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The Effects of Molybdenum, Wolfram and Copper on the Solubility of Graphite in Liquid Iron and a Method for Calculation of the Activity Coefficient of Carbon in Multicomponent Alloys

By

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The effects of molybdenum, wolfram and copper on the solubility of graphite in liquid iron have been studied at 1550°C. Interaction parameters at graphite saturation are given as follows:

$$\left(\frac{\partial \ln \gamma_c}{\partial N_{Mo}}\right)_{N_{c'}=0.207} = -3.20, \quad \left(\frac{\partial \ln \gamma_c}{\partial N_W}\right)_{N_{c'}=0.207} = -1.31, \quad \left(\frac{\partial \ln \gamma_c}{\partial N_{Cu}}\right)_{N_{c'}=0.207} = +4.77$$

A general approximate equation for calculating the activity coefficient of carbon in a multicomponent alloy can be given as follows:

$$(\log \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\log \gamma_c')_{N_c} + \sum \left(\frac{\partial \log \gamma_c}{\partial N_{j_1}}\right)_{N_c, 0, 0, \dots} \cdot N_{j_1}$$

The validity of this equation was discussed by using the present data. Interaction parameters for infinitely dilute and graphite saturated solutions were compared and discussed.

1. Introduction

One of the authors investigated the effects of arsenic and tin on the solubility of graphite in liquid iron at 1550°C, and found that both of these elements increase the activity of carbon¹⁾. The present investigation was performed to determine the effects of molybdenum, wolfram and copper on the solubility of graphite in alloys of iron-carbon-molybdenum, iron-carbon-wolfram and iron-carbon-copper respectively. In addition, solubility measurements were also made concerning the alloys iron-carbon-molybdenum-wolfram, iron-carbon-molybdenum-copper, iron-carbon-wolfram-copper and iron-carbon-molybdenum-wolfram-copper.

2. Method of the Experiment

Basic electric furnace pure iron was used as a raw material, and the pure iron was charged into a graphite Tammann tube which contained small pieces of

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graphite, melted in vacuo and then cast into a dry sand mould at ca. 1600°C. The composition of the mother alloy iron-carbon thus manufactured is shown in Table 1. The purity of the metallic molybdenum and wolfram used as additives was higher than 99.99 pct. Electrolytic copper was used for the copper alloys.

Table 1. Chemical composition of the mother alloy iron-carbon.

| | | | | | | | | |
|---------|-----------|-------|---------|-----------|--------|--------|--------|-------|
| Element | C | Si | Mn | P | S | Cu | Ni | Cr |
| % | 4.23~5.28 | 0.110 | tr. | 0.010 | 0.007 | 0.017 | 0.022 | 0.007 |
| Element | Mo | W | sol. Al | insol. Al | H | O | N | |
| % | 0.004 | 0.003 | 0.0020 | 0.0008 | 0.0002 | 0.0067 | 0.0013 | |

The content of carbon in the mother alloy is lower than the saturation value at 1600°C because the flaky graphite was partly separated during solidification and floated up to the surface of the cast ingot. Graphite was also observed in the section of the ingot causing some variation in the values of carbon content.

The mother alloy weighing ca. 100 g and the required amount of the added metal were charged into a graphite crucible¹⁾ of 25 mm i.d. and 60 mm height, and the crucible was then put into a Tammann furnace whose lower half was filled with cryptol grains. Dried argon gas was led into the furnace from the bottom and after the air within the furnace was almost completely replaced by the argon gas the charge was melted by heating the furnace. The molten alloy was agitated by a graphite rod after being held about 30 min. at 1550°C, and after holding a definite time at that temperature sampling was made by using a silica suction tube of 4 mm o.d., the sample thus taken being rapidly quenched in water to prevent graphitization. After the sampling operation, the required amount of mother alloy or metal was added to the remaining molten metal by passing through a silica tube. The alloys iron-carbon-molybdenum and iron-carbon-wolfram were thoroughly agitated after waiting a period of 30 minutes following the addition of metallic molybdenum or wolfram, while the alloy iron-carbon-copper was agitated after waiting a period of only one or two min. following the addition of copper because the added copper dissolved immediately. In the case of the alloys of iron-carbon-copper, the solubility of graphite was measured for the range up to 5 pct of copper because alloys containing more than 5 pct of copper separate into two liquid phases.

Besides the above mentioned experiments, the solubility of graphite in the binary alloy iron-carbon was also measured.

The temperature of the alloys was measured with a Pt-PtRh thermocouple which was calibrated by measuring the melting point of electrolytic nickel. The alloys were kept at $1550 \pm 10^\circ\text{C}$ throughout the experiments.

3. Method of Analysis

The samples were crushed and screened. Oversize of 35 mesh was used for the determination of carbon. The results of analyses for molybdenum, wolfram and copper were independent of the size, but the undersize of 48 mesh was used for the determination of these elements because a long time was necessary to dissolve the oversize of 48 mesh.

3-1 Analysis of carbon

Combustion and gravimetric method corresponding to JIS G 1211²⁾ was applied. The standard sample No. 6(b) was analysed to check the accuracy of analysis before and after the analysis of samples.

3-2 Analysis of molybdenum

Colorimetric method for the solution of potassium thiocyanomolybdate corresponding to JIS G 1218³⁾ was applied. The standard line was checked by analysing the standard sample No. 9(a) and No. IV (Cr-Mo steel).

3-3 Analysis of wolfram

Colorimetric method by means of hydroquinon reported by Kamimori and Mukaewaki⁴⁾ was applied. The standard line was checked by analysing the standard sample No. 11 and No. 9(a).

3-4 Analysis of copper

Colorimetric method extracting the complex salt of diethyldithiocarbamic acid with carbon tetrachloride corresponding to JIS G 1219⁵⁾ was applied. 20 ml of carbon tetrachloride solution was used for the extraction and the time of agitation was 4 min. because one min. agitation was insufficient for the complete extraction of copper.

4. Results of the Experiment

4-1 Solubility of graphite in alloy iron-carbon

The solubility of graphite in alloy iron-carbon at 1550°C was determined to be 5.28 pct. The mother alloy used for the experiments contained 0.11 pct of silicon and because the solubility of graphite is decreased by the addition of silicon, the authors corrected the molar fraction N_c' of the solubility of graphite at 1550°C to 0.207 (i.e. 5.31 wt. pct). All of the results of analyses shown later were corrected in view of the effect of the silicon present as an impurity.

4-2 Relation between the holding time and the changes of composition of alloys iron-carbon-molybdenum, iron-carbon-wolfram and iron-carbon-copper

The holding time necessary to attain equilibrium was investigated at 1550°C. Results of the experiments are shown in Figs. 1 to 3.

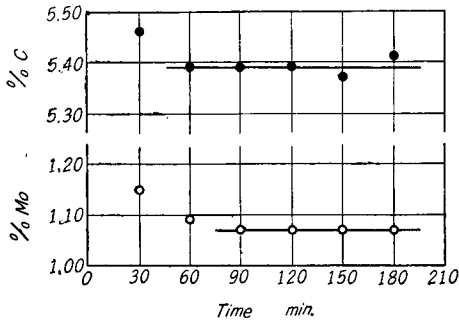


Fig. 1. Relation between the composition of alloy Fe-C-Mo and holding time at 1550°C.

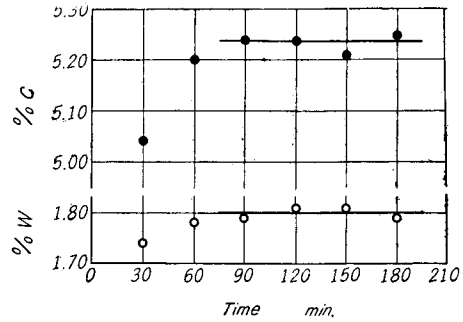


Fig. 2. Relation between the composition of alloy Fe-C-W and holding time at 1550°C.

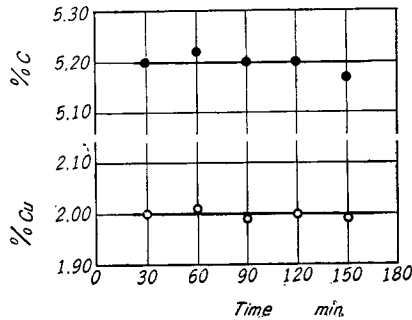


Fig. 3. Relation between the composition of alloy Fe-C-Cu and holding time at 1550°C.

