

Activity of Carbon and Solubility of Carbides in the FCC Fe-Mo-C, Fe-Cr-C, and Fe-V-C Alloys

T. WADA, H. WADA, J. F. ELLIOTT, AND J. CHIPMAN

The activity of carbon in austenitic Fe-Mo-C, Fe-Cr-C, and Fe-V-C alloys has been studied by equilibration with controlled CH₄-H₂ atmospheres at temperatures in the range 850° to 1200°C. The observations included a number of compositions in the two-phase fields, γ + carbide. Equations are given for the activity coefficient of carbon as a function of temperature and composition in the austenite field and from these the other thermodynamic properties of the solution may be computed as desired. The phase boundaries γ/γ + carbide were determined by breaks in the isoactivity lines. This was supplemented in the case of Fe-Mo-C alloys by metallographic linear analysis of equilibrated samples. The results confirm certain published phase diagrams and discredit others.

THE effects of various alloying elements on the activity of carbon in austenite have been studied by a number of investigators. This paper is the third in a series of studies by the authors, the first two having to do with Fe-Ni-C alloys¹ and Fe-Mn-C and Fe-Si-C alloys.² The activity of carbon can be measured with simple equipment and when this is known as a function of composition and temperature other thermodynamic properties may be calculated.

While the primary purpose of this investigation was to determine the effects of three carbide-forming elements on the activity of carbon, an equally important secondary objective was an evaluation of the solubility of the several carbides in austenite. This second part was not in itself a complete study, but its results serve as a basis for discrimination among the grossly disagreeing data of earlier observers. Published work in both areas will be cited in connection with our results on the three systems.

EXPERIMENTAL PROCEDURE

Materials

The Fe-Mo, Fe-Cr, and Fe-V alloys were prepared by induction melting in alumina crucibles under an argon atmosphere. Electrolytic iron and alloying elements of at least 99.9 pct purity were used. A master Fe-Mo alloy was prepared, and pieces of chromium and tungsten added to the molten iron for the other two systems. Melts were cast by suction into 5 mm ID vycor tubes and then rolled into 0.25 mm sheets. Compositions were determined by chemical analysis. Nitrogen analyses of several specimens containing up to 7.66 pct Cr or 1.05 pct V showed a maximum of only 31 ppm.

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Procedure

The experimental procedure was similar to that used in the previous studies,^{1,2} equilibration with controlled mixtures of methane and hydrogen. Samples are treated in groups containing several alloy specimens accompanied always by one sample of pure iron. When equilibrium is reached, the activity of carbon is constant within the group and its value is determined by the carbon content of the pure Fe-C alloy.

The time for equilibration was 44 to 50 h at 1200°C, 49 to 91 h at 1000°C, and 185 to 284 h at 850°C. In a number of instances equilibrium was approached from both the high-carbon and the low-carbon sides with generally satisfactory agreement.

Results

The experimental results are shown in Tables I, II, and III. Alloy compositions are shown as y_M , the atom fraction of M in the carbon-free base alloy. Carbon content is shown as wt percent. The activity of carbon, a_C , was calculated from the following equation based on the CO-CO₂ equilibrium data of Ban-ya, Elliott, and Chipman³ and earlier observers:

$$\log a_C = 2300/T - 0.92 + (3860/T)y_C + \log z_C \quad [1]$$

where T is degrees Kelvin and

$$y_C = n_C/(n_{Fe} + n_M); \quad z_C = y_C/(1 - y_C) \quad [2]$$

Fe-Mo-C ALLOYS

Activity of Carbon

All high-carbon samples were examined metallographically and those which contained carbides were excluded from calculations of the activity coefficient. In Fig. 1 the logarithm of the activity coefficient, $\log \Psi_C$, is plotted with the standard state being graphite ($\Psi_C = a_C/z_C$). Points approached from the high-carbon side are indicated by arrows. Lines are drawn parallel to the lines for the Fe-C binary.³ For the small concentrations involved and within the limits of accuracy of the data, a slope dependent upon alloy concentrations would not be warranted. The intercepts, $\log \Psi_C^0$ at $y_C = 0$ are plotted against y_{Mo} in Fig. 2. The

Table I. Experimental Results of Equilibrium Carbon Content (Wt Pct) in Fe-Mo-C Alloys

