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Effects of Aluminium, Sulphur and Vanadium on the Solubility of Graphite in Liquid Iron

By

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The effects of aluminium and sulphur on the solubility of graphite in liquid iron were studied at 1550°C, and that of vanadium at 1350°, 1450° and 1550°C.

The activity of carbon is increased by the presence of aluminium or sulphur, while it is decreased by the addition of vanadium.

The interaction parameters at a constant concentration N_C' of graphite saturation at the above-mentioned temperatures are given as follows:

$$\left(\frac{\partial \ln \gamma_C}{\partial N_{Al}}\right)_{N_C'} = 6.93, \quad \left(\frac{\partial \ln \gamma_C}{\partial N_S}\right)_{N_C'} = 13.8 \quad \text{at} \quad 1550^{\circ}\text{C},$$

$$\left(\frac{\partial \ln \gamma_C}{\partial N_V}\right)_{N_C'} = -4.87 \quad \text{at} \quad 1550^{\circ}\text{C},$$

$$\left(\frac{\partial \ln \gamma_C}{\partial N_V}\right)_{N_C'} = -4.77 \quad \text{at} \quad 1450^{\circ}\text{C},$$

$$\left(\frac{\partial \ln \gamma_C}{\partial N_V}\right)_{N_C'} = -4.52 \quad \text{at} \quad 1350^{\circ}\text{C},$$

where γ_C is the activity coefficient of carbon, N_X is the molar fraction of the added element.

1. INTRODUCTION

One of the authors has investigated the effects of arsenic1), copper2), molybdenum2), nickel3), phosphorus3), sulphur4), tin1),3) and wolfram2) on the solubility of graphite in liquid iron at 1550°C. The present study was performed as one of the series in this investigation to know the effects of aluminium, sulphur and vanadium on the solubility of graphite in liquid alloys iron-carbon-aluminium, iron-carbon-sulphur and iron-carbon-vanadium; moreover solubility measurements were made concerning the alloy iron-carbon-aluminium-sulphur.

2. METHOD OF THE EXPERIMENT

2. 1. Materials

Basic electric furnace pure iron was used as a raw material, the pure iron

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was charged into a graphite Tammann tube which contained small pieces of graphite (ash content $<0.01\%$) and it was melted in vacuum by using a high-frequency induction furnace and then cast into a dry sand mould of a cylindrical type ca. 10 mm ϕ and ca. 150 mm long at about 1600°C. An example of the chemical composition of the mother alloys iron-carbon thus manufactured is shown in Table 1.

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

C	Si	Mn	P	S	Cu	Ni	Cr	ΣAl	H	O	N
~4.35	0.022	0.017	0.005	0.010	0.016	0.03	0.0013	0.002	0.0002	0.0055	0.0012

The chemical composition of the mother alloys used in this investigation was almost the same as shown in Table 1 except for the slight change in carbon content. The purity of metallic aluminium and vanadium used as additional elements is respectively 99.99 pct and 99.7 pct. Sulphur was added as a mother alloy iron-sulphur which was made from pure iron and crystal sulphur under an atmosphere of dried argon gas using a magnesia crucible. A Tammann furnace was used for melting the mother alloys iron-sulphur.

2. 2. Experimental apparatus

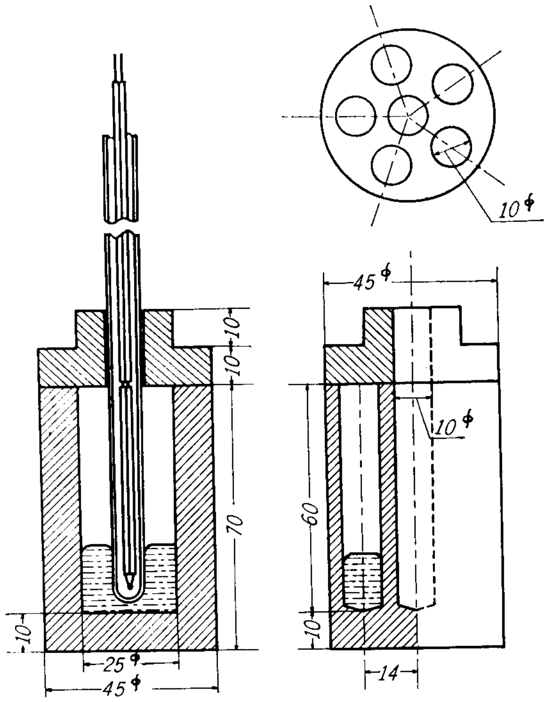
Samples were melted in the Tammann furnace, the resistance body of which is a graphite tube of 60 mm i.d. and 300 mm long. Cryptol grains were charged as a crucible supporter in order to keep the liquid alloys at the middle height of the furnace, and after the required amounts of the mother alloy and the added metal were charged into the graphite crucible, the crucible was then put into the Tammann furnace. Dried argon gas was led into the furnace atmosphere from the bottom of the furnace and after the air in the furnace was almost replaced by the argon gas the charge was melted under the average flow rate of 75 cc/min argon gas.

The temperature of the liquid alloys was measured by a Pt–PtRh thermocouple which was calibrated by measuring the melting points of electrolytic nickel and pure iron, or paradium and platinum by means of the wire-method. The thermocouple was put into a fused alumina tube and then it was inserted into the crucible as shown in Fig. 1(a). In the case of using the multi-hole crucible shown in Fig. 1(b), the thermocouple was inserted into the center hole which contained the molten mother alloy iron-carbon. Crucibles used in this experiment were made of high purity graphite. The crucible shown in Fig. 1(a) was used to measure the solubility of graphite in the binary alloy iron-carbon and to determine the holding time necessary to attain equilibrium in liquid ternary alloys, and the other crucible shown in Fig. 1(b) was used to measure the solubility of graphite in the alloys iron-carbon-aluminium, iron-carbon-sulphur, iron-carbon-aluminium-sulphur and iron-carbon-vanadium.

2. 3. Experimental procedure

2. 3. 1. Temperature measurements

The mother alloy iron-carbon was charged into the center hole of the crucible [Fig. 1(b)] to measure the temperature of the liquid alloys, and the temperature difference between the center hole and the outside holes was not recognized.



(a) (b)

Fig. 1. Shape of graphite crucibles.

The liquid alloys were kept at each constant temperature within a range of temperature deviation ±5° to 10°C throughout the experiments.

After melting samples at 1350°, 1450° and 1550°C, the carbon content of the liquid mother alloy in the center hole was analysed to check the accuracy of the holding temperature. The carbon content in the binary alloys iron-carbon was, for example, 4.78 pct and 4.80 pct at 1350°C, 5.01 pct and 5.04 pct at 1450°C, 5.25 pct and 5.24 pct at 1550°C. These values are in good agreement with that of the solubility of graphite in the binary alloys at each temperature as shown in the later section.

2. 3. 2. Solubility of graphite in alloys iron-carbon and determination of the holding time to attain equilibrium in alloys iron-carbon-aluminium, iron-carbon-sulphur and iron-carbon-vanadium

The mother alloy iron-carbon weighing ca. 100 g was charged into a crucible [Fig. 1(a)] which was put in the Tammann furnace and then heated up to the holding temperature. The molten alloy was agitated by a graphite rod and after being kept for a definite time at that temperature, sampling of about 10 g was made by using a silica suction tube of 4 mmϕ. The sample thus taken was rapidly quenched into water to prevent graphitization. The surface of the sample was ground and then it was broken to several small pieces of about 0.3 to 0.4 g, and after crushing the piece into fine particles the whole particles were used for carbon analysis.

The holding time for the alloy series iron-carbon-aluminium necessary to attain equilibrium was examined by sampling and analysing the specimens taken from the ternary alloy containing ca. 3.7 pct aluminium at 1550°C. The procedure is quite the same in the case of the alloy iron-carbon-sulphur. The content of sulphur was selected as ca. 0.7 pct in this case. The holding time was determined at 1350°C in the case of the alloy series iron-carbon-vanadium, because the higher the temperature of the liquid alloy becomes, the greater the diffusion velocity of the dissolved element in the alloy is. Two levels of vanadium content were examined to determine the holding time for the vanadium containing ternary alloys.