Complete equilibrium conditions were found to be attained within 1.5 hrs after agitation for the alloys iron-carbon-molybdenum and iron-carbon-wolfram, and within 0.5 hr after agitation for the alloys iron-carbon-copper, but the holding times were set at 2.5 hrs in the alloys iron-carbon-molybdenum and iron-carbon-wolfram, and 1.5 hrs in the alloy iron-carbon-copper for certainty.

4-3 Solubility of graphite in alloys iron-carbon-molybdenum, iron-carbon-wolfram, iron-carbon-copper, iron-carbon-molybdenum-wolfram, iron-carbon-molybdenum-copper, iron-carbon-wolfram-copper and iron-carbon-molybdenum-wolfram-copper

Results of the experiments are shown in Tables 2 to 5 and also in Figs. 4 to 6. The data of Koros and Chipman⁸⁾ and Fuwa, Fujikura and Matoba⁹⁾ are also shown in these figures.

Table 2. Solubility of graphite in alloys of iron-carbon-molybdenum at 1550°C.

| Heat No. | C | | Mo | |
|----------|------|-------|-------|----------|
| | % | N_C | % | N_{Mo} |
| Mo 03-1 | 5.32 | 0.207 | 0.36 | 0.00176 |
| Mo 02-1 | 5.33 | 0.208 | 0.59 | 0.00288 |
| Mo 03-2 | 5.37 | 0.209 | 0.71 | 0.00346 |
| Mo 01 | 5.39 | 0.210 | 1.07 | 0.00522 |
| Mo 02-2 | 5.33 | 0.208 | 1.08 | 0.00528 |
| Mo 02-3 | 5.35 | 0.210 | 2.45 | 0.0120 |
| Mo 03-4 | 5.42 | 0.213 | 3.70 | 0.0182 |
| Mo 02-4 | 5.39 | 0.212 | 4.07 | 0.0201 |
| Mo 02-5 | 5.37 | 0.214 | 6.55 | 0.0326 |
| Mo 03-5 | 5.37 | 0.215 | 7.79 | 0.0390 |
| Mo 02-6 | 5.42 | 0.218 | 10.04 | 0.0505 |
| Mo 03-6 | 5.45 | 0.220 | 10.84 | 0.0547 |
| Mo 02-7 | 5.53 | 0.227 | 16.52 | 0.0849 |
| Mo 03-7 | 5.56 | 0.228 | 16.60 | 0.0852 |

Table 3. Solubility of graphite in alloys of iron-carbon-wolfram at 1550°C.

| Heat No. | C | | W | |
|----------|------|-------|------|---------|
| | % | N_C | % | N_W |
| W 4-1 | 5.32 | 0.208 | 0.37 | 0.00094 |
| W 5-7 | 5.33 | 0.208 | 0.47 | 0.00120 |
| W 5-6 | 5.26 | 0.206 | 0.66 | 0.00169 |
| W 6 | 5.24 | 0.207 | 1.80 | 0.00464 |
| W 4-3 | 5.26 | 0.207 | 1.82 | 0.00469 |
| W 5-4 | 5.22 | 0.208 | 3.61 | 0.00941 |
| W 4-4 | 5.21 | 0.208 | 3.91 | 0.0102 |
| W 5-3 | 5.16 | 0.208 | 5.09 | 0.0134 |
| W 4-5 | 5.18 | 0.211 | 6.79 | 0.0181 |
| W 5-2 | 5.07 | 0.209 | 7.93 | 0.0213 |
| W 4-6 | 5.01 | 0.209 | 9.80 | 0.0267 |
| W 5-1 | 4.93 | 0.210 | 12.8 | 0.0357 |
| W 4-7 | 4.85 | 0.213 | 16.7 | 0.0481 |

Table 4. Solubility of graphite in alloys of iron-carbon-copper at 1550°C.

| Heat No. | C | | Cu | |
|----------|------|-------|------|----------|
| | % | N_C | % | N_{Cu} |
| Cu 5-1 | 5.29 | 0.206 | 0.50 | 0.00369 |
| Cu 4-6 | 5.28 | 0.206 | 0.57 | 0.00420 |
| Cu 5-2 | 5.24 | 0.205 | 1.00 | 0.00738 |
| Cu 4-5 | 5.23 | 0.204 | 1.15 | 0.00850 |
| Cu 6 | 5.20 | 0.204 | 2.00 | 0.0148 |
| Cu 4-4 | 5.20 | 0.204 | 2.25 | 0.0167 |
| Cu 5-3 | 5.04 | 0.198 | 2.28 | 0.0170 |
| Cu 5-4 | 4.94 | 0.195 | 3.36 | 0.0250 |
| Cu 4-3 | 4.98 | 0.197 | 3.43 | 0.0256 |
| Cu 4-2 | 4.96 | 0.196 | 4.60 | 0.0344 |

Table 5. Solubility of graphite in alloys of iron-carbon-molybdenum-wolfram, iron-carbon-molybdenum-copper, iron-carbon-wolfram-copper and iron-carbon-molybdenum-wolfram-copper at 1550°C.

| Heat No.* | C | | Mo | | W | | Cu | |
|-----------|------|-------|------|----------|------|---------|-------|----------|
| | % | N_C | % | N_{Mo} | % | N_W | % | N_{Cu} |
| Mo2W2Cu0 | 5.34 | 0.212 | 2.25 | 0.0112 | 1.81 | 0.00468 | 0.016 | 0.00012 |
| Mo5W2Cu0 | 5.25 | 0.212 | 5.24 | 0.0265 | 1.99 | 0.00529 | 0.016 | 0.00012 |
| Mo5W5Cu0 | 5.21 | 0.213 | 4.79 | 0.0245 | 4.90 | 0.0131 | 0.015 | 0.00012 |
| Mo0W2Cu2 | 4.97 | 0.198 | 0 | 0 | 1.98 | 0.00516 | 1.98 | 0.0146 |
| Mo2W0Cu2 | 5.13 | 0.203 | 2.58 | 0.0128 | 0 | 0 | 1.93 | 0.0145 |
| Mo2W2Cu2 | 5.03 | 0.203 | 2.35 | 0.0118 | 2.18 | 0.00572 | 1.93 | 0.0147 |
| Mo2W4Cu4 | 4.90 | 0.200 | 2.16 | 0.0110 | 3.80 | 0.01009 | 3.00 | 0.0231 |
| Mo2W2Cu4 | 5.03 | 0.203 | 2.17 | 0.0110 | 2.60 | 0.00684 | 3.57 | 0.0272 |
| Mo2W4Cu2 | 4.99 | 0.203 | 2.34 | 0.0119 | 3.96 | 0.0105 | 1.79 | 0.0138 |

* Each heat was kept for 2.5 hrs at 1550°C before sampling.

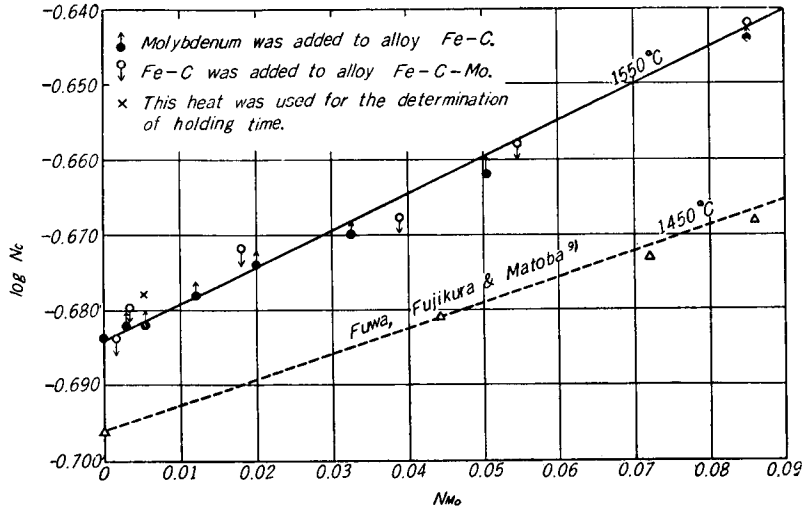


Fig. 4. Effect of molybdenum on solubility of graphite in alloys Fe-C-Mo at 1550°C.