Run No.	Temperature, °C	a_C	y_{Mo}				
			0.00	0.0033	0.0075	0.0139	0.0248
68	1197	0.385	1.23	1.25	1.28	1.34	
66	1197	0.234	0.85	0.87	0.89	0.91	0.99
67	1197	0.0860	0.37	0.38	0.39	0.42	0.46
				0.37†		0.40†	
62	997	0.771	1.29	1.31	1.33	1.39*	1.56*
63	997	0.516	0.98	1.00	1.04	1.07*	1.27*
				0.99†		1.10†*	
64	997	0.413	0.83	0.85	0.87	0.95	0.96*
60	997	0.285	0.62	0.64	0.65	0.70	0.74*
65	997	0.135	0.33	0.34	0.37	0.41	0.44*
				0.34†		0.40†	
112	848	0.725	0.81	0.83	0.89(*)	0.92*	1.02*
111	848	0.520	0.63	0.64	0.66	0.74*	0.84*
110	848	0.353	0.46	0.49	0.50	0.57*	0.68*
115	848	0.274	0.37		0.40		

*Carbides present. Parenthesis indicates less certainty
 †Equilibrium approached from higher carbon.

Table II. Experimental Results of Equilibrium Carbon Content (Wt Pct) in Fe-Cr-C Alloys

Run No.	Temperature, °C	a_C	y_{Cr}					
			0.00	0.0203	0.0412	0.0611	0.0818	0.120
84	1201	0.290	1.01	1.16	1.30	1.43	1.89*‡	
90	1201	0.180	0.70†	0.81	0.90	1.01	1.12*	
					0.92			
85	1201	0.106	0.45	0.53	0.61	0.67	0.77	0.93*‡
				0.53†	0.61†			
86	1201	0.0366	0.17†	0.20†	0.24†	0.30†	0.32†	0.41†
79	1000	0.442	0.88	0.99	1.19*			
81	1000	0.191	0.45	0.53	0.63	0.75	1.05*‡	1.83*‡
82	1000	0.168	0.40	0.47	0.55	0.66	0.90*‡	1.67*‡
92	1000	0.0815	0.21	0.25	0.30	0.35	0.43	0.88*‡
115	850	0.262	0.36	0.46	0.59*			
114	850	0.166	0.24	0.33	0.41			
			0.24	0.32†	0.40†			
113	850	0.0859	0.13‡	0.17	0.22	0.30*		

*Carbides present.
 †Equilibrium approached from higher carbon.
 ‡Calculated from weight gain.
 ‡Extrapolated from Fe-Cr Alloys

relation is obviously linear and the slopes may be expressed as

$$d \log \Psi_C / dy_{Mo} = -9500/T + 2.5 \quad [3]$$

From this equation, the value of $(\partial \ln f_C / \partial x_C)_{x_{Fe} \rightarrow 1} = \epsilon_C^{Mo}$ at 1000°C is -11.4. The activity coefficient of carbon is given by the equation:

$$\log \Psi_C = 2300/T - 0.92 + (3860/T)y_C - (9500/T - 2.5)y_C \quad [4]$$

An entirely comparable series of results at 1000°C has been published by Nishizawa.⁴ When the activity of carbon in his Fe-C specimens is calculated from our Eq. [1] and applied to the alloy samples, the results

are parallel with the lines of Fig. 1. They are somewhat more closely spaced as indicated by their intercepts shown in Fig. 2 and thus they indicate a smaller value of ϵ_C^{Mo} .

On the other hand, the data of Bungardt, Schürmann, Preisendanz, Schüler, and Osing⁵ at 1000° and 1100°C

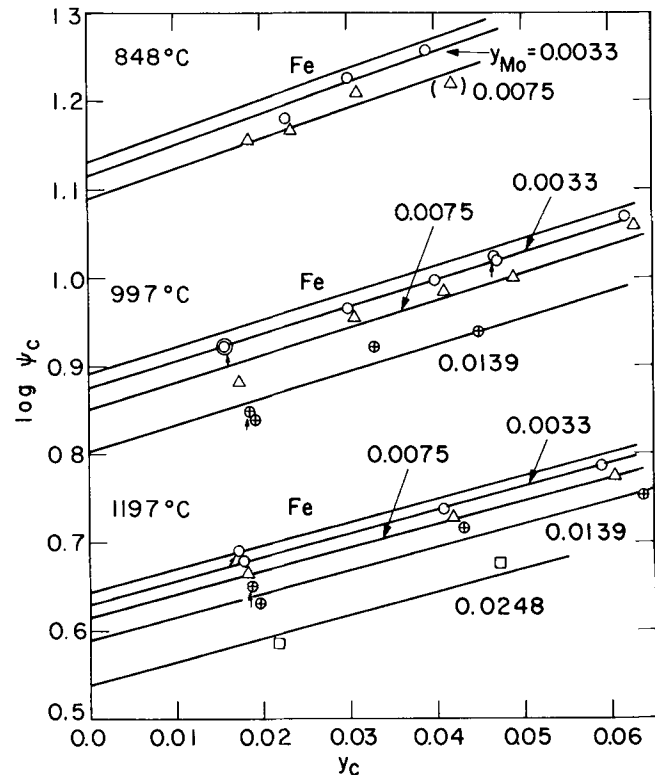


Fig. 1—Activity coefficient of carbon in Fe-Mo-C alloys. Points marked by arrows approached from high-carbon side.