2.3.3. Solubility of graphite in alloys iron-carbon-aluminium, iron-carbon-sulphur, iron-carbon-vanadium and iron-carbon-aluminium-sulphur

The mother alloy and the added metal were charged into the outside holes of the above-mentioned crucible. The total weight of each charge was 8 to 10 g. The mother alloy weighing ca. 10 g was charged into the center hole, and then the crucible was put in the Tammann furnace. After dissolving the charge under an atmosphere of argon gas, the molten alloys were thoroughly agitated by a graphite rod. After being kept for a required time at a constant temperature the crucible was pulled out as soon as possible with tongs and was quenched into water. The samples thus obtained were analysed for equilibrium content of carbon and added element.

3. METHOD OF ANALYSIS

Combustion and gravimetric method corresponding to JIS G 1211[5] was applied for the determination of carbon. The standard sample No. 6 was analysed to check the accuracy of analysis before and after the analysis of samples.

The gravimetric method of oxine precipitates corresponding to JIS G 1224[6] was used for the analysis of aluminium. A standard sample containing 0.79 pct aluminium which was prepared in the authors' laboratory was frequently analysed to check the accuracy of analysis.

Combustion and volumetric method which is a modification[7] of JIS G 1215[8] was applied for the determination of sulphur. A standard sample containing 0.61 pct sulphur which was prepared in the authors' laboratory was analysed before and after the analysis of samples.

The quantitative method⁹⁾ of oxidizing vanadium with perchloric acid was applied for the determination of vanadium. A standard sample containing 3.82 pct vanadium was frequently analysed to check the accuracy of analysis.

4. RESULTS OF THE EXPERIMENT

4.1. Solubility of graphite in the alloy iron-carbon at 1350°, 1450° and 1550°C

The relation between the carbon content of liquid iron and the holding time at 1350°, 1450° and 1550°C are shown in Fig. 2. The solubility of graphite at 1550°C was determined to be 5.29 pct. The mother alloy used for the experiments contained 0.022 pct silicon and 0.01 pct sulphur as impurities, and therefore the authors calibrated the molar fraction N'_{c} of the solubility of graphite at 1550°C as 0.2068 (i.e. 5.31 wt. pct). By applying the above-mentioned calibration, the solubility of graphite at 1450°C and at 1350°C were determined respectively to be 5.03 pct ($N'_{c}=0.1976$) and 4.80 pct ($N'_{c}=0.1899$). All of the results of the analyses for carbon concentration shown later were calibrated in view of the effects of silicon and sulphur.

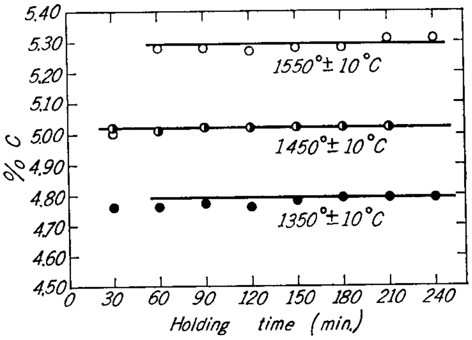


Fig. 2. Relation between the carbon content and the holding time in alloys Fe-C at 1350°, 1450° and 1550°C.

4.2. Relation between the holding time and the chemical composition of the alloys iron-carbon-aluminium, iron-carbon-sulphur and iron-carbon-vanadium

Results of the experiments are shown in Fig. 3 to 6. Complete equilibrium conditions were found to be attained within 1.5 hrs for the alloy iron-carbon-aluminium, within 2.5 hrs for the alloy iron-carbon-sulphur and within 3 hrs for the alloy iron-carbon-vanadium, but the holding times were determined to be 2.5 hrs for the alloy iron-carbon-aluminium and 4 hrs for the alloy iron-carbon-sulphur. E. T. Turkdogan and R. A. Hancock¹⁰⁾ kept the alloy iron-carbon-sulphur for more than 4 hrs, while T. Fuwa and J. Chipman¹¹⁾ kept it for 3 to 4 hrs and T. Hatakeyama⁴⁾ selected 3 or 4 hrs as the holding time. The holding time for the alloy iron-carbon-vanadium was determined to be 3 hrs from the results shown in Fig. 5 and Fig. 6. Though the vanadium content for 3 hrs in Fig. 5 was somewhat higher than the average value, it seemed to be due to insufficient agitation of the molten alloy.

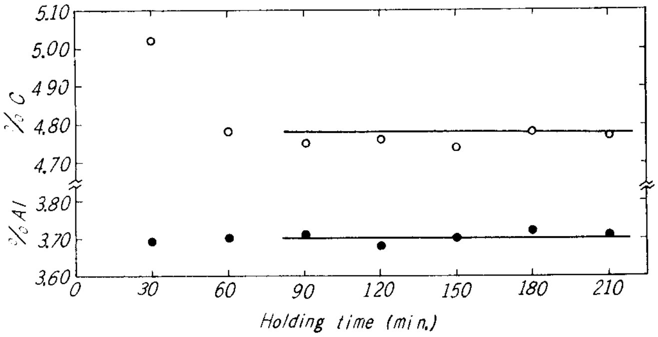


Fig. 3. Relation between the chemical composition of the alloy Fe-C-Al and the holding time at 1550°C.

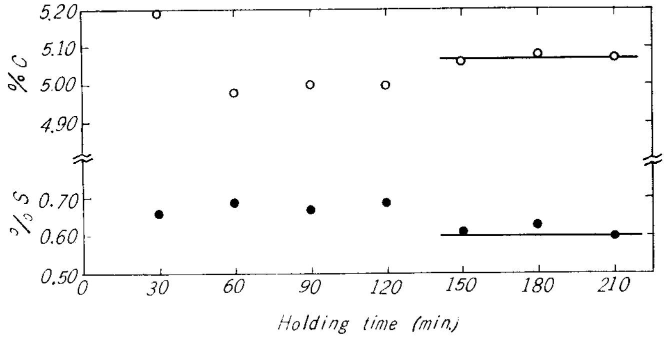


Fig. 4. Relation between the chemical composition of the alloy Fe-C-S and the holding time at 1550°C.

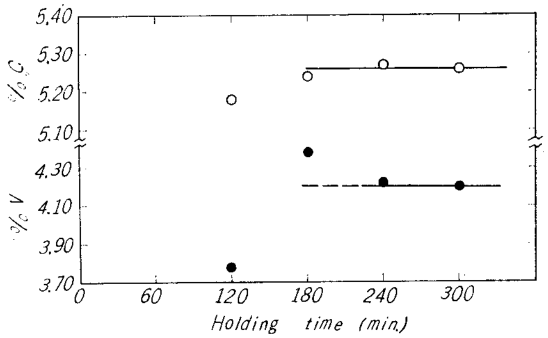


Fig. 5. Relation between the chemical composition of the alloy Fe-C-V and the holding time at 1350°C.

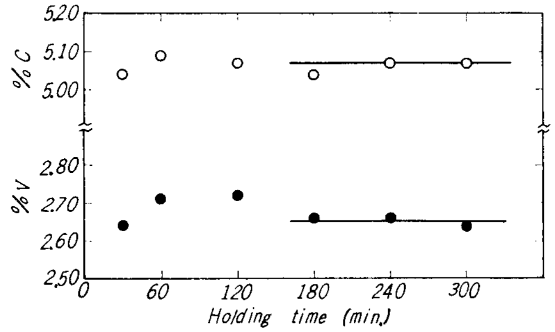


Fig. 6. Relation between the chemical composition of the alloy Fe-C-V and the holding time at 1350°C.