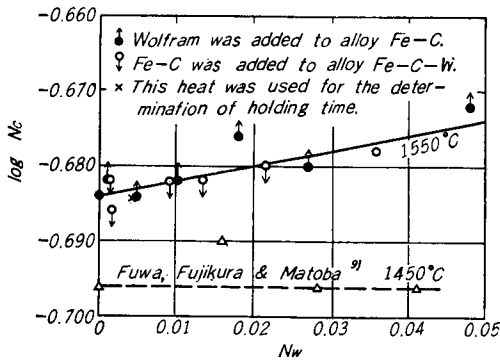


Fig. 5. Effect of wolfram on solubility of graphite in alloys Fe-C-W at 1550°C.

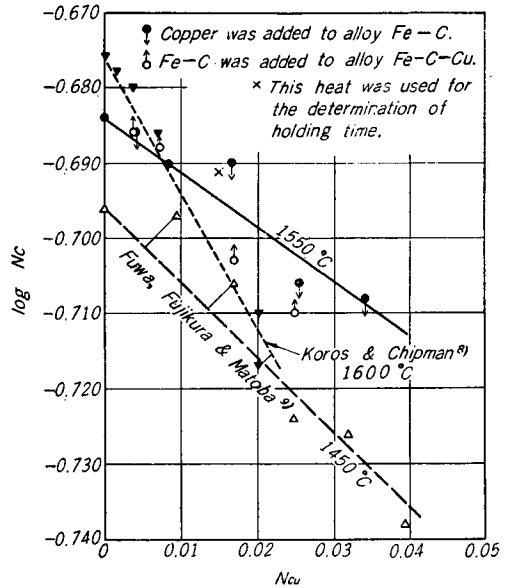


Fig. 6. Effect of copper on solubility of graphite in alloys Fe-C-Cu at 1550°C.

5. Consideration

When the molar fractions of carbon and a solute j are given as N_c and N_j in a ternary solution iron-carbon- j at a constant temperature and pressure, the logarithm of the activity coefficient of carbon γ_c can be expressed as a function of N_c and N_j , i.e.

$$\ln \gamma_c = f(N_c, N_j)$$

or

$$\ln \gamma_c = f_1(\ln N_c, N_j) \quad (1)$$

If the activity of carbon a_c is constant, $\ln N_c$ is a function of N_j , i.e.

$$\ln N_c = f_2(N_j) \quad (2)$$

The following equation can be derived from eq. (1) and (2),

$$\left(\frac{d \ln \gamma_c}{d N_j}\right)_{a_c} = \left(\frac{\partial \ln \gamma_c}{\partial \ln N_c}\right)_{N_j} \left(\frac{d \ln N_c}{d N_j}\right)_{a_c} + \left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{\ln N_c} \quad (3)$$

Furthermore

$$\ln \gamma_c = \ln a_c - \ln N_c \quad (4)$$

Combination of eq. (3) with eq. (4) gives

$$\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{\ln N_c} = -\left\{1 + \left(\frac{\partial \ln \gamma_c}{\partial N_c}\right)_{N_j} \cdot N_c\right\} \left(\frac{d \ln N_c}{d N_j}\right)_{a_c} \quad (5)$$

When the value of N_c is taken as the saturation value of graphite i.e. $a_c=1$, and that of N_j is equal to zero, the corresponding value of $\ln N_c$ is that of $\ln N_c'$. Therefore, from eq. (5)

$$\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c'} = -\left\{1 + \left(\frac{\partial \ln \gamma_c}{\partial N_c}\right)_{N_j=0} \cdot N_c\right\} \left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1} \quad (5)'$$

or

$$\left(\frac{\partial \log \gamma_c}{\partial N_j}\right)_{N_c'} = -\left\{1 + \left(\frac{\partial \ln \gamma_c}{\partial N_c}\right)_{N_j=0} \cdot N_c\right\} \left(\frac{d \log N_c}{d N_j}\right)_{a_c=1} \quad (5)''$$

The first term of the right side in eq. (5)'' can be given for this case as follows:

$$1 + \left(\frac{\partial \ln \gamma_c}{\partial N_c}\right)_{N_j=0} \cdot N_c = 1 + 2.303 \left(\frac{d \log \gamma_c'}{d N_c'}\right)_{N_c'} \quad (6)$$

where γ_c' and N_c' are the activity coefficient and molar fraction of carbon in the binary alloy iron-carbon.

According to Rist and Chipman¹⁰⁾, the activity coefficient of carbon in the binary alloy iron-carbon at 1550°C can be expressed as follows:

$$\log \gamma_c' = 2.437(2N_c' - N_c'^2) - 0.223 \quad (7)$$

By differentiation of eq. (7) by N_c' and by putting $N_c'=0.207$, the right side of

eq. (6) can be calculated, i.e.

$$1 + 2.303 \left(\frac{d \log \gamma_c'}{dN_c'} \right)_{N_c'} = 2.84 \quad (8)$$

The second term of the right side in eq. (5)'' is given as the tangent of the line shown in Figs. 4 to 6, i.e.

$$\left. \begin{aligned} \left(\frac{d \log N_c}{dN_{Mo}} \right)_{a_c=1} &= 0.49 \\ \left(\frac{d \log N_c}{dN_W} \right)_{a_c=1} &= 0.20 \\ \left(\frac{d \log N_c}{dN_{Cu}} \right)_{a_c=1} &= -0.73 \end{aligned} \right\} \quad (9)$$

The interaction parameters of carbon at graphite saturation can be calculated by substituting eqs. (8) and (9) into eq. (5)'', i.e.

$$\left. \begin{aligned} \left(\frac{\partial \log \gamma_c}{\partial N_{Mo}} \right)_{N_c'=0.207} &= -1.39 & \left(\frac{\partial \ln \gamma_c}{\partial N_{Mo}} \right)_{N_c'=0.207} &= -3.20 \\ \left(\frac{\partial \log \gamma_c}{\partial N_W} \right)_{N_c'=0.207} &= -0.57 & \left(\frac{\partial \ln \gamma_c}{\partial N_W} \right)_{N_c'=0.207} &= -1.31 \\ \left(\frac{\partial \log \gamma_c}{\partial N_{Cu}} \right)_{N_c'=0.207} &= +2.07 & \left(\frac{\partial \ln \gamma_c}{\partial N_{Cu}} \right)_{N_c'=0.207} &= +4.77 \end{aligned} \right\} \quad (10)$$

The activity coefficient γ_c of carbon in a multicomponent solution iron-carbon- j_1 - j_2 -... can be expressed as a function of the molar fractions of carbon, j_1, j_2, \dots at a constant temperature and pressure. If $\ln \gamma_c$ is expanded as a Taylor series at a point $N_c = N_c^*, N_{j_1} = N_{j_1}^*, N_{j_2} = N_{j_2}^*, \dots$ and the terms of second and higher derivatives are disregarded, the following equation is approximately valid.

$$\begin{aligned} (\ln \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} &= (\ln \gamma_c)_{N_c^*, N_{j_1}^*, N_{j_2}^*, \dots} + \left(\frac{\partial \ln \gamma_c}{\partial N_c} \right)_{N_c^*, N_{j_1}^*, N_{j_2}^*, \dots} (N_c - N_c^*) \\ &+ \sum \left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}} \right)_{N_c^*, N_{j_1}^*, N_{j_2}^*, \dots} (N_{j_1} - N_{j_1}^*) \end{aligned} \quad (11)$$

If the relations $N_c^* = N_c, N_{j_1}^* = 0, N_{j_2}^* = 0, \dots$ are put into eq. (11), then

$$(\ln \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\ln \gamma_c)_{N_c, 0, 0, \dots} + \sum \left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}} \right)_{N_c, 0, 0, \dots} \cdot N_{j_1} \quad (12)$$

The value of $(\ln \gamma_c)_{N_c, 0, 0, \dots}$ in eq. (12) is equal to that of $\ln \gamma_c' = f_n(N_c')$ in a binary solution of iron-carbon with N_c substituted for N_c' . The value of $\left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}} \right)_{N_c, 0, 0, \dots}$ can be calculated as the tangent at a point $N_{j_1} \rightarrow 0$ and $N_c =$ constant in a ternary solution of iron-carbon- j_1 . It should be noticed that the value of the activity of carbon is not constant in this case. Many experimental measurements must, therefore, be carried out and the points of the same value

of N_c must be selected in order to calculate the value of $\left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c, 0}$, but this value is supposed to show only a slight change if the change in the molar fractions of carbon is not very great. In order to know the effect of the third element j_1 in a ternary solution iron-carbon- j_1 in the range near graphite saturation, the value of $\left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c', 0}$ i.e. that at the graphite saturation may well be applied instead of $\left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c, 0}$. Furthermore, the above substitution is sufficient so long as $\left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c', 0}$ is nearly equal to $\left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c, 0}$ even if the value of N_c is different from that of the graphite saturation.