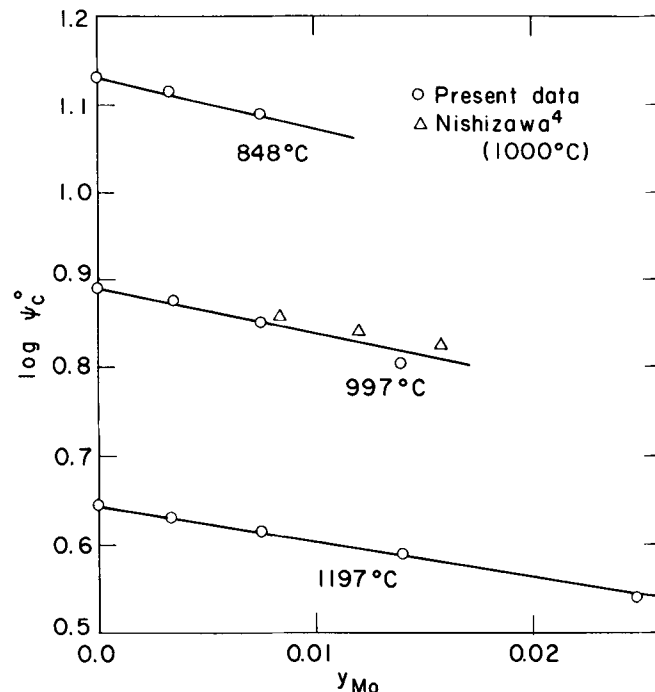


Fig. 2—Activity coefficient of carbon at infinite dilution in Fe-Mo-C alloys.

Table III. Experimental Results of Equilibrium Carbon Content (Wt Pct) in Fe-V-C Alloys

Run No.	Temperature, °C	a_C	γ_V							
			Wt Pct C							
			0.00	0.0022	0.0054	0.0069	0.0116	0.0119	0.0165	0.0211
88	1201	0.103	0.436	0.438	0.461	0.470	0.510	0.513		
91	1201	0.0499	0.229	0.232	0.238	0.258				
89	1201	0.0389	0.180	0.201	0.195	0.204	0.229			
79	997	0.440	0.870	0.876	0.931†*	0.194†				
80	997	0.179	0.420	0.430†	0.462	0.485*	0.603*			
78	997	0.0901	0.230	0.236	0.246	0.268(*)		0.380*		
77	997	0.0596	0.155	0.155	0.170	0.186	0.255*		0.321*	
76	997	0.0560	0.146	0.149	0.154	0.155	0.208*		0.283*	0.385*
93	997	0.0422	0.112†	0.113†	0.120†	0.127†	0.157†*			
94	997	0.0256	0.0690†	0.0695†	0.0714†	0.0744†		0.0861†	0.111†*	
115	850	0.274	0.370	0.394*	0.437*					
114	850	0.166	0.240	0.261*	0.298*	0.334*				
				0.254†*	0.298†*					

*Carbides present. Parenthesis indicates less certainty.

†Equilibrium approached from higher carbon.

are more difficult to compare. Their results are not given in tabular form and their base line for Fe-C as read from their graphs is very substantially different from ours and also different from the earlier results of Bungardt, Preisendanz, and Lehnert.⁶ We are inclined to conclude that the method is less accurate than ours, but that the qualitative agreement regarding the effect of molybdenum on the activity of carbon offers good approximate confirmation. A simple comparison is found in the value of $\epsilon_C^{(Mo)} = d \ln f_C / dx_{Mo}$ for which Bungardt *et al.* report -9.63 whereas our value is -11.4 .

Solubility of Carbides in the Fe-Mo-C System

Murakami's reagent was used to identify the species of carbide. This reagent does not attack cementite, attacks weakly ξ -carbide and colors it to light brown and markedly attacks M_6C carbide. Mo_2C is delineated by this reagent. Thus, the carbides which formed during equilibration can be distinguished from cementite formed during quenching of specimen. An example of the microstructure is shown in Fig. 3. Fine particles of M_6C -type carbides are well distinguished from bainitic carbides as shown by the left-hand side picture which was etched by Murakami's reagent, while the right-hand side picture shows the microstructure of the same area with picral etching.