4.3. Solubility of graphite in the alloy iron-carbon-aluminium at 1550°C

Results of the experiments are shown in Table 2 and Fig. 7. The line in Fig. 7 was drawn by the method of least squares through the point (Al=O pct, C=5.31 pct) from the point of view that there was a quadratic relation between the weight percent aluminium and weight percent carbon. This relation is expressed as follows:

Table 2. Solubility of graphite in liquid alloys Fe-C-Al at 1550°±10°C.

Heat No.	C			Al	
	wt %	N_C	log N_C	wt %	N_{Al}
C-C	5.31	0.2068	−0.684	0	0
Al-1-1	5.12	0.199	−0.702	0.98	0.0170
Al-5-2	5.06	0.193	−0.714	2.99	0.0509
Al-3-1	4.67	0.180	−0.745	3.33	0.0572
Al-2-2	4.62	0.178	−0.749	3.53	0.0606
Al-0	4.78	0.183	−0.737	3.70	0.0631
Al-5-4	4.36	0.168	−0.776	4.73	0.0810
Al-2-3	4.16	0.159	−0.799	6.20	0.1054
Al-3-2	4.18	0.160	−0.797	7.60	0.1292
Al-2-5	3.89	0.148	−0.829	8.11	0.1393
Al-5-5	3.78	0.143	−0.845	8.49	0.1431
Al-1-3	3.74	0.142	−0.849	8.52	0.1437
Al-3-3	3.36	0.125	−0.905	12.13	0.2005
Al-4-1	3.26	0.121	−0.917	12.51	0.2068
Al-4-2	3.08	0.114	−0.944	14.05	0.2315
Al-4-5	2.53	0.092	−1.035	17.00	0.2762
Al-3-4	2.74	0.099	−1.002	17.27	0.2783
Al-4-3	2.69	0.097	−1.015	18.42	0.2945

N: Molar fraction

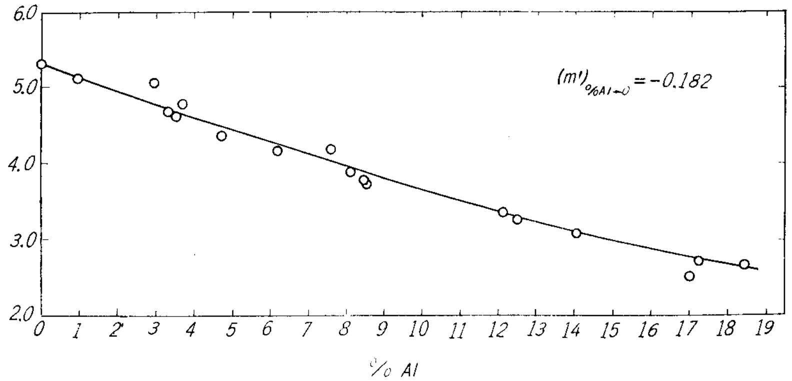


Fig. 7. Effect of aluminium on the solubility of graphite in liquid alloys Fe-C-Al at 1550°C.

$$(\%C) = 5.31 - 0.1824(\%Al) + 0.001685(\%Al)^2$$

The slope (m') of the line at zero concentration of aluminium is calculated to be ca. -0.182 from the above equation.

4.4. Solubility of graphite in the alloy iron-carbon-sulphur at 1550°C

Results of the experiments are shown in Table 3 and Fig. 8. The line in Fig. 8 was drawn through the point (S=O pct, C=5.31 pct) by the method of

Table 3. Solubility of graphite in liquid alloys Fe-C-S at 1550°±10°C.

Heat No.	C			S	
	wt %	N_C	log N_C	wt %	N_S
C-1	5.31	0.2068	−0.6844	0	0
S- 8-1	5.27	0.2053	−0.6882	0.11	0.00161
S- 8-3	5.24	0.2043	−0.6904	0.15	0.00219
S-10-3	5.10	0.1993	−0.7011	0.46	0.00674
S- 6-2	5.15	0.2009	−0.6968	0.53	0.00775
S- 0	5.07	0.1981	−0.7033	0.60	0.00878
S- 9-3	4.89	0.1917	−0.7167	1.05	0.01541
S- 6-4	4.91	0.1922	−0.7167	1.09	0.01598
S-11-3	4.86	0.1904	−0.7212	1.26	0.01849
S- 9-1	4.80	0.1884	−0.7258	1.27	0.01867
S- 9-2	4.88	0.1910	−0.7190	1.31	0.01921
S-12-4	4.75	0.1865	−0.7282	1.46	0.02147
S- 6-5	4.70	0.1846	−0.7328	1.59	0.02340
S-12-1	4.66	0.1833	−0.7375	1.63	0.02401
S-12-3	4.68	0.1838	−0.7352	1.73	0.02545
S-12-2	4.56	0.1796	−0.7447	1.89	0.02788
S- 7-5	4.73	0.1851	−0.7328	2.04	0.02991

N: Molar fraction

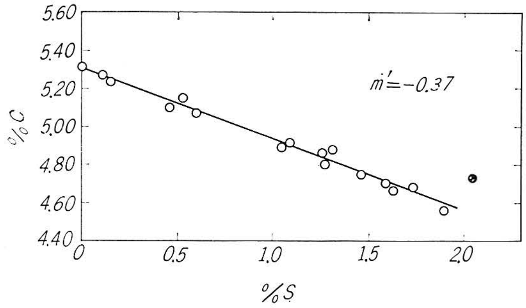
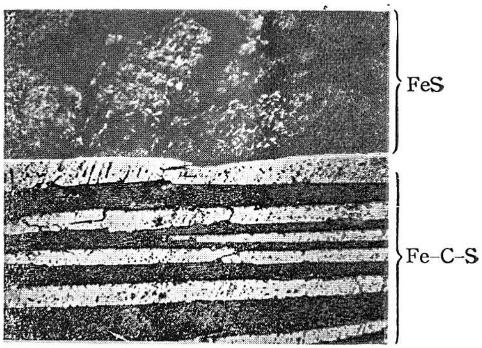


Fig. 8. Effect of sulphur on the solubility of graphite in liquid alloys Fe–C–S at 1550°C.



Picral etch ×100

Fig. 9. Micro-structure of the sulphur saturated alloy Fe–C–S at the phase boundary.

least squares from the point of view that the relation between the weight percent sulphur and that of carbon was linear. The slope (m') is -0.37. The sample containing 2.04 pct sulphur and 4.73 pct carbon separated into two layers, the upper layer of which was the sulphur rich phase and the lower layer the carbon rich phase. The micro-photograph of the quenched specimen is shown in Fig. 9. The phase boundary is clearly shown in the photograph.

4. 5. Solubility of graphite in the alloy iron-carbon-vanadium at 1550°, 1450° and 1350°C

The relations between the content of carbon and that of vanadium are shown in Table 4 to 6 and also in Fig. 10. The slopes (m') in Fig. 10 were

Table 4. Solubility of grlphite in liquid alloys Fe–C–V at 1550°±10°C.

Heat No.	C			V	
	wt %	N_C	log N_C	wt %	N_V
C–1	5.31	0.2068	−0.6844	0	0
15–3–3	5.37	0.2087	−0.6805	0.41	0.00376
15–1–5	5.44	0.2109	−0.6759	0.72	0.00658
15–3–5	5.52	0.2134	−0.6718	1.45	0.01321
15–1–3	5.55	0.2143	−0.6690	1.75	0.01593
15–3–1	5.58	0.2151	−0.6673	2.61	0.02372
15–1–1	5.59	0.2153	−0.6669	3.15	0.02861
15–2–5	5.68	0.2181	−0.6613	3.73	0.03377
15–3–2	5.71	0.2190	−0.6595	3.98	0.03599
15–2–4	5.85	0.2234	−0.6520	4.50	0.04050
15–3–4	5.89	0.2245	−0.6488	5.08	0.04565
15–1–2	5.86	0.2236	−0.6506	5.20	0.04677
15–2–3	5.87	0.2238	−0.6502	5.76	0.05176
15–1–4	5.94	0.2259	−0.6461	6.04	0.05415
15–2–2	6.03	0.2286	−0.6410	6.91	0.06175
15–2–1	6.20	0.2337	−0.6314	7.67	0.06815

N: Molar fraction

Table 5. Solubility of graphite in liquid alloys Fe-C-V at 1450°±10°C.