If the relation between the interaction coefficient and the interaction parameter of carbon in a ternary solution of iron-carbon- j_1 at the concentration N_c of carbon is defined as

$$\left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c, 0} \times N_{j_1} \equiv (\ln \gamma_c^{(j_1)})_{N_c} \quad (13)$$

eq. (12) can be written as follows:

$$(\ln \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\ln \gamma_c)_{N_c} + \sum (\ln \gamma_c^{(j_1)})_{N_c} \quad (14)$$

or
$$(\gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\gamma_c' \cdot \gamma_c^{(j_1)} \cdot \gamma_c^{(j_2)} \cdot \dots)_{N_c} \quad (14)'$$

The form of eq. (14) is quite the same as Wagner's equation¹¹⁾ which was applicable to a dilute multicomponent solution.

Let us now consider another modification of eq. (11). If eq. (11) is expanded at a point $N_c^* = N_c'$, $N_{j_1}^* = 0$, $N_{j_2}^* = 0, \dots$, it can be written as follows:

$$\begin{aligned} (\ln \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} &= (\ln \gamma_c)_{N_c', 0, 0, \dots} + \left(\frac{\partial \ln \gamma_c}{\partial N_c}\right)_{N_c', 0, 0, \dots} \cdot (N_c - N_c') \\ &+ \sum \left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c', 0, 0, \dots} \cdot N_{j_1} \end{aligned} \quad (15)$$

When the activity of carbon is equal in a binary alloy of iron-carbon and in a multicomponent alloy of iron-carbon- j_1 - j_2 - \dots , i.e.

$$a_c = (\gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} \cdot N_c = (\gamma_c')_{N_c'} \cdot N_c' \quad (16)$$

eq. (17) can be derived from the combination of eq. (15) and (16),

$$\ln N_c' - \ln N_c = \left(\frac{\partial \ln \gamma_c}{\partial N_c}\right)_{N_c', 0, 0, \dots} \cdot (N_c - N_c') + \sum \left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}}\right)_{N_c', 0, 0, \dots} \cdot N_{j_1} \quad (17)$$

If $|N_c' - N_c| \ll 1$, the following equation is approximately valid.

$$\ln N_c - \ln N_c' = \ln \left(1 - \frac{N_c' - N_c}{N_c'}\right) \approx -\frac{N_c' - N_c}{N_c'} \quad (18)$$

Combination of eq. (18) with (17) and rearranging gives

$$\frac{N_c' - N_c}{N_c'} \left\{ \left(\frac{\partial \ln \gamma_c}{\partial N_c} \right)_{N_c', 0, 0, \dots} \cdot N_c' + 1 \right\} = \sum \left(\frac{\partial \ln \gamma_c}{\partial N_{j_1}} \right)_{N_c', 0, 0, \dots} \cdot N_{j_1} \quad (19)$$

Therefore, from eqs. (19) and (5),

$$\frac{N_c' - N_c}{N_c'} = - \sum \left(\frac{d \ln N_c}{d N_{j_1}} \right)_{a_c} \cdot N_{j_1} \quad (20)$$

If the temperature, pressure and the activity of carbon are constant in a ternary alloy iron-carbon- j_1 , the value of $\left(\frac{d \ln N_c}{d N_{j_1}} \right)_{a_c}$ is constant in the range of small N_{j_1} . $(N_c' - N_c)/N_c'$ or $N_c' - N_c$ or, furthermore, N_c/N_c' is, therefore, proportional to N_{j_1} . These relations have been shown to be valid by many experimental data particularly in Turkdogan and his coworkers' reports^{12,13,14}.

Combination of eqs. (16), (18) and (20) gives

$$(\ln \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\ln \gamma_c')_{N_c'} - \sum \left(\frac{d \ln N_c}{d N_{j_1}} \right)_{a_c} \cdot N_{j_1} \quad (21)$$

When common logarithms are used instead of natural logarithms, eqs. (12) and (21) are given as follows:

$$(\log \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\log \gamma_c')_{N_c'} + \sum \left(\frac{\partial \log \gamma_c}{\partial N_{j_1}} \right)_{N_c', 0, 0, \dots} \cdot N_{j_1} \quad (12)'$$

$$(\log \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\log \gamma_c')_{N_c'} - \sum \left(\frac{d \log N_c}{d N_{j_1}} \right)_{a_c} \cdot N_{j_1} \quad (21)'$$

These two equations may be considered to be general approximate equations to calculate the activity coefficient or activity of carbon in a given multicomponent alloy of iron-carbon- j_1 - j_2 - \dots .

The value of $\left(\frac{\partial \log \gamma_c}{\partial N_{j_1}} \right)_{N_c', 0, 0, \dots}$ cannot be obtained directly from the results of the present experiments, but that of $\left(\frac{\partial \log \gamma_c}{\partial N_{j_1}} \right)_{N_c', 0}$ was used instead of $\left(\frac{\partial \log \gamma_c}{\partial N_{j_1}} \right)_{N_c', 0, 0, \dots}$ for the calculation of $(\log \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots}$ in eq. (12)' and the validity of this equation was checked by calculating the difference between the value of a_c calculated by this equation and the theoretical value i.e. $a_c = 0.996$. The comparison are shown in Table 6.

Δa_c in Table 6 is expressed as follows:

$$\Delta a_c = a_c - 0.996$$

When $N_c' = 0.207$, $\log \gamma_c' = 0.682$ according to eq. (7) and also $\log N_c' = 0.684$, therefore, $a_c = 0.996$. This is the reason why the authors used the above relation for the calculation of Δa_c . According to the results of calculation shown in Table 6, the agreement is good for alloys of iron-carbon-molybdenum and iron-carbon-

Table 6. Comparison of values of activity of carbon calculated by eq. (12)' and the theoretical value.