Campbell, Reynolds, Ballard, and Carroll⁷ determined the phase diagram of the iron-corner of Fe-Mo-C system over the temperature range from 720° to 1300°C using metallographic methods. Their results indicate that the homogeneous austenite range is relatively narrow at temperatures around 1000°C. Bungardt *et al.*⁵ reported the austenite-carbide boundary at 1000° and 1100°C according to their equilibrium measurements. Their results showed an appreciably wider austenite range than that given by Campbell *et al.* Nishizawa⁴ determined the boundary from his equilibrium measurements and the microprobe analysis of austenite and carbide phases, and obtained remark-

ably larger austenite range than those by Campbell *et al.* and Bungardt *et al.*⁵ Recently, Harvig and Uhrenius⁸ redetermined the boundary with similar but improved techniques using equilibration times up to 1000 h at 1000°C, and the results are very close to Nishizawa's. The phase boundaries at 1000°C by these four groups are shown in Fig. 4, together with the results of the present work.

The presence of carbides observed metallographically in the present work, shown by black points in Fig. 4 and their absence shown by open circles support the highest solubility by Nishizawa⁴ and Harvig and Uhrenius.⁸

To obtain more quantitative results, the amount of carbides formed in the specimens of 4.19 pct Mo ($\gamma_{Mo} = 0.0139$) were determined by a metallographic linear analysis.⁹ The results and further conversion to the molybdenum concentration in matrix are shown in Table IV. The compositions of the phase boundary, as shown in the last column in Table IV and in Fig. 4 are again in good agreement with those by Nishizawa⁴ and Harvig and Uhrenius.⁸ It is difficult to select only one from these two.

Bungardt *et al.*⁵ did not include Mo_2C in their diagram. The metallographic observations in the present work showed, however, by etching with Murakami's reagent, that specimens 4006 and 4005, Table IV, contained delineated carbide particles which are most probably M_2C -type carbide. Recent work by Harvig and Uhrenius⁸ also showed that M_2C -type carbide is stable at 1000°C.

Fe-Cr-C ALLOYS

Activity of Carbon

The activity of carbon in fcc Fe-Cr alloys has been studied at 1000°C by Schenck and Kaiser,¹⁰ Brigham and Kirkaldy,¹¹ Flender and Wever,¹² Bungardt, Preisendanz and Lehnert,⁶ and more recently by Nishizawa.⁴ Results of the first four were reviewed by Chipman and Brush¹³ who found substantial agreement

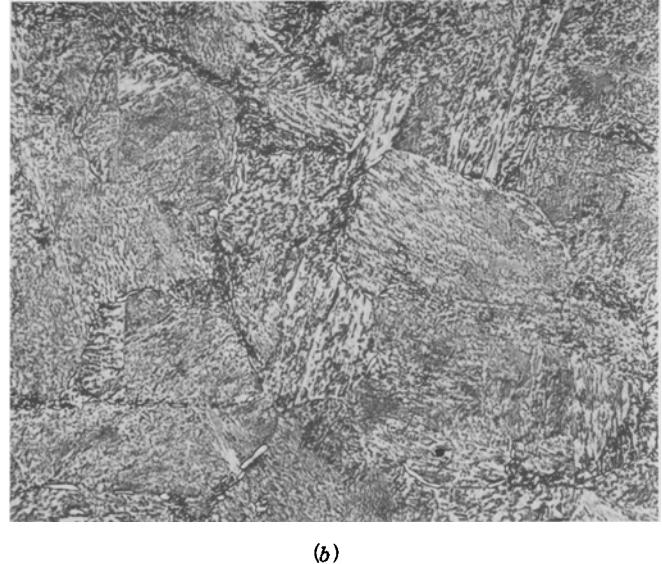
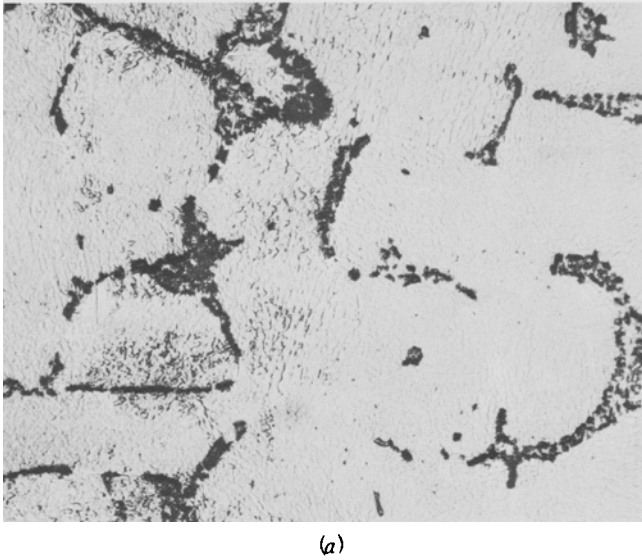


Fig. 3—Microstructure of specimen 4007 containing 4.21 pct Mo, 0.44 pct C equilibrated at 997°C; left, Murakami's reagent; right, Picral. Magnification 385 times.

as to the effect of chromium when all data were referred to a common Fe-C base line.

