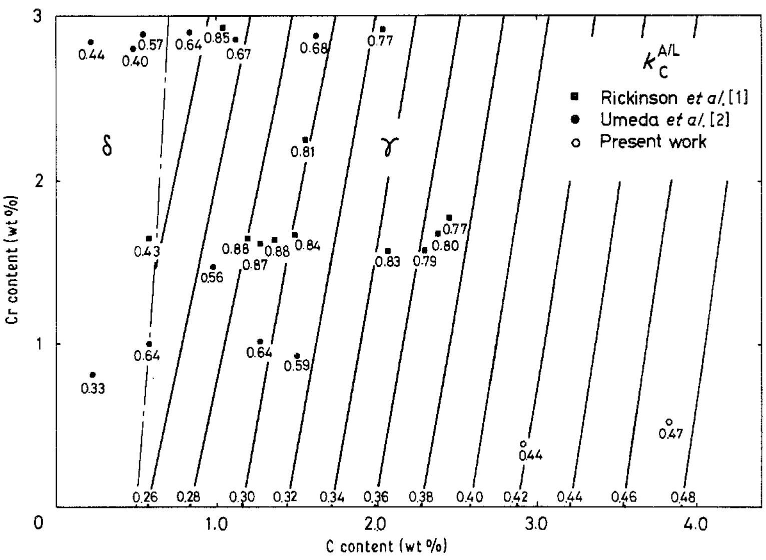


Figure 8 Partition coefficient diagram for carbon in the Fe–C–Cr system.

It is demonstrated from an equation given by Lupis [17] that the partition coefficient between eutectic and liquid is closely related to the graphitization of cast iron. The equation is similar to van't Hoff's equation for a binary system, representing a linear relationship between an increment of binary eutectic temperature, δT_E, with a small addition of a third element, and the equilibrium partition coefficient k_0 of the element between eutectic and liquid, which is expressed as follows:

$$\delta T_E = -\frac{RT_E^2}{\Delta H_E}(1-k_0), \qquad (30)$$

where T_E is the eutectic temperature of the binary system, ΔH_E is the latent heat-of-fusion of the eutectic, and R is the gas constant. For the iron–carbon system, the value of ΔH_E is 8677 J mol^{-1} for the stable eutectic system and 8936 J mol^{-1} for the metastable eutectic system [18], and the following equations are obtained for the eutectic systems:

for the stable eutectic system

$$\delta T_E = -19.5(1-k_0) \qquad (31)$$

and for the metastable eutectic system

$$\delta T'_E = -18.8(1-k'_0). \qquad (32)$$

When chromium is used as the third element, the calculated values of δT_E and $\delta T'_E$ amount to -10 K at% Cr^{-1} and 5 K at% Cr^{-1}, respectively, from the data of the zone-melting experiment, and are in good agreement with measured values by other workers ($\delta T_E = -9$ K at% Cr^{-1} [19] and $\delta T'_E = 6$ K at% Cr^{-1} [3]).

As shown above, the theoretical thermodynamic calculation of partition coefficients can be useful, provided that the necessary thermodynamic data are available. The theoretical method is applicable to other multi-component systems and is advantageous where there are experimental difficulties in obtaining data more directly.

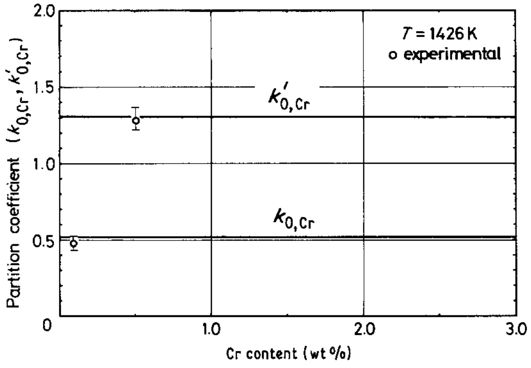


Figure 9 The dependence of partition coefficients of chromium between eutectic and its liquid on chromium content.