| Heat No. | $(\log \gamma_C)_{N_C, N_{X_0}}$ | $\log N_C$ | Δa_c | Heat No. | $(\log \gamma_C)_{N_C, N_{M_0}}$ | $\log N_C$ | Δa_c |
|----------|---|------------|--------------|----------|---|------------|--------------|
| Mo 03-1 | 0.680 | -0.684 | -0.005 | Mo 02-4 | 0.673 | -0.674 | +0.002 |
| Mo 02-1 | 0.681 | -0.682 | +0.002 | Mo 02-5 | 0.663 | -0.670 | -0.012 |
| Mo 03-2 | 0.684 | -0.680 | +0.013 | Mo 03-5 | 0.658 | -0.668 | -0.019 |
| Mo 01 | 0.686 | -0.678 | +0.023 | Mo 02-6 | 0.654 | -0.662 | -0.014 |
| Mo 02-2 | 0.678 | -0.682 | -0.005 | Mo 03-6 | 0.655 | -0.658 | -0.003 |
| Mo 02-3 | 0.676 | -0.678 | 0 | Mo 02-7 | 0.640 | -0.644 | -0.005 |
| Mo 03-4 | 0.680 | -0.672 | +0.023 | Mo 03-7 | 0.644 | -0.642 | +0.009 |
| Heat No. | $(\log \gamma_C)_{N_C, N_W}$ | $\log N_C$ | Δa_c | Heat No. | $(\log \gamma_C)_{N_C, N_W}$ | $\log N_C$ | Δa_c |
| W 4-1 | 0.684 | -0.682 | +0.009 | W 5-3 | 0.677 | -0.682 | -0.007 |
| W 5-7 | 0.684 | -0.682 | +0.009 | W 4-5 | 0.689 | -0.676 | +0.034 |
| W 5-6 | 0.677 | -0.686 | -0.016 | W 5-2 | 0.677 | -0.680 | -0.003 |
| W 6 | 0.679 | -0.684 | -0.007 | W 4-6 | 0.674 | -0.680 | -0.010 |
| W 4-3 | 0.679 | -0.684 | -0.007 | W 5-1 | 0.673 | -0.678 | -0.007 |
| W 5-4 | 0.680 | -0.682 | 0 | W 4-7 | 0.678 | -0.672 | +0.018 |
| W 4-4 | 0.679 | -0.682 | -0.003 | | | | |
| Heat No. | $(\log \gamma_C)_{N_C, N_{Cu}}$ | $\log N_C$ | Δa_c | Heat No. | $(\log \gamma_C)_{N_C, N_{Cu}}$ | $\log N_C$ | Δa_c |
| Cu 5-1 | 0.686 | -0.686 | +0.004 | Cu 4-4 | 0.705 | -0.690 | +0.039 |
| Cu 4-6 | 0.687 | -0.686 | +0.006 | Cu 5-3 | 0.682 | -0.703 | -0.043 |
| Cu 5-2 | 0.689 | -0.688 | +0.006 | Cu 5-4 | 0.687 | -0.710 | -0.048 |
| Cu 4-5 | 0.688 | -0.690 | 0 | Cu 4-3 | 0.696 | -0.706 | -0.019 |
| Cu 6 | 0.701 | -0.690 | +0.030 | Cu 4-2 | 0.710 | -0.708 | +0.009 |
| Heat No. | $(\log \gamma_C)_{N_C, N_{j_1}, \dots}$ | $\log N_C$ | Δa_c | Heat No. | $(\log \gamma_C)_{N_C, N_{j_1}, \dots}$ | $\log N_C$ | Δa_c |
| Mo2W2Cu0 | 0.683 | -0.674 | +0.025 | Mo2W2Cu2 | 0.677 | -0.693 | -0.032 |
| Mo6W2Cu0 | 0.657 | -0.676 | -0.039 | Mo2W4Cu4 | 0.681 | -0.699 | -0.055 |
| Mo5W5Cu0 | 0.664 | -0.672 | -0.014 | Mo2W2Cu4 | 0.703 | -0.693 | +0.016 |
| Mo0W2Cu2 | 0.674 | -0.704 | -0.063 | Mo2W4Cu2 | 0.672 | -0.693 | -0.043 |
| Mo2W0Cu2 | 0.678 | -0.693 | -0.030 | | | | |

wolfram, but the difference becomes large for alloys of iron-carbon-copper as the content of copper is increased, and is generally even larger for multicomponent alloys.

The values of $(\log \gamma_C)_{N_C, N_{j_1}, N_{j_2}, \dots}$ were also calculated by using eq. (21)' and the values Δa_c thus obtained are shown in Table 7. The values of Δa_c in Table 7 show quite the same tendency as those shown in Table 6, but it is obvious that the former are generally smaller than the latter. It is apparent, therefore, that eq. (21)' is more applicable than eq. (12)'. This is thought to be due to the fact that 1) the value of $\left(\frac{\partial \log \gamma_C}{\partial N_{j_1}}\right)_{N_C', 0, 0, \dots}$

Table 7. Comparison of the values of the activity of carbon calculated by eq. (21)' and the theoretical value.

| Heat No. | Δa_c | Heat No. | Δa_c | Heat No. | Δa_c | Heat No. | Δa_c |
|----------|--------------|----------|--------------|----------|--------------|----------|--------------|
| Mo 03-1 | -0.003 | W 4-1 | +0.004 | Cu 5-1 | +0.002 | Mo2W2Cu0 | +0.009 |
| Mo 02-1 | +0.002 | W 5-7 | +0.004 | Cu 4-6 | +0.002 | Mo5W2Cu0 | -0.014 |
| Mo 03-2 | +0.004 | W 5-6 | -0.005 | Cu 5-2 | +0.002 | Mo5W5Cu0 | -0.005 |
| Mo 01 | +0.006 | W 6 | -0.003 | Cu 4-5 | 0 | Mo0W2Cu2 | -0.021 |
| Mo 02-2 | -0.003 | W 4-3 | -0.003 | Cu 6 | +0.011 | Mo2W0Cu2 | -0.012 |
| Mo 02-3 | 0 | W 5-4 | 0 | Cu 4-4 | +0.013 | Mo2W2Cu2 | -0.012 |
| Mo 03-4 | +0.006 | W 4-4 | 0 | Cu 5-3 | -0.016 | Mo2W4Cu4 | -0.012 |
| Mo 02-4 | 0 | W 5-3 | -0.003 | Cu 5-4 | -0.019 | Mo2W4Cu4 | +0.009 |
| Mo 02-5 | -0.005 | W 4-5 | +0.009 | Cu 4-3 | -0.010 | Mo2W4Cu2 | -0.016 |
| Mo 03-5 | -0.007 | W 5-2 | 0 | Cu 4-2 | +0.002 | | |
| Mo 02-6 | -0.007 | W 4-6 | -0.003 | | | | |
| Mo 03-6 | -0.003 | W 5-1 | -0.003 | | | | |
| Mo 02-7 | -0.005 | W 4-7 | +0.004 | | | | |
| Mo 03-7 | 0 | | | | | | |

were used for the calculation instead of $\left(\frac{\partial \log \gamma_c}{\partial N_{j_1}}\right)_{N_c, 0, 0, \dots}$, and, therefore, the error became greater as the absolute value of $|N_c - N_c'|$ became large, 2) that $\left(\frac{\partial \log \gamma_c}{\partial N_{j_1}}\right)_{N_c, 0}$ is not equal to $\left(\frac{\partial \log \gamma_c}{\partial N_{j_1}}\right)_{N_c, N_{j_1}, N_{j_2}}$ i.e. the interaction parameters are affected by the presence of the fourth element j_2 , 3) that the accuracy of $(\log \gamma_c')_{N_c}$ calculated by Rist and Chipman's equation has not been experimentally confirmed for binary alloys in which the carbon content is comparatively lower than the graphite saturation value.

The interaction parameters that have been reported^{1, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20, 24)} including the present study are shown in Tables 8 and 9. Those which have been experimentally determined by Fuwa and Chipman¹⁵⁾ are the values of $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c, N_j=0}$ in the alloys containing 0.1 to 0.3 pct of carbon, but these may well be considered to be nearly equal to those of $\epsilon_c^{(j)}$ i.e. $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c=0, N_j=0}$. The values in parentheses in Table 8 are values estimated by the authors, the method of estimation being explained later. The values of $-\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ were derived by the authors by calculating the tangents at $N_j \rightarrow 0$ in the figures of $\log N_c$ vs. N_j drawn by using the original data and, therefore, the numerical values are somewhat different from those reported in the original papers. The values of $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c=\text{sat.}, N_j=0}$ were calculated by eq. (5)'. The values superscripted by stars were derived by inter- or extrapolation. The values of N_j in the fourth column are the maximum limit within which $\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ is constant, and the values that have no inequality sign are the maximum content experimentally measured

Table 8. Intraction parameters

| Element j | $\varepsilon_c^{(j)}$ | Temperature °C | References |
|----------------|-----------------------|-------------------|------------|
| C | +11.2*, +9.9† | 1550*, 1560† | 10)*, 15)† |
| Nb | -23.0 | 1580 | 15) |
| V | -8.0 | 1560 | 15) |
| Cr | -4.9 | 1560 | 15) |
| Mo | -3.5*, -0.79† | 1560*, 1600† | 15)*, 16)† |
| Mn | (-2.4) | 1550 | |
| W | -2.3 | 1560 | 15) |
| Co | +2.9 | 1560 | 15) |
| Ni | +2.9 | 1560 | 15) |
| Cu | +4.2 | 1560*, 1600† | 15)*, 8)† |
| Al | +6.7 | 1600 | 17), 18) |
| Si | +10.1 | 1600 | 16) |
| As | (+11) | 1550 | 1) |
| P | (+11) | 1575 | 1) |
| S | +12 | 1560 | 15) |
| Sn | 0.0 | 1560 | 15) |

Symbols "*" and "†" correspond to each other.
(): estimated values.

and the values of $\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ remain constant up to these concentrations.