Heat No.	C			V	
	wt %	N_C	log N_C	wt %	N_V
C-2	5.03	0.1976	−0.7042	0	0
14-1-1	5.05	0.1982	−0.7029	0.32	0.00296
14-2-2	5.10	0.1998	−0.6993	0.56	0.00517
14-2-5	5.18	0.2024	−0.6949	1.30	0.01197
14-2-4	5.21	0.2032	−0.6920	1.90	0.01747
14-1-2	5.33	0.2071	−0.6839	2.37	0.02171
14-1-5	5.27	0.2050	−0.6882	2.91	0.02669
14-1-3	5.40	0.2092	−0.6794	3.23	0.02950
14-1-4	5.48	0.2116	−0.6746	4.62	0.04205
14-2-3	5.55	0.2137	−0.6701	5.05	0.04585

N: Molar fraction

Table 6. Solubility of graphite in liquid alloys Fe-C-V at 1350°±10°C.

Heat No.	C			V	
	wt %	N_C	log N_C	wt %	N_V
C-3	4.80	0.1899	−0.7214	0	0
13-2-1	4.82	0.1905	−0.7200	0.36	0.00336
13-1-5	4.85	0.1915	−0.7178	0.55	0.00512
13-1-3	4.95	0.1948	−0.7105	1.16	0.01076
13-2-3	4.95	0.1947	−0.7107	1.67	0.01548
13-1-2	5.00	0.1963	−0.7071	2.11	0.01953
13-1-4	5.02	0.1969	−0.7068	2.59	0.02394
C-V-10	5.07	0.1985	−0.7022	2.65	0.02446
13-2-5	5.14	0.2007	−0.6975	3.36	0.03093
13-2-2	5.14	0.2007	−0.6975	3.65	0.03359
C-V-5	5.26	0.2045	−0.6893	4.15	0.03804
13-1-1	5.16	0.2012	−0.6965	4.63	0.04255
13-2-4	5.27	0.2047	−0.6889	4.97	0.04551

N: Molar fraction

calculated by the method of least squares as mentioned above, and these are 0.106 at 1550°C, 0.102 at 1450°C and 0.094 at 1350°C respectively.

4.6. Solubility of graphite in the alloy iron-carbon-aluminium-sulphur at 1550°C

The solubility of graphite in the quaternary alloys are shown in Table 7. Each heat was kept for 4.5 hrs at 1550°C before sampling.

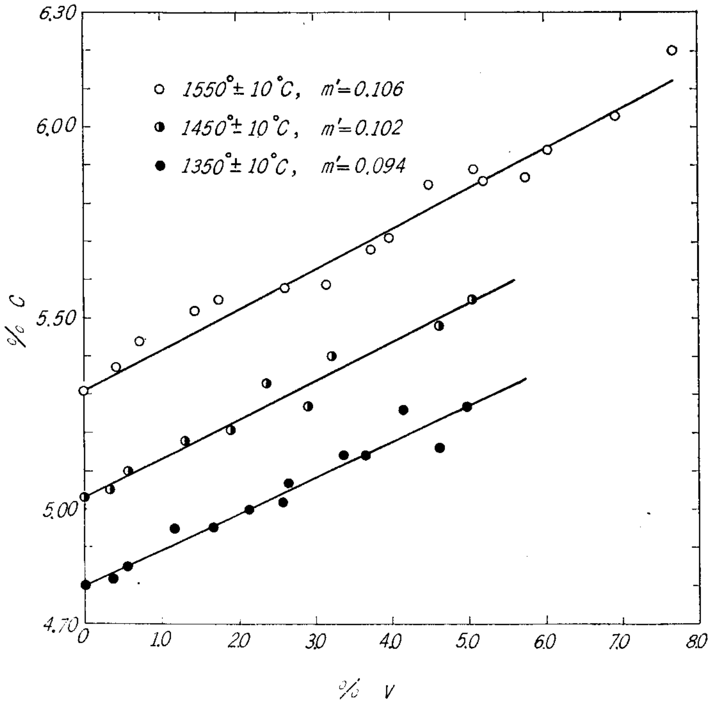


Fig. 10. Effect of vanadium on the solubility of graphite in liquid alloys Fe–C–V at 1350°, 1450° and 1550°C.

Table 7. Solubility of graphite in liquid alloys Fe–C–Al–S at 1550°±10°C.

Heat No.	C		Al		S	
	wt %	N_C	wt %	N_{Al}	wt %	N_S
S-Al-1	4.78	0.1873	0.37	0.0064	1.17	0.0213
S-Al-2	4.48	0.1716	4.55	0.0776	0.21	0.0030
S-Al-3	4.77	0.1868	0.51	0.0089	1.06	0.0156
S-Al-4	5.01	0.1949	0.77	0.0134	0.58	0.0085
S-Al-5	5.00	0.1943	1.11	0.0192	0.30	0.0044
S-Al-6	4.70	0.1829	1.50	0.0263	0.97	0.0142
S-Al-7	3.82	0.1434	9.15	0.1530	0.16	0.0023
S-Al-9	4.51	0.1760	1.72	0.0299	1.31	0.0192

N: Molar fraction

5. CONSIDERATION

5.1. Activity coefficient of carbon in a multicomponent alloy iron-carbon-X_1-X_2-···

When the molar fraction of carbon and a solute X are given as N_c and

N_x in a ternary solution iron-carbon-X at a constant temperature and pressure, the next equation can be generally derived[2]:

$$\left(\frac{\partial \log \gamma_c}{\partial N_x}\right)_{N_c'} = -\left\{1+2.303\left(\frac{d \log \gamma_c'}{dN_c'}\right)N_c'\right\}\left(\frac{d \log N_c}{dN_x}\right)_{a_c=1} . \qquad (1)$$

Here, γ_c is the activity coefficient and a_c is the activity of carbon in the ternary alloy, and γ_c' and N_c' are respectively the activity coefficient and the molar fraction in the binary alloy iron-carbon.

According to A. Rist and J. Chipman[12], the activity coefficient γ_c' can be expressed as follows:

$$\log \gamma_c' = \frac{4350}{T}\{1+4\cdot 10^{-4}(T-1770)\}(1-N_{Fe}^2)+\frac{1180}{T}-0.87 , \qquad (2)$$

where T is the absolute temperature and N_{Fe} is the molar fraction of iron in the binary alloy iron-carbon. The activity of carbon in the molten alloy saturated with graphite was taken as unity in this equation. The logarithms of γ_c' can be derived from eq. (2) at each temperature as follows:

$$\log \gamma_c' = 2.437(2N_c'-N_c'^2)-0.223 \qquad \text{at } 1550^\circ\text{C} , \qquad (3)$$
$$\log \gamma_c' = 2.476(2N_c'-N_c'^2)-0.185 \qquad \text{at } 1450^\circ\text{C} , \qquad (4)$$
$$\log \gamma_c' = 2.523(2N_c'-N_c'^2)-0.143 \qquad \text{at } 1350^\circ\text{C} . \qquad (5)$$

By differentiation of eqs. (3), (4) and (5) by N_c' and putting N_c' values into them, the first term of the right side in eq. (1) can be calculated, e.g.