6. Conclusion

The equilibrium partition coefficients for chromium between austenite and liquid iron for iron–carbon hypo-eutectic alloys with 0.4 to 0.5 wt% chromium content were determined by the rapid-cooling experiment from a coexisting solid–liquid state. Chromium was rejected to liquid on the crystallization of primary austenite, the equilibrium partition coefficient having been smaller than unity. As the temperature at which austenite was in equilibrium with liquid was increased, the equilibrium partition coefficient for chromium approached unity. Therodynamically-calculated partition coefficient values for chromium in iron–carbon–chromium ternary alloys agreed well with the experimental values. It was also shown that the calculated partition coefficient of carbon between austenite and liquid iron decreased with an increase in chromium content.

The results of the calculated partition coefficients of chromium and carbon between austenite and liquid iron indicated that chromium shifted the solidus to the low-carbon side in contradiction with the results recently obtained experimentally by some workers [1, 2]. However, this shift may be reasonable, because chromium is one of the elements that form a γ-loop.

On the other hand, the results of the zone-melting experiments with iron–carbon eutectic alloys containing 0.1 or 0.5 to 0.6 wt % chromium showed that the equilibrium partition coefficients of chromium between eutectic and liquid iron was smaller than unity for the stable eutectic system and larger than unity for the metastable eutectic system, resulting from rejection of chromium into cementite rather than into liquid iron. The observed partition coefficient values of chromium for both the eutectic systems agreed well with the thermodynamically calculated values. The thickness of the boundary layer in eutectic liquid ahead of the solid–liquid interface amounted to 0.17 mm for the stable eutectic solidification and 0.11 mm for the metastable eutectic solidification.

Acknowledgement

The authors wish to thank Mrs M. Horihata for the chemical analysis of the specimens and Mr K. Iwata for the computation of the partition coefficients.

References

1. B. A. RICKINSON and D. H. KIRKWOOD, *Metal Sci.* **12** (1978) 138.
2. T. UMEDA, Y. KIMURA, M. SUZUKI and T. OGATA, The 4th Japan–Germany Seminar on Basic Principles of Solidification of Steel with special regard to Continuous Casting Nov. 1980, Tokyo (Iron and Steel Institute of Japan, Tokyo, 1980) p. 106.
3. K. BUNGARDT, E. KUNZE and E. HORN, *Arch. Eisenhüttenwes.* **29** (1958) 193.
4. A. KAGAWA and T. OKAMOTO, *Metal Sci.* **14** (1980) 519.
5. S. BAN-YA, J. F. ELLIOTT and J. CHIPMAN, *Met. Trans.* **1** (1970) 1313.
6. J. CHIPMAN, *ibid.* **1** (1970) 2163.
7. G. KIRCHNER, T. NISHIZAWA and B. UHRENIUS, *ibid.* **4** (1973) 167.
8. O. KUBASCHEWSKI and C. B. ALCOCK, "Metallurgical Thermochemistry" 5th edn. (Pergamon Press, Oxford, 1979) p. 328.
9. J. CHIPMAN, "Basic Open-Hearth Steelmaking" (Iron and Steel Division, American Institute of Metallurgical Engineers, New York, 1951) p. 632.
10. E. SCHÜRMANN and J. H. RIMKUS, *Giessereiforschung* **27** (1975) 19.
11. E. SCHÜRMANN, K. H. HARRE and J. H. RIMKUS, *ibid.* **26** (1974) 31.
12. L. KAUFMAN and H. NESOR, *Z. Metallkde* **64** (1973) 249.
13. J. A. BURTON, R. C. PRIMM and W. P. SLICHTER, *J. Chem. Phys.* **21** (1953) 1987.
14. P. M. SHURYGIN and V. D. SHANTARIN, *Fiz. Metal. Metalloved.* **17** (1964) 471.
15. W. TOFAUTE, C. KÜTTNER and A. BÜTTINGHAUS, *Arch. Eisenhüttenwes.* **9** (1935) 607.
16. M. KO, T. SAKUMA and T. NISHIZAWA, *Nihon kinzoku gakkai shi* **40** (1976) 593.
17. C. H. P. LUPIS, *Met. Trans.* **9B** (1978) 231.
18. M. HILLERT and S. RAO V. V., "The Solidification of Metals" (Iron and Steel Institute, London, 1967) p. 204.
19. W. OLDFIELD, *Brit. Cast Iron Res. Assoc. J.* **9** (1961) 506.

Received 20 March
and accepted 15 June 1981