There are several papers^{6,12,14)} in which the values of $\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ have been taken to be constant and independent of temperature, but a tendency of the absolute value of $\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ to increase as the temperature is lowered is found in Table 9.

If N_c is nearly equal to zero, the first term of the right side in eq. (5) becomes unity, and, therefore, $-\left(\frac{d \ln N_c}{d N_j}\right)_{a_c}$ is equal to $\varepsilon_c^{(j)}$ in case both N_c and N_j tend to zero. When the values of $-\left(\frac{d \ln N_c}{d N_j}\right)_{a_c}$ or $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c, N_j=0}$ are plotted against that of N_c' , Figs. 7 and 8 are derived from Tables 8 and 9. Experimental data at the intermediate range of N_c' have been reported by Richardson and Dennis²¹⁾ and by Ohtani²²⁾ concerning the alloys of iron-carbon-chromium. Ohtani²³⁾ measured, furthermore, the activity of carbon in alloys of iron-carbon-manganese. The values of N_c corresponding to 0, 10 and 23 pct of chromium at constant activities of carbon i.e. 0.01, 0.02, 0.03 and 0.04 were calculated from the curves at 1560°C in Fig. 4 shown in Richardson and Dennis's paper, and the values of $-\left(\frac{d \ln N_c}{d N_{Cr}}\right)$ at constant carbon activities were then calculated. These values are plotted in Fig. 7 by the full points. The points lie a little above the straight line drawn through the two points, one of which is the point corresponding to

Table 9. Values of $-\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ and $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c=\text{sat.}, N_j=0}$ in alloys iron-carbon-*j*.

| Element <i>j</i> | $-\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ | $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c=\text{sat.}, N_j=0}$ | N_j | Temperature °C | References |
|------------------|---|--|--------|----------------|------------------|
| C | +8.9 | — | — | 1550 | 10) |
| Nb | -3.91 | -11.1 | <0.02 | 1580 | 15) |
| | -4.37 | -12.4 | <0.02 | 1620 | 15) |
| V | -2.20 | -6.3 | <0.06 | 1560 | 15) |
| Cr | -1.25 | -3.55 | <0.04 | 1545±10 | 6) |
| Mo | -1.13 | -3.20 | 0.085† | 1550±10 | This study 9) |
| | -0.78 | -2.2 | <0.20 | 1450 | |
| Mn | -0.41 | -1.19 | <0.4 | 1690 | 7), 19) |
| | -0.48* | -1.35 | | 1550 | |
| | -0.51 | -1.43 | <0.3 | 1490 | 7), 19) |
| | -0.54 | -1.51 | <0.15 | 1500±10 | |
| | -0.58 | -1.67 | <0.3 | 1290 | 7), 19) |
| | -0.55 | -1.56 | <0.2 | 1490 | |
| | -0.77 | -2.24 | <0.1 | 1290 | |
| W | -0.46 | -1.31 | 0.048† | 1550±10 | This study 9) |
| | 0 | 0 | 0.041† | 1450 | |
| Co | +0.46 | +1.31 | <0.65 | 1550 | 14) |
| | +0.60 | +1.67 | <0.5 | 1350 | 14) |
| | +0.60 | +1.74 | <0.4 | 1450 | 20) |
| Ni | +0.74 | +2.09 | <0.2 | 1550 | 14) |
| | +1.12 | +3.34 | <0.4 | 1350 | 14) |
| | +0.95 | +2.70 | <0.46 | 1550±10 | 24) |
| | +1.01 | +2.87 | 0.27† | 1550 | 20) |
| | +1.24 | +3.5 | <0.5 | 1450 | 9) |
| Cu | +4.14 | +11.8 | 0.02† | 1600 | 8) |
| | +1.68 | +4.77 | 0.035† | 1550±10 | This study 9) |
| | +2.30 | +6.4 | 0.04† | 1450 | |
| Al | +2.7 | +7.5 | 0.36† | 1600 | 17), 18) |
| Si | +3.91 | +11.2 | <0.08 | 1690 | 7) |
| | +4.19* | +11.9 | | 1550 | |
| | +4.30 | +12.2 | <0.10 | 1490 | 7) |
| | +4.67 | +13.5 | <0.14 | 1290 | 7) |
| | +3.75 | +10.6 | <0.07 | 1540±10 | 6) |
| | +4.61 | +13.1 | 0.085† | 1550 | 20) |
| As | +4.4 | +12.5 | 0.08† | 1550 | 1) |
| P | +4.33 | +12.4 | <0.045 | 1575 | 12) |
| | +4.49 | +12.7 | <0.045 | 1490 | 12) |
| | +4.61 | +13.4 | <0.03 | 1290 | 12) |
| | +4.49 | +12.8 | 0.037† | 1550 | 20) |
| | +4.60 | +13.1 | <0.056 | 1550±10 | 24) |
| S | +3.9* | +11.0 | <0.02† | 1550 | 13) |
| | +3.86 | +10.9 | <0.02† | 1500 | |
| | +3.86 | +10.8 | <0.02† | 1350 | 13) |
| | +3.86 | +10.6 | <0.02† | 1200 | 13) |
| | +3.52 | +10 | <0.03 | 1550±10 | 24) |
| Sn | +6.49 | +18.1 | <0.4 | 1450 | 9) |
| | +7.07 | +20.1 | <0.076 | 1550±10 | 24) |

*: Calculated by inter- or extrapolation.

†: Maximum content measured.

$\epsilon_c^{(Cr)}$ i.e. -4.9 given by Fuwa and Chipman¹⁵⁾ and the other is the point corresponding to $-\left(\frac{d \ln N_c}{dN_{Cr}}\right)$ i.e. -1.25 at the carbon saturated solution given by Sanbongi, Ohtani and Toita⁶⁾. The values of $\left(\frac{\partial \ln \gamma_c}{\partial N_{Cr}}\right)_{N_c}$ were calculated by 1) putting the values of $-\left(\frac{d \ln N_c}{dN_{Cr}}\right)$ into the second term of the right side of eq. (5), and 2) calculating the first term by using eq. (6). The points thus calculated are shown in Fig. 8 by full points. These points lie in this case a little below the straight line drawn through the points corresponding to $\epsilon_c^{(Cr)}$ and $\left(\frac{\partial \ln \gamma_c}{\partial N_{Cr}}\right)$

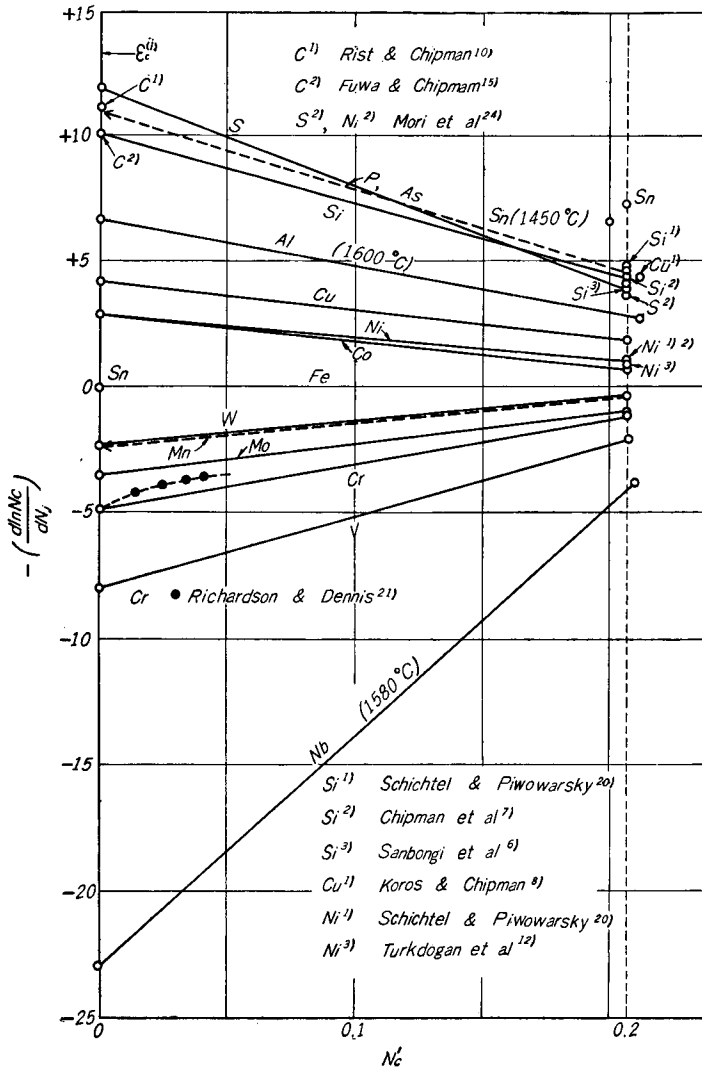


Fig. 7. Relation between N_c' and $-\left(\frac{d \ln N_c}{dN_j}\right)$.