$$1+2.303\left(\frac{d \log \gamma_c'}{dN_c'}\right)N_c' = 2.84 \qquad \text{for } N_c' = 0.2068 , \qquad (3)'$$
$$1+2.303\left(\frac{d \log \gamma_c'}{dN_c'}\right)N_c' = 2.81 \qquad \text{for } N_c' = 0.1976 , \qquad (4)'$$
$$1+2.303\left(\frac{d \log \gamma_c'}{dN_c'}\right)N_c' = 2.79 \qquad \text{for } N_c' = 0.1899 . \qquad (5)'$$

The second term of the right side in eq. (1) can be evaluated by the present experimental data; consequently the interation parameter at a constant carbon concentration i.e. $(\partial \log \gamma_c/\partial N_x)_{N_c'}$ or $(\partial \ln \gamma_c/\partial N_x)_{N_c'}$ can be calculated at each temperature. Furthermore, the next two equations are given as approximate equations to calculate the activity coefficient or activity of carbon in a given multicomponent alloy iron-carbon-X_1-X_2-$\cdots$[3]:

$$(\log \gamma_c)_{N_c,N_{x_1},N_{x_2},\cdots} = (\log \gamma_c')_{N_c}+\Sigma\left(\frac{\partial \log \gamma_c}{\partial N_x}\right)_{N_x,0,0,\cdots}\times N_x , \qquad (6)$$

$$(\log \gamma_c)_{N_c,N_{x_1},N_{x_2},\cdots} = (\log \gamma_c')_{N_c'}-\Sigma\left(\frac{d \log N_c}{dN_x}\right)_{a_c=1,0,0,\cdots}\times N_x . \qquad (7)$$

The activity of graphite in the quaternary alloys was calculated by these two equations and the validity of these equations is discussed later.

5.2. Relation between $\log N_c$ and N_x or ΔN_c^x and N_x in the carbon saturated ternary alloys

The experimental data in the case of the alloy iron-carbon-aluminium are shown in Fig. 11 and Fig. 12. The relation between $\log N_c$ and N_{Al} is given as:

$$\log N_c = -0.684 - 1.06 N_{Al} - 0.28 N_{Al}^2 .$$

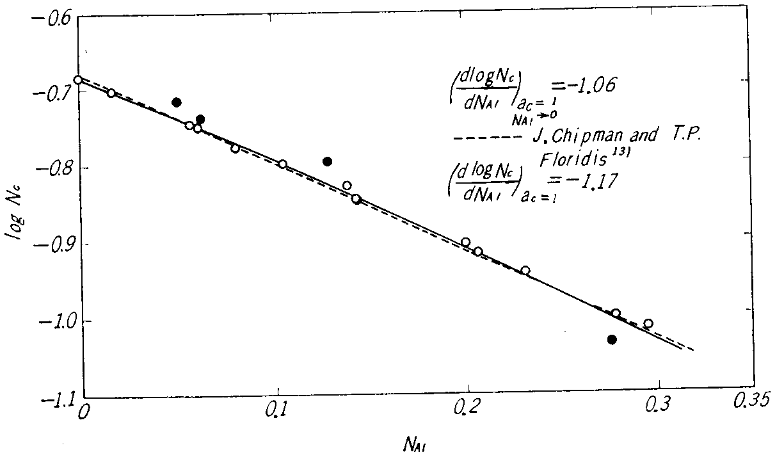


Fig. 11. Relation $\log N_c$ and N_{Al}.

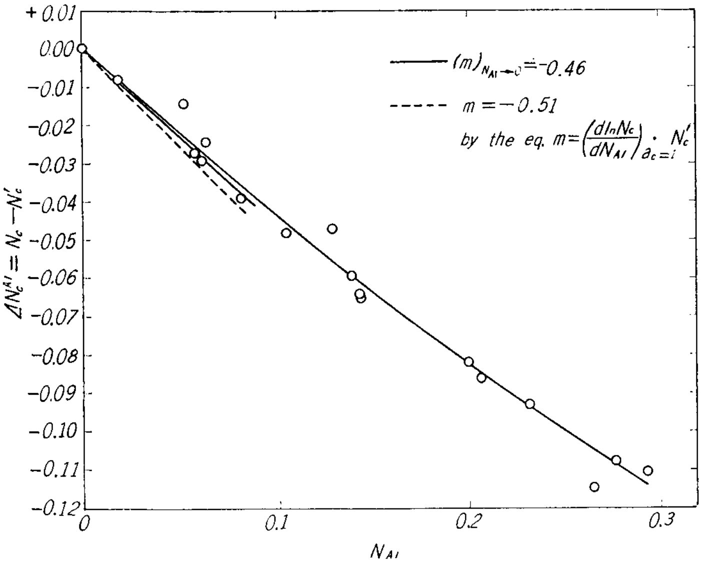


Fig. 12. Effect of aluminium on the difference of carbon solubility in alloys Fe-C-Al at 1550°C.

The black points in Fig. 11 were omitted from the calculation because these were out of the standard deviation calculated by using the whole experimental data. The value of $(d\log N_c/dN_{Al})_{a_c=1}$ is almost constant in the range $N_{Al}<0.3$, while J. Chipman and T. P. Floridis[13] gave the following equation at 1600°C:

$$\log N_c = -0.68-1.17N_{Al} \qquad (N_{Al}<0.36).$$

The interaction parameter of carbon at graphite saturation can be calculated by putting the values of $(d\log N_c/dN_{Al})_{a_c=1}$ and eq. (3′) into eq. (1), i.e.

$$\left(\frac{\partial \log \gamma_c}{\partial N_{Al}}\right)_{N_c'} = -2.84\times(-1.06)=3.01$$

or

$$\left(\frac{\partial \ln \gamma_c}{\partial N_{Al}}\right)_{N_c'} = 6.93\,.$$

J. Chipman and T. P. Floridis[13] obtained the values of $(d\log N_c/dN_{Al})_{a_c=1}$ to be -1.17 at 1600°C in the range $N_{Al}<0.36$. From this value and eq. (1),

$$\left(\frac{\partial \log \gamma_c}{\partial N_{Al}}\right)_{N_c'} = 3.32$$

or

$$\left(\frac{\partial \ln \gamma_c}{\partial N_{Al}}\right)_{N_c'} = 7.65\,.$$

Fig. 12 shows the relation between $\Delta N_c^{Al}=N_c-N_c'$ and N_{Al}, where N_c is the molar fraction of carbon in the graphite saturated ternary alloy and N_c' is that in the graphite saturated binary alloy. It is thought from Fig. 12 that the relation between ΔN_c^{Al} and N_{Al} is not linear. As the result of calculation by the method of least squares through the point $(N_{Al}=0,\ \Delta N_c^{Al}=0)$, the following equation was obtained:

$$\Delta N_c^{Al} = -0.4612N_{Al}+0.2474N_{Al}^2\,.$$

This equation is shown in Fig. 12 as the solid curved line. The solid straight line is the slope at $N_{Al}\rightarrow 0$ and the dotted line shows the slope calculated by eq. (10) which will be mentioned below.

According to E. T. Turkdogan and L. E. Leake[14] the value of ΔN_c^x is independent of the temperature and the concentration of carbon at a constant carbon activity, and has a linear relation to the molar fraction of an added element N_x, e.g.

$$\Delta N_c^x = N_c-N_c' = mN_x\,, \tag{8}$$

or

$$N_c = N_c'+mN_x\,, \tag{8$'$}$$

where m is a constant characteristic to the added element. Differentiation of the natural logarithm of eq. (8)′ by N_x gives,

$$\left(\frac{d\ln N_c}{dN_x}\right)_{a_c}=\frac{m}{N_c'+mN_x}. \tag{9}$$

When $N_x \to 0$, eq. (9) can be given as follows:

$$\left(\frac{d\ln N_c}{dN_x}\right)_{a_c, N_x\to 0}=\frac{m}{N_c'}. \tag{10}$$

The value m can be calculated, therefore, as follows:

$$\begin{aligned} m &= 2.303\times(-1.06)\times 0.2068 \\ &= -0.51 \end{aligned}$$

which is shown as the dotted line in Fig. 12.