Our experimental data, Table II, omitting all samples that contained carbide, are plotted in Figs. 5 and 6. Points approached from higher carbon are indicated by arrows. The lines are drawn parallel to the base lines for Fe-C alloys and spaced in proportion to the chromium content.

In Fig. 7 the results of Bungardt *et al.*⁶ and of Nishizawa⁴ at 1000°C are replotted after converting their carbon activity to the same base line used for the Fe-C system in the present work. In both cases the correction is small since the binary data do not differ greatly from that of Eq. [1]. The larger adjustments required for comparison of the data of Schenck and Kaiser¹⁰ and of Flender and Wever¹² were estimated by Chipman and Brush,¹³ but the data are omitted here. The data in Fig. 7 may be represented adequately by lines parallel to that of the Fe-C binary.

The intercepts, $\log \Psi_C^0$ at $y_C = 0$ for the several lines for 1000°C are shown in Fig. 8, together with our data for 850° and 1201°C. As noted by Chipman and Brush,¹³ two of the lines of Bungardt *et al.* are incompatible with the other data and these are omitted from Figs. 7 and 8. The agreement among the other data at 1000°C is very good and the slopes at all three temperatures may be represented by

$$d \log \Psi_C^0 / dy_{Cr} = -9500/T + 3.05 \quad [5]$$

The value of $\epsilon_{(Cr)}^C$ at 1000°C is -10.2 in excellent agreement with -10.7 found by Brigham and Kirkaldy.¹¹ The activity coefficient of carbon is given by the equation:

$$\log \Psi_C = 2300/T - 0.92 + (3860/T)y_C - (9500/T - 3.05)y_{Cr} \quad [6]$$

Solubility of Carbides in the Fe-Cr-C System

As shown in Fig. 9, the experimental isoactivity lines when continued beyond the homogeneous austenite

region produce a second system of lines in the two-phase γ + carbide region. The intersections of the two sets of lines gives the position of the phase boundary. While our data are insufficient to establish the boundary, they do offer a basis for selection among the published diagrams. The phase boundaries reported by Bungardt, Preisendanz, and Lehnert,⁶ by Bungardt, Kunze, and Horn¹⁴ and, by Nishizawa⁴ are shown in Fig. 9. The breaks in our lines correspond fairly well with the diagrams of Bungardt, Preisendanz, and Lehnert and of Nishizawa.

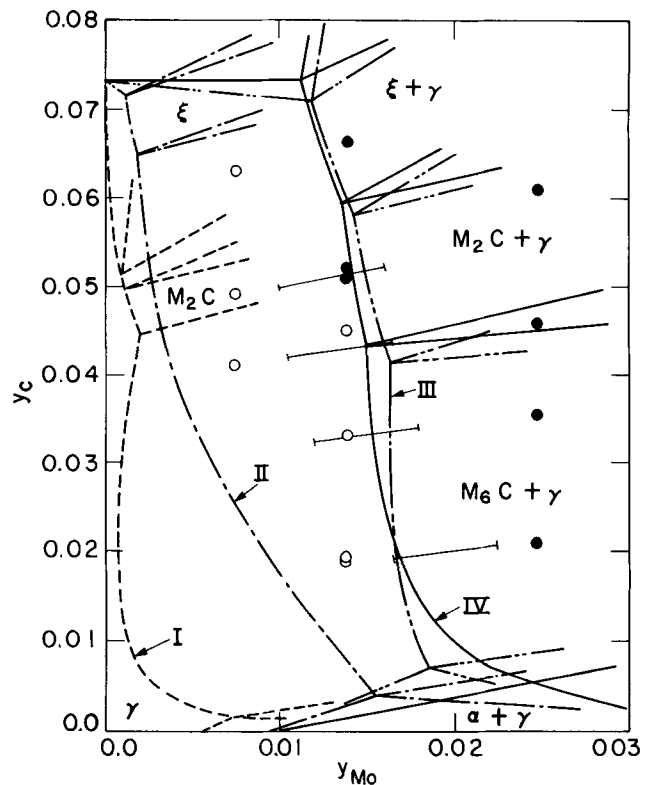


Fig. 4—The austenite/carbide phase boundaries in Fe-Mo-C alloys at 1000°C. I) Campbell *et al.*⁷ II) Bungardt *et al.*⁵ III) Nishizawa.⁴ IV) Harvig and Uhrenius.⁸ Circles, this work; ● carbides observed, ○ carbides absent; bars, limits of range of γ field estimated by quantitative metallography.