i.e. -3.55 for the carbon saturated solution. The values of a_c and N_{Cr} corresponding to $0.04 N_c$ were also calculated from Richardson and Dennis's Fig. 4, and then the values of $\log \gamma_c$ were calculated from those values, and $\left(\frac{\partial \ln \gamma_c}{\partial N_{Cr}}\right)$ was, furthermore, calculated directly from these data. The results thus obtained are shown in Fig. 8 by the mark " \ddagger ". The triangular full point is the mean value, and the mark " \lceil " shows its range. Similar calculations were made from the a_c , N_c and N_{Cr} relation diagram concerning the alloys iron-carbon-chromium given by

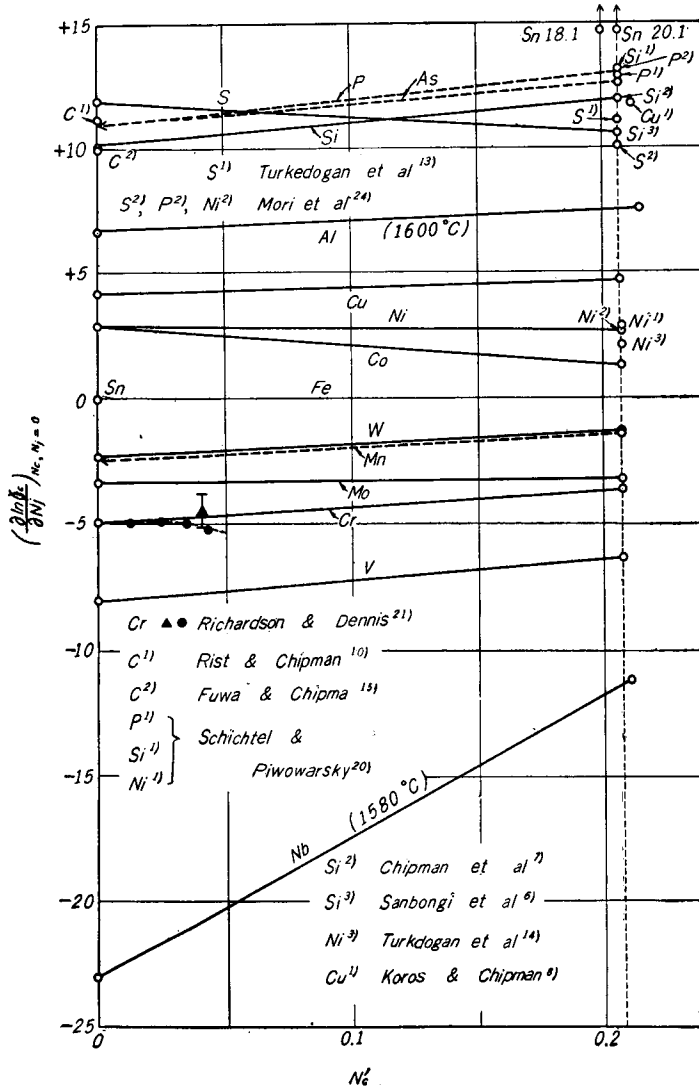


Fig. 8. Relation between N_c' and $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c, N_j=0}$.

Ohtani²²⁾, but the results are scattered because of the small figure of his original paper, and, therefore, these results are not shown in the authors' figures. The change of the value of the interaction parameter is not always shown by a straight line drawn through the point $\varepsilon_c^{(Cr)}$ and the point $\left(\frac{\partial \ln \gamma_c}{\partial N_{Cr}}\right)$ for the carbon saturated solution. Generally speaking, this line is expected to be a curved line, but the data available for the discussion are limited to the above two papers^{21,22)}, and, therefore, all the lines are shown by straight lines in Fig. 8. Quite the same discussion can be applied to Fig. 7. The broken lines in these two figures are the estimated ones based on the values of $-\left(\frac{d \ln N_c}{d N_j}\right)$ for the carbon saturated solution. The values of $\varepsilon_c^{(j)}$ for infinite dilution estimated by these broken lines are shown in Table 8 with parentheses.

Large differences are apparent between the values of the interaction parameter of tin in dilute solution reported by Fuwa and Chipman and those at carbon saturation by Fuwa, Fujikura and Matoba and by Mori et alli, and also among the values for the interaction parameter of copper reported by Koros and Chipman, Fuwa, Fujikura and Matoba and the present study. Further experimental study is desirable concerning these values.

Let us now consider the equation expressing the relation between the concentrations of carbon and the added element at carbon saturation. Substitution of the values of eq. (9) and $N_c' = 0.207$ into eq. (20) gives

$$\left. \begin{aligned} N_c &= 0.207 + 0.234 N_{Mo} \\ N_c &= 0.207 + 0.095 N_W \\ N_c &= 0.207 - 0.348 N_{Cu} \end{aligned} \right\} \quad (22)$$

If the weight per centages are used instead of the molar fractions, eq. (22) can be expressed as follows:

$$\left. \begin{aligned} [\%C] &= 5.31 + 0.013 [\%Mo] \\ [\%C] &= 5.31 - 0.030 [\%W] \\ [\%C] &= 5.31 - 0.085 [\%Cu] \end{aligned} \right\} \quad (23)$$

Eqs. (22) and (23) show that the activity of carbon is increased by the addition of molybdenum and is decreased by the addition of copper. Wolfram shows somewhat different behaviour because it decreases the activity of carbon when the relation between the concentrations of carbon and wolfram are expressed as molar fractions, while it increases the activity of carbon when the relation between those two elements are expressed as weight per centages.

The interaction parameters at infinite dilution have the following relation:

$$\left(\frac{\partial \log f_c}{\partial \%j}\right)_{\%C=0, \%j=0} = \frac{0.2425}{M_j} \left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c=0, N_j=0} \quad (24)$$

where f_c is the activity coefficient of carbon, the reference state being at infinite dilution. These two parameters have, therefore, the same sign. But when the concentration of carbon is high such as in the present study, eq. (24) is not adequate, while eq. (25) is generally valid between f_c and γ_c .

$$f_c = \frac{\gamma_c}{\gamma_c^\circ} \frac{1}{\frac{\%C}{M_c} + \frac{\%j}{M_j} + \frac{100 - \%C - \%j}{M_{Fe}}} \frac{100}{M_{Fe}} \quad (25)$$

where γ_c° is the activity coefficient of carbon at infinite dilution when the activity is expressed as molar fraction. Partial differentiation of $\ln f_c$ by $\%j$ gives

$$\begin{aligned} \frac{\partial \ln f_c}{\partial \%j} &= \frac{\partial \ln \gamma_c}{\partial N_j} \frac{1}{M_j} \left(\frac{\%C}{M_c} + \frac{\%j}{M_j} + \frac{100 - \%C - \%j}{M_{Fe}} \right) - \frac{\%j}{M_j} \left(\frac{1}{M_j} - \frac{1}{M_{Fe}} \right) \\ &\quad - \frac{\frac{1}{M_j} - \frac{1}{M_{Fe}}}{\left(\frac{\%C}{M_c} + \frac{\%j}{M_j} + \frac{100 - \%C - \%j}{M_{Fe}} \right)^2} \end{aligned} \quad (26)$$

Calculation of eq. (26) for the conditions $\%j = 0$, $\%C = 5.31$, $M_j = M_W$ and $\left(\frac{\partial \ln \gamma_c}{\partial N_W} \right)_{N_c=0, 20\%}^{N_W=0} = -1.31$ gives

$$\left(\frac{\partial \log f_c}{\partial \%W} \right)_{\%C=5.31, \%W=0} = +0.0011 \quad (27)$$

Eq. (27) shows that the activity coefficient of carbon becomes larger than unity by the addition of wolfram. Alloys whose interaction parameters have opposite signs such as iron-carbon-wolfram have not been known besides wolfram, but such a case can occur when the value of $\left(\frac{\partial \ln \gamma_c}{\partial N_j} \right)$ is negative and of comparatively small absolute value together with a large difference between the atomic weights of the added element and the solvent iron.