The relation between $\log N_c$ or ΔN_c^s and N_s in the alloy iron-carbon-sulphur is shown in Fig. 13 and Fig. 14. The relation between $\log N_c$ and N_s is thought to be linear as shown in Fig. 13, and therefore the slope of the line i.e. the value of $(d\log N_c/dN_s)_{a_c=1}$ was calculated by the above-mentioned method of least squares. The result of calculation is as follows:

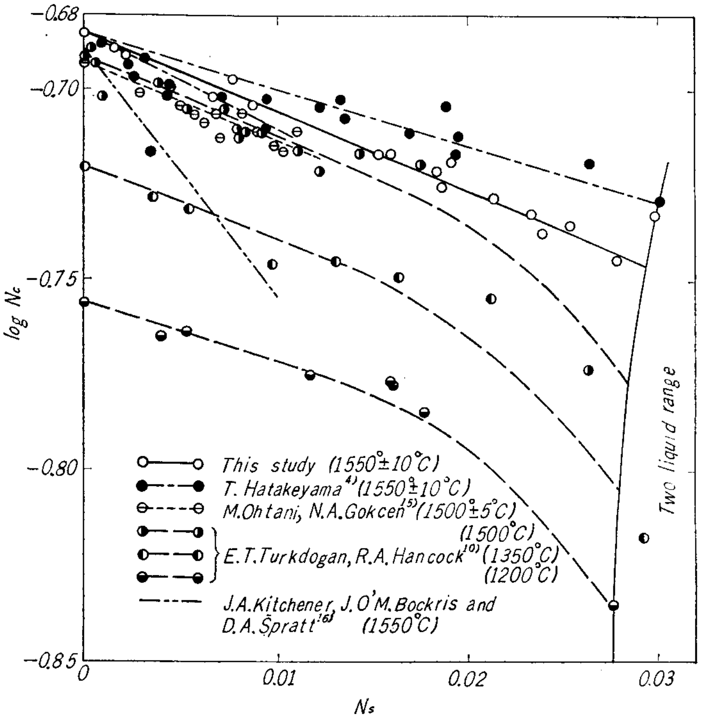


Fig. 13. Relation between $\log N_c$ and N_s.

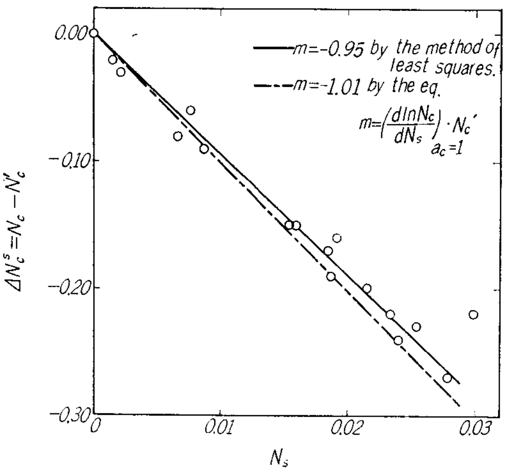


Fig. 14. Effect of sulphur on the difference of carbon solubility in alloys Fe-C-S at 1550°C.

$$\left(\frac{d\log N_c}{dN_s}\right)_{N_c'} = -2.11$$

$$\text{for } N_s < 0.03\,.$$

Calculation of the interaction parameter by eq. (1) gives,

$$\left(\frac{\partial\log\gamma_c}{\partial N_s}\right)_{N_c'} = 5.99\,,$$

or

$$\left(\frac{\partial\ln\gamma_c}{\partial N_s}\right)_{N_c'} = 13.8\,.$$

The results of other investigators are also shown in Fig. 13 and the values of the interaction parameter are compared in Table 8.

Experimental data by T. Hatakeyama[4] are more or less scattered as shown in the figure, and therefore the slope was separately measured in the range $N_s<0.0302$ and $N_s<0.01$, which were -1.53 and -2.58 respectively. The plot of data by E. T. Turkdogan and R. A. Hancock[10] shows a wave form which was seemed to be doubtful to the authors. The solubility measurements were carried out again, therefore, for the ternary alloys.

Table 8. Comparison of the values of $(d\log N_C/dN_S)_{a_C=1}$ and $(\partial\ln\gamma_C/\partial N_S)_{N_C'}$.

$\left(\frac{d\log N_C}{dN_S}\right)_{a_C=1}$	$\left(\frac{\partial\ln\gamma_C}{\partial N_S}\right)_{N_C'}$	N_S	Temperature °C	References
−2.11	+13.8	0.03	1550±10	This study
−2.58	+16.8	0.01	"	T. Hatakeyama[4]
−1.53	+10	0.03	"	"
−1.68	+10.9	0.02	1500	E. T. Turkdogan and R. A. Hancock[10]
−1.68	+10.8	0.02	1350	"
−1.68	+10.6	0.02	1200	"
−2.09	+13.6	0.01	1500±5	M. Ohtani and N. A. Gokcen[15]
−6.44	+42.1	0.012	1550	J. A. Kitchener, J. O'M. Bockris and D. A. Spratt[16]

In the present experiments a linear relation was obtained with comparatively small deviation in the range $N_s<0.03$. Value of the interaction parameter is in good agreement to that reported by M. Ohtani and N. A. Gokcen[15] though the temperature is somewhat different. J. A. Kitchener, J. O'M. Bockris and D. A. Spratt[16] presented the following equation for the relations between the solubility of graphite, the content of sulphur and the temperature:

$$(\%C) = 1.19 + 0.0262t - (\%S)\{1.67 - 0.001(t - 1200)\}$$
$$t = 1200^\circ \sim 1700^\circ C,$$
$$\%S = 0 \sim 0.84 \quad (N_s < 0.012).$$

This equation becomes at 1550°C,

$$(\%C) = 5.25 - 1.32(\%S).$$

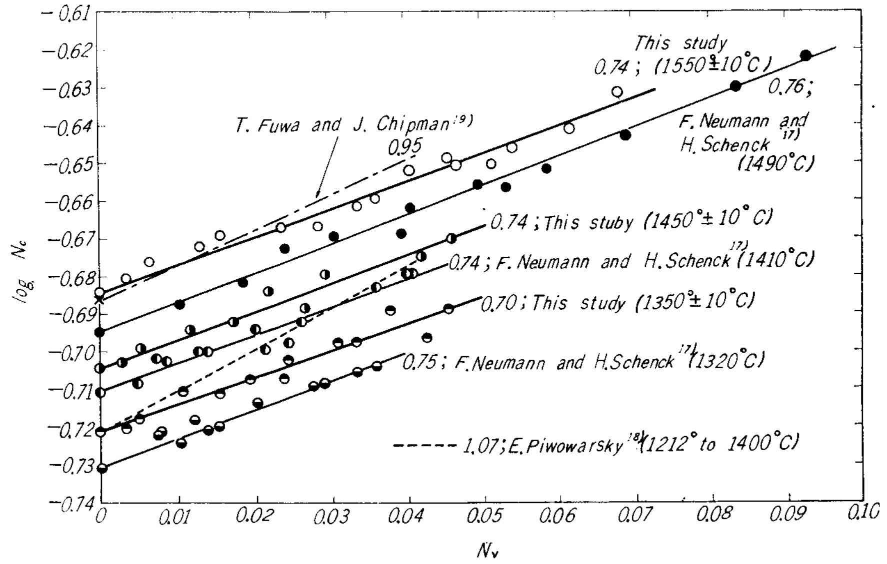


Fig. 15. Relation between log N_c and N_v.

Conversion for the weight percent into the molar fraction gives,

$$N_c = 0.205 - 3.04 N_s.$$

The slope i.e. the value m was calculated from this equation and then the value of $(d \log N_c / dN_s)_{a_c=1}$ was calculated by using eq. (10), e.g.

$$\left(\frac{d \log N_c}{dN_s}\right)_{a_c=1} = -\frac{3.04}{0.205} \times \frac{1}{2.303} = -6.44.$$

This value differs considerably from the other ones as shown in Fig. 13 and Table 8.