Table IV. Amount of Carbide Determined by Linear Analysis and Estimated Austenite/Carbide Phase Boundary in the System Fe-Mo-C

Specimen No.	Total Composition		Vol. Pct of Carbide	Carbide Phases		<i>D</i> Carbide/cm ³ ¶	Wt Pct of Carbide	Phase Boundary	
	Pct Mn	Pct C		Possible Type	Composition Estimated Wt Pct			Pct Mo	$y_{Mo} \times 10^2$
4007	4.19	0.44	1.4 ± 0.4	<i>M</i> ₆ C	57.6Mo, 38.5Fe, 3.9C ^{1*}	9.1	1.6 ± 0.5	3.3 ± 0.4	1.95 ± 0.3
4001	4.91	0.74	2.5 ± 0.4	<i>M</i> ₆ C	57.6Mo, 38.5Fe, 3.9C ^{1*}	9.1	2.9 ± 0.5	2.5 ± 0.4	1.50 ± 0.3
4006	4.19	0.96	2.3 ± 0.4	<i>M</i> ₆ C + <i>M</i> ₂ C	70.5Mo, 24.4Fe, 5.1C ^{2†}	9.0	2.7 ± 0.5	2.3 ± 0.4	1.35 ± 0.3
4005	4.19	1.27	2.1 ± 0.4	<i>M</i> ₂ C	83.4Mo, 10.3Fe, 6.3C ^{3‡}	9.0	2.4 ± 0.5	2.2 ± 0.4	1.30 ± 0.3

*The ratio of Mo:Fe is selected as 60:40 in weight, a mid point of the composition determined by Harvig and Uhrenius.⁸

†Assumed a mixture of equal weight *M*₆C and *M*₂C.

‡The ratio Mo:Fe is selected as 89:11 in weight.⁸

¶Calculated from crystal structures of these carbides

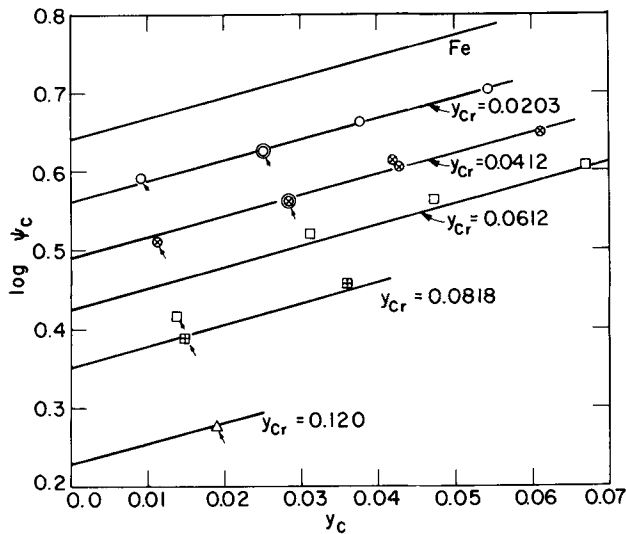


Fig. 5—Activity coefficient of carbon in Fe-Cr-C alloys at 1201°C. Points marked by arrows approached from high-carbon side.

It is interesting to extrapolate the two lines in the two-phase field to the theoretical composition *M*₇C₃ at which $y_C = 0.43$. It turns out that at this composition $y_{Cr} \approx 0.49$. This is to be regarded merely as indicative of nearly equal concentrations of iron and chromium in this carbide.

Fe-V-C ALLOYS

Activity of Carbon

The austenite field in the Fe-V-C system is narrowly constricted by the limited solubility of the carbides and the intrusion of the $\alpha + \gamma$ area in low-carbon alloys. All of our specimens equilibrated at 850°C and some of those treated at 997°C were found to contain carbides. Activity coefficients in the carbide-free specimens are plotted in Fig. 10. In view of the limited concentration range, the slopes of the lines cannot be determined and they are drawn parallel to the lines for Fe-C.

This system was studied by Zupp and Stevenson¹⁶ at 1000°C using CH₄-H₂ mixtures and including Fe-C samples for reference. The bulk of their data fell into the two-phase fields $\alpha + \gamma$ or $\gamma + \text{carbide}$. Their data were reviewed by Chipman and Brush¹³ who were able to show that the data for $y_V = 0.0026$ and $y_V = 0.0054$

were self consistent. Actually they lie, with somewhat greater scatter, very close to our lines for $y_V = 0.0022$ and $y_V = 0.0054$. At higher vanadium concentrations, the data were irregular and the specimens contained the α phase so satisfactory evaluation was not possible. The system was also studied by Flender and Wever¹² and by Ebeling and Wever.¹⁵ Their base line for the activity of carbon in the Fe-C binary was derived from earlier data on the CH₄-H₂ equilibrium in which we have no confidence.¹³ Some of their experimental points appear to have been in a multiphase region. Their experimental data were not tabulated and their graphs cannot be interpolated with accuracy. Their only experimental series which is evidently in