The activity of carbon in multicomponent alloys iron-carbon- j_1 - j_2 -... kept at 1550°C can generally be calculated by eq. (12)'. Though calculation by eq. (21)' gives a more correct value than eq. (12)', eq. (21)' cannot be used because $(\log \gamma_c')_{N_c}$ is generally unknown.

Calculation by eq. (12)' can be performed as follows:

- 1) Calculate the molar fractions N_c , N_{j_1} , N_{j_2} , ... by chemical analyses.
- 2) Calculate the value of $(\log \gamma_c')_{N_c}$ by the equation of $\log \gamma_c'$ such as given in eq. (7).
- 3) Find the interaction parameters of each added element which correspond to the value of N_c by using Fig. 8, and then calculate the second term of the

right side of eq. (12)'.

- 4) The activity of carbon can be calculated by the relation $a_c = \gamma_c \cdot N_c$ into which the value of γ_c obtained from eq. (12)' and that of N_c should be introduced.

The straight lines shown in Fig. 8 are all estimated lines and not observed ones, and, therefore, it is necessary to determine the values of interaction parameters in the intermediate range of the concentration of carbon by experiment for the purpose of acquiring accurate values of the activity coefficient of carbon by eq. (12)'.

6. Summary

(1) The solubility change of graphite in alloys iron-carbon-molybdenum, iron-carbon-wolfram, iron-carbon-copper, iron-carbon-molybdenum-wolfram, iron-carbon-wolfram-copper, iron-carbon-molybdenum-copper and iron-carbon-molybdenum-wolfram-copper was measured at 1550°C.

(2) The relations between the solubility of graphite and the concentration of the added elements at 1550°C are given as follows:

$$\begin{aligned} \text{Fe-C-Mo : } \quad N_c &= 0.207 + 0.234 N_{Mo} \\ [\%C] &= 5.31 + 0.013 [\%Mo] \end{aligned}$$

$$\begin{aligned} \text{Fe-C-W : } \quad N_c &= 0.207 + 0.095 N_W \\ [\%C] &= 5.31 - 0.030 [\%W] \end{aligned}$$

$$\begin{aligned} \text{Fe-C-Cu : } \quad N_c &= 0.207 - 0.348 N_{Cu} \\ [\%C] &= 5.31 - 0.085 [\%Cu] \end{aligned}$$

(3) The interaction parameters of carbon by the added elements at 1550°C and at graphite saturation are given as follows:

$$\left(\frac{\partial \ln \gamma_c}{\partial N_{Mo}} \right)_{N_c' = 0.207} = -3.20$$

$$\left(\frac{\partial \ln \gamma_c}{\partial N_W} \right)_{N_c' = 0.207} = -1.31$$

$$\left(\frac{\partial \ln \gamma_c}{\partial N_{Cu}} \right)_{N_c' = 0.207} = +4.77$$

(4) The activity of carbon is decreased by the addition of molybdenum and is increased by the addition of copper. Wolfram decreases the activity of carbon when the relation between the content of wolfram and the solubility of graphite in the alloys iron-carbon-wolfram is expressed in molar fractions, while it increases the activity of carbon when the relation is expressed in weight per centages. An explanation was offered.

(5) The general equation applicable to the calculation of the activity of

carbon in a multicomponent alloy iron-carbon- j_1 - j_2 -... can be given as follows :

$$(\log \gamma_c)_{N_c, N_{j_1}, N_{j_2}, \dots} = (\log \gamma_c)_{N_c} + \sum \left(\frac{\partial \log \gamma_c}{\partial N_{j_1}} \right)_{N_c, 0, 0, \dots} \cdot N_{j_1}$$

The validity of this equation was discussed by using the present experimental data.

(6) The values of $-\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ and $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c=\text{sat.}, N_j=0}$ in alloys of iron-carbon- j at graphite saturation were summarized by using the present data and other reported data and the relation between $-\left(\frac{d \ln N_c}{d N_j}\right)_{a_c=1}$ or $\left(\frac{\partial \ln \gamma_c}{\partial N_j}\right)_{N_c=\text{sat.}, N_j=0}$ and the interaction parameter $\varepsilon_c^{(j)}$ at infinite dilution was explained with the aid of two figures.

References

- 1) H. Sawamura, T. Mori, H. Kobayashi and T. Miyashita; SUIYŌ KWAISHI, **13**, 771-774 (1959).
- 2) JIS G 1211 (1953), Analytical Method of Carbon in Iron and Steel.
- 3) JIS G 1218 (1954), Analytical Method of Molybdenum in Iron and Steel.
- 4) O. Kamimori and K. Mukaewaki; GAKUSAIN 19th Committee, Report No. 2679 Nov. (1952).
- 5) JIS G 1219 (1954), Analytical Method of Copper in Iron and Steel.
- 6) K. Sanbongi, M. Ohtani and K. Toita; SENKEN IHŌ, **12**, 97-106 (1956).
- 7) J. Chipman, K. M. Alfred, L. W. Gott, R. B. Small, D. M. Wilson, C. N. Thomson, D. L. Guernsey and J. C. Fulton; Trans. Amer. Soc. Metals, **44**, 1215-1230 (1952).
- 8) P. Koros and J. Chipman; J. of Metals, **8**, 1102-1104 (1956).
- 9) T. Fuwa, M. Fujikura and S. Matoba; GAKUSHIN 19th Committee, Report No. 5430 Apr. (1959), see TETSU TO HAGANE **46**, 235-237 (1960).
- 10) A. Rist and J. Chipman; Rev. de Métallurgie, **53**, 796-807 (1956).
- 11) C. Wagner; "Thermodynamics of Alloys" **51**, (1952).
- 12) E. T. Turkdogan and L. E. Leake; J. Iron and Steel Inst., **179**, 39-43 (1955).
- 13) E. T. Turkdogan and R. A. Hancock; *ibid.*, **179**, 155-159 (1955).
- 14) E. T. Turkdogan, R. A. Hancock, S. I. Herlitz and J. Dentan; *ibid.*, **183**, 69-72 (1956).
- 15) T. Fuwa and J. Chipman; Trans. Meta. Soc. ATME, **215**, 708-716 (1959).
- 16) J. Chipman; J. Iron and Steel Inst., **180**, 97-106 (1955).
- 17) T. P. Floridis and J. Chipman; Acta Metallurgica, **3**, 456-459 (1955).
- 18) T. Mori; SUIYŌ KWAISHI **13**, 139-141 (1956).
- 19) Discussion by R. G. Ward; J. Iron and Steel Inst., **184**, 52-57 (1956).
- 20) K. Schichtel and E. Piwowsky; Arch. Eisenhüttenw., **3**, 139-147 (1929/30).
- 21) F. D. Richardson and W. E. Dennis; J. Iron and Steel Inst., **175**, 257-263 (1953).
- 22) M. Ohtani; TETSU TO HAGANE, **42**, 1095-1101 (1956).
- 23) M. Ohtani; *ibid.*, **43**, 1211-1215 (1957).
- 24) T. Mori, T. Ogasawara, H. Hasegawa, T. Hatakeyama and T. Yamada; *ibid.*, **46**, 1147-1150 (1960).