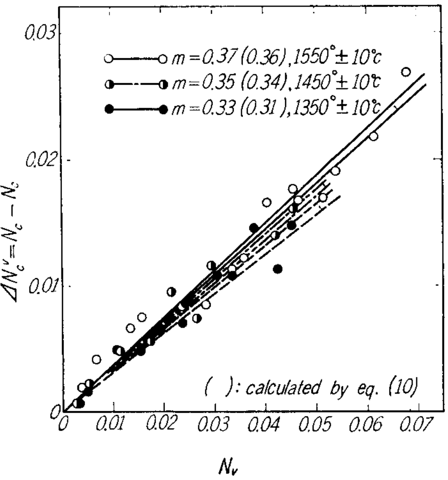


Fig. 16. Effect of vanadium on the difference of carbon solubility in alloys Fe–C–V at 1350°, 1450° and 1550°C,

The relation between $\Delta N_c^s = N_c - N_c'$ and N_s is shown in Fig. 14, which shows that there is a linear relation between ΔN_c^s and N_s.

Experimental results for the alloy iron-carbon-vanadium are shown in Fig. 15 and Fig. 16. The relation between $\log N_c$ and N_v can be regarded as linear as shown in Fig. 15. The slope i.e. $(d\log N_c/dN_v)_{a_c=1}$ was calculated by the method of least squares. These results are given as follows:

$$\left(\frac{d\log N_c}{dN_v}\right)_{a_c=1} = 0.70_4 \quad (N_v < 0.046) \quad \text{at} \quad 1350^\circ \pm 10^\circ\text{C},$$

$$\left(\frac{d\log N_c}{dN_v}\right)_{a_c=1} = 0.73_7 \quad (N_v < 0.046) \quad \text{at} \quad 1450^\circ \pm 10^\circ\text{C},$$

$$\left(\frac{d\log N_c}{dN_v}\right)_{a_c=1} = 0.74_5 \quad (N_v < 0.068) \quad \text{at} \quad 1550^\circ \pm 10^\circ\text{C}.$$

The interaction parameters calculated from these values are given as follows:

$$\left(\frac{\partial\log\gamma_c}{\partial N_v}\right)_{N_c'} = -1.96$$

or

$$\left(\frac{6\ln\gamma_c}{\partial N_v}\right)_{N_c'} = -4.52 \quad \text{at} \quad 1350^\circ\text{C} \pm 10^\circ\text{C},$$

$$\left(\frac{\partial\log\gamma_c}{\partial N_v}\right)_{N_c'} = -2.07$$

or

$$\left(\frac{\partial\ln\gamma_c}{\partial N_v}\right)_{N_c'} = -4.77 \quad \text{at} \quad 1450^\circ \pm 10^\circ\text{C},$$

$$\left(\frac{\partial\log\gamma_c}{\partial N_v}\right)_{N_c'} = -2.12$$

or

$$\left(\frac{\partial\ln\gamma_c}{\partial N_v}\right)_{N_c'} = -4.87 \quad \text{at} \quad 1550^\circ \pm 10^\circ\text{C}.$$

The values of other authors shown in Fig. 15 are summarized in Table 9. Though the present value of interaction parameter at 1350°C is somewhat lower than the others, there is a fair agreement between those by F. Neumann and

Table 9. Comparison of the values of $(d\log N_C/dN_V)_{a_C=1}$ and $(\partial\ln\gamma_C/\partial N_V)_{N_C'}$.

$\left(\frac{d\log N_C}{dN_V}\right)_{a_C=1}$	$\left(\frac{\partial\ln\gamma_C}{\partial N_V}\right)_{N_C'}$	N_V	Temperature °C	References
$+0.70_4$	−4.52	0.046	1350±10	This study
$+0.73_7$	−4.77	0.046	1450±10	"
$+0.74_5$	−4.87	0.068	1550±10	"
+0.75	−4.78	0.036	1320	F. Neumann and H. Schenck[17]
+0.74	−4.77	0.041	1410	"
+0.76	−4.95	0.093	1490	"
+0.95	−6.10	0.09	1560	T. Fuwa and J. Chipman[19]
+1.07	−6.88	0.045	1212~1400	E. Piwowarsky[18]

H. Schenck(17) and that by the authors. It seems logical that the interaction parameter is constant and independent of temperature in this temperature range. The value by E. Piwowarsky(18) calculated by using the next equation at 1350°C, e.g.

$$\Delta N_c^v = 0.42 N_v \quad \left(\begin{array}{c} N_v < 0.045 \\ 1212^\circ \sim 1400^\circ\mathrm{C} \end{array} \right),$$

and the value by T. Fuwa and J. Chipman(19) by using the next formula and eq. (1) at 1560°C, give a little higher values:

$$\log N_c = -0.687 + 0.95 N_v .$$

Fig. 16 shows the differences of m values at various temperatures which were calculated 1) from eq. (10) by using the values $(d\log N_c/dN_v)_{a_c=1}$ and N_c', and 2) from the values m which were calculated by the method of least squares directly from the relation between ΔN_c^v and N_v. The arrows show the change of each slope at each temperature, though the differences may be negligible at the same temperature.

The general relation between the interaction parameter expressed in weight percent and that in molar fraction is written as follows(2):

$$\left(\frac{\partial \log f_c}{\partial \%\mathrm{X}}\right)_{\%\mathrm{C}} = \left(\frac{\partial \log \gamma_c}{\partial N_x}\right)_{N_c} \frac{\dfrac{1}{M_x}\left(\dfrac{\%\mathrm{C}}{M_c}+\dfrac{\%\mathrm{X}}{M_x}+\dfrac{100-\%\mathrm{C}-\%\mathrm{X}}{M_{Fe}}\right)-\dfrac{\%\mathrm{X}}{M_x}\left(\dfrac{1}{M_x}-\dfrac{1}{M_{Fe}}\right)}{\left(\dfrac{\%\mathrm{C}}{M_c}+\dfrac{\%\mathrm{X}}{M_x}+\dfrac{100-\%\mathrm{C}-\%\mathrm{X}}{M_{Fe}}\right)^2}$$
$$-\frac{1}{2.303}\cdot\frac{\dfrac{1}{M_x}-\dfrac{1}{M_{Fe}}}{\dfrac{\%\mathrm{C}}{M_c}+\dfrac{\%\mathrm{X}}{M_x}+\dfrac{100-\%\mathrm{C}-\%\mathrm{X}}{M_{Fe}}} .$$

Here, M_c, M_{Fe} and M_x correspond to the atomic weight of carbon, iron and the added element X respectively; and f_c is the activity coefficient of carbon, the reference state of which is infinite dilution. From the above equation the interaction parameters expressed in percent unit at each temperature are abtained as follows:

$$\left(\frac{\partial \log f_c}{\partial \%\mathrm{V}}\right)_{\%\mathrm{C}=4.80,\,\%\mathrm{V}=0} = -0.019 \quad (\%\mathrm{V} < 4.97) \quad \text{at} \quad 1350^\circ\mathrm{C} \pm 10^\circ\mathrm{C},$$

$$\left(\frac{\partial \log f_c}{\partial \%\mathrm{V}}\right)_{\%\mathrm{C}=5.03,\,\%\mathrm{V}=0} = -0.020 \quad (\%\mathrm{V} < 5.05) \quad \text{at} \quad 1450^\circ\mathrm{C} \pm 10^\circ\mathrm{C},$$

$$\left(\frac{\partial \log f_c}{\partial \%\mathrm{Al}}\right)_{\%\mathrm{C}=5.31,\,\%\mathrm{Al}=0} = 0.048 \quad (\%\mathrm{Al} < 8)$$

$$\left(\frac{\partial \log f_c}{\partial \%\mathrm{S}}\right)_{\%\mathrm{C}=5.31,\,\%\mathrm{S}=0} = 0.085 \quad (\%\mathrm{S} < 2.04)$$

$$\left(\frac{\partial \log f_c}{\partial \%\mathrm{V}}\right)_{\%\mathrm{C}=5.31,\,\%\mathrm{V}=0} = -0.020 \quad (\%\mathrm{V} < 7.67) \quad \text{at} \quad 1550^\circ \pm 10^\circ\mathrm{C},$$