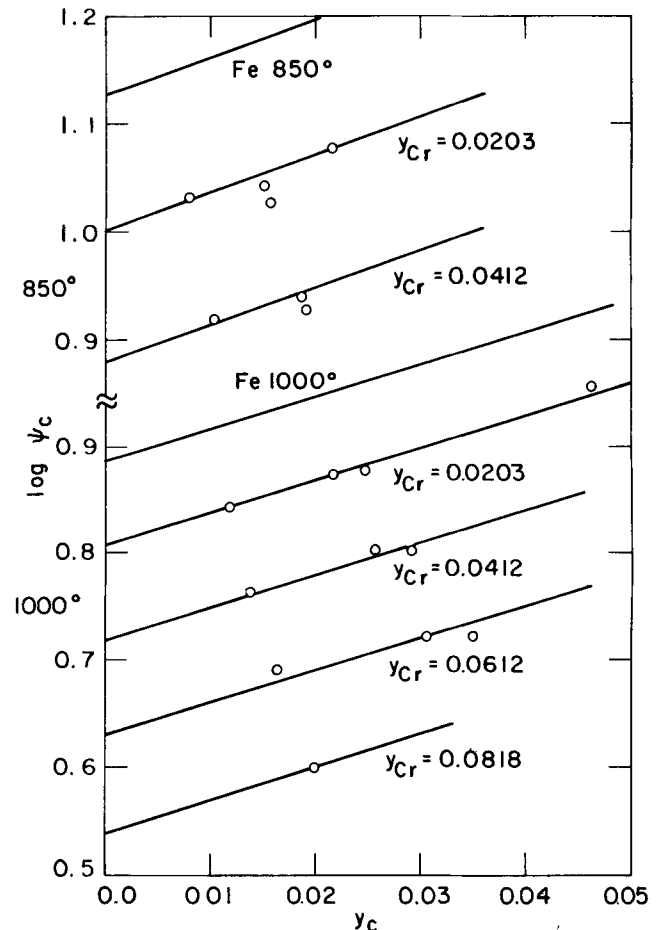


Fig. 6—Activity coefficient of carbon in Fe-Cr-C alloys at 850°C (upper) and 1000°C (lower).

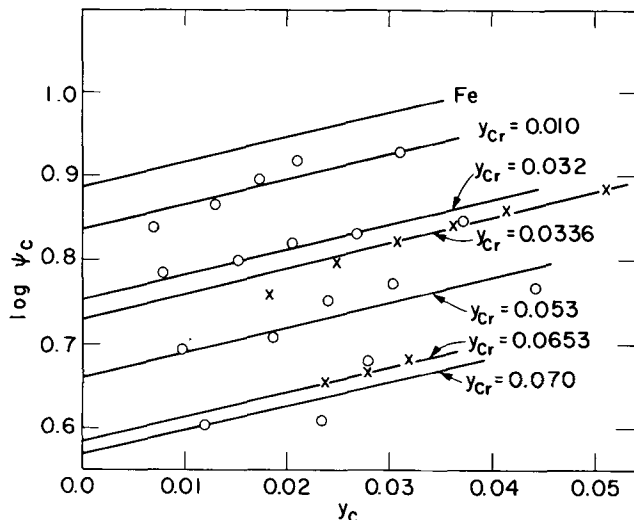


Fig. 7—Activity coefficient of carbon in Fe-Cr-C alloys at 1000°C. Results of Nishizawa,⁴ circles, and of Bungardt *et al.*,⁶ crosses.

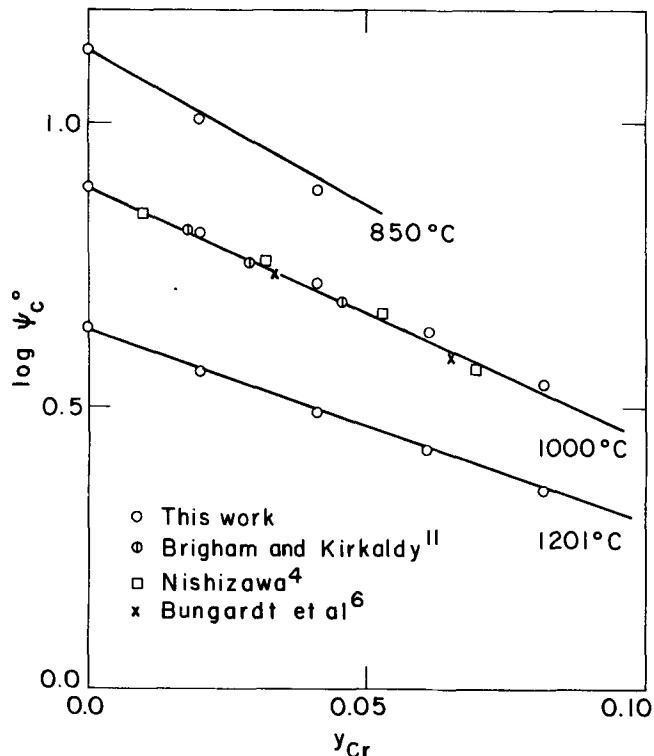


Fig. 8—Effect of chromium on the activity coefficient of carbon at infinite dilution in Fe-Cr-C alloys.

the austenite range is that at 0.6 pct V at 1050°C. Reading approximately their plotted carbon contents of binary and ternary alloys and referring to Eq. [1] for the binary, we have calculated the point shown in Fig. 11.

The solid lines of Fig. 11 represent our conclusions regarding the effect of vanadium on the activity coefficient of carbon at infinite dilution. The lines are not accurately determined because of the limited concentration range. They are drawn according to the expression:

$$d \log \Psi_C / dy_V = -10,700/T \quad [7]$$

This corresponds to a value $\epsilon_C^{(V)} = -19.4$ at 1000°C and

-18.6 at 1050°C. These values are slightly less negative than those reported by Ebeling and Wever¹⁵ which are represented by the broken lines of Fig. 11. The activity coefficient of carbon in Fe-V-C alloys may be represented by the equation

$$\log \Psi_C = 2300/T - 0.92 + (3860/T)y_C - (10,700/T)y_V \quad [8]$$

Solubility of Carbides in Fe-V-C Alloys

In order to determine the solubility limit of carbide in austenite, the experimental observations on carbides at 997°C are plotted in Fig. 12. The carbide phase VC_{1-x} is known as having a composition range from $VC_{0.88}$ to $VC_{0.73}$,^{17,18} depending upon the carbon activity. Using these values, the straight lines can be drawn through points of constant activity of carbon. The intersection of these straight lines with corresponding isoactivity lines in the austenite range gives the phase boundary. The resulting boundary lies appreciably lower in carbon than that of Zupp and Stevenson.¹⁶

Zupp and Stevenson determined the phase boundary from the break points of their lines without metallographic observations. Because of the scattering of experimental points, this method may not be of high accuracy. As a matter of fact, two typical runs from Zupp and Stevenson's paper plotted in Fig. 12 illustrate that their isoactivity lines may be better explained by the phase boundary of the present work.

Flender and Wever¹² determined the solubility limit of vanadium carbide in austenite on the basis of limited data on thermodynamic properties of this system. Especially they estimated an unknown parameter, the ac-

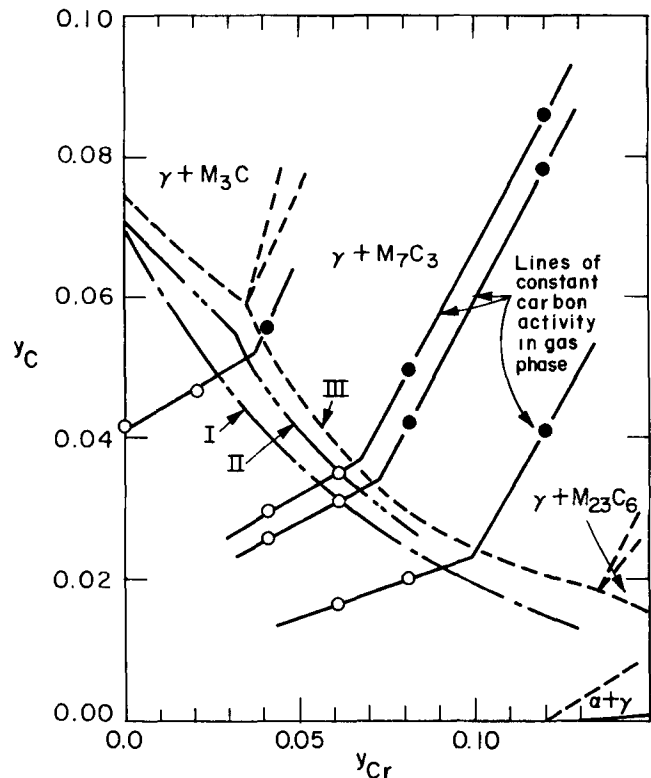


Fig. 9—The austenite/carbide phase boundaries in Fe-Cr-C alloys at 1000°C. I) Bungardt, Kunze, and Horn;¹⁴ II) Bungardt, Preisendanz, and Lehnert;⁶ III) Nishizawa.⁴ Isoactivity lines