Now, the formulae which show the relation between N_c and N_x or %C and %X at each temperature are summarized as follows:

$$\begin{aligned} N_c &= 0.190+0.325N_v \\ \%C &= 4.80+0.095\%V \quad \text{at } 1350°C, \\ N_c &= 0.198+0.350N_v \\ \%C &= 5.03+0.108\%V \quad \text{at } 1450°C, \\ N_c &= 0.207-0.4612N_{Al}+0.2474N_{Al}^2 \\ \%C &= 5.31-0.1824(\%Al)+0.001685(\%Al)^2 \\ N_c &= 0.207-0.946N_s \\ \%C &= 5.31-0.462\%S \\ N_c &= 0.207+0.371N_v \\ \%C &= 5.31+0.124\%V \quad \text{at } 1550°C. \end{aligned}$$

5.3. The relation between the interaction parameter and the atomic number

The relation between the interaction parmeter or $\Delta\%C/\%X$ and the atomic number has been discussed by several investigators,15),17)~22) and at present it is recognized as empirical fact that there is a close relation between these values. F. Neumann and H. Schenck17) have shown a regular relation between the value $-(\partial \ln N_c/\partial N_x)_{a_c}$ and the atomic number of the element by comparing the experimental values and the estimated values. Here the present results and the above-mentioned values by F. Neumann and H. Schenck are compared as follows:

	Present results	Experimental values17)	Estimated values
$(\partial \ln N_c/\partial N_{Al})$	-2.44	-2.525	-2.476
$(\partial \ln N_c/\partial N_s)$	-4.86	-4.855	-4.952
	$+1.62$ (1350°C)		
$(\partial \ln N_c/\partial N_v)$	$+1.70$ (1450°C)		
	$+1.72$ (1550°C)	$+1.743$	$+1.602$

The regularity between the interaction parameter and the atomic number proposed by F. Neumann and H. Schenck can be said to be valid also in the present data.

5.4. Activity of carbon in the alloy iron-carbon-aluminium-sulphur at 1550°C

Values of activity of carbon calculated by eqs. (6), (7) and theoretical values are shown in Table 10. In the calculation of Δa_c the next equation was used at 1550°C:

$$\Delta a_c = a_c - 0.996.$$

The reason why the value 0.996 was employed had been explained elsewhere2),

Table 10. Comparison of the values of activity of carbon calculated by eqs. (6), (7) and the theoretical value in alloys Fe-C-Al-S at 1550°±10°C.

Heat No.	$\log N_C$	$(\log \gamma_C)_{N_C,N_{Al},N_S}$ by eq. (6)	a_C	Δa_C	$(\log \gamma_C)_{N_C,N_{Al},N_S}$ by eq. (7)	a_C	Δa_C
S-Al-1	−0.728	0.7509	1.054	+0.058	0.7337	1.013	+0.017
S-Al-2	−0.766	0.7936	1.066	+0.070	0.7706	1.011	+0.015
S-Al-3	−0.729	0.7223	0.980	−0.016	0.7243	0.989	−0.007
S-Al-4	−0.710	0.7252	1.036	+0.040	0.7141	1.010	+0.014
S-Al-5	−0.712	0.7162	1.010	+0.014	0.7117	0.999	+0.003
S-Al-6	−0.738	0.7533	1.036	+0.040	0.7399	1.004	+0.008
S-Al-7	−0.844	0.9003	1.138	+0.142	0.8490	1.012	+0.016
S-Al-9	−0.755	0.7640	1.021	+0.025	0.7542	0.998	+0.002

As shown in this table the calculated activity values by eq. (7) are more accurate than those by eq. (6), and this trend was also observed in the previous studies.[2),3)]

6. SUMMARY

(1) The solubility of graphite was measured in liquid alloys iron-carbon-aluminium and iron-carbon-sulphur at 1550°±10°C, and in liquid alloys iron-carbon, iron-carbon-vanadium at 1350°±10°C, 1450°±10°C and 1550°±10°C.

(2) The solubility of graphite was also measured in liquid alloys iron-carbon-aluminium-sulphur at 1550±10°C.

(4) The relations between the saturated concentration of carbon and the added element are given as follows:

$$
\begin{aligned}
N_c &= 0.190+0.325N_v \\
\%\mathrm{C} &= 4.80+0.095\%\mathrm{V} \quad \text{at } 1350^\circ\mathrm{C}, \\
N_c &= 0.198+0.350N_v \\
\%\mathrm{C} &= 5.03+0.108\%\mathrm{V} \quad \text{at } 1450^\circ\mathrm{C}, \\
N_c &= 0.207-0.4612N_{Al}+0.2472N_{Al}^2 \\
\%\mathrm{C} &= 5.31-0.1824(\%\mathrm{Al})+0.001685(\%\mathrm{Al})^2 \\
N_c &= 0.207-0.946N_s \\
\%\mathrm{C} &= 5.31-0.462\%\mathrm{S} \\
N_c &= 0.207+0.371N_v \\
\%\mathrm{C} &= 5.31+0.124\%\mathrm{V} \quad \text{at } 1550^\circ\mathrm{C}.
\end{aligned}
$$

(4) The interaction parameters for the graphite saturated solutions in molar fraction unit given as follows:

$$\left(\frac{\partial \ln \gamma_c}{\partial N_V}\right)_{N_C'=0.190} = -4.52 \quad (N_v < 0.046) \quad \text{at } 1350^\circ \pm 10^\circ\mathrm{C},$$

$$\left(\frac{\partial \ln \gamma_c}{\partial N_V}\right)_{N'_C=0.198} = -4.77 \quad (N_V < 0.046) \quad \text{at} \quad 1450° \pm 10°\text{C},$$

$$\left(\frac{\partial \ln \gamma_c}{\partial N_V}\right)_{N'_C=0.207} = -4.87 \quad (N_V < 0.068)$$

$$\left(\frac{\partial \ln \gamma_c}{\partial N_{Al}}\right)_{N'_C=0.207} = 6.93 \quad (N_{Al} < 0.14)$$

$$\left(\frac{\partial \ln \gamma_c}{\partial N_s}\right)_{N'_C=0.207} = 13.8 \quad (N_s < 0.03) \quad \text{at} \quad 1550° \pm 10°\text{C}.$$

(5) The interaction parameters for the graphite saturated solutions in weight percent unit are given as follows:

$$\left(\frac{\partial \log f_c}{\partial \% V}\right)_{\% C=4.80} = -0.019 \quad (\% V < 4.97) \quad \text{at} \quad 1350° \pm 10°\text{C},$$

$$\left(\frac{\partial \log f_c}{6\% V}\right)_{\% C=5.03} = -0.020 \quad (\% V < 5.05) \quad \text{at} \quad 1450° \pm 10°\text{C},$$

$$\left(\frac{\partial \log f_c}{\partial \% V}\right)_{\% C=5.31} = -0.020 \quad (\% V < 7.67)$$

$$\left(\frac{\partial \log f_c}{\partial \%_{Al}}\right)_{\% C=5.31} = 0.048 \quad (\% Al < 8)$$

$$\left(\frac{\partial \log f_c}{\partial \% S}\right)_{\% C=5.31} = 0.085 \quad (\% S < 2.04) \quad \text{at} \quad 1550° \pm 10°\text{C}.$$

(6) The activity of carbon in liquid iron is increased by the addition of aluminium or sulphur, while it is decreased by vanadium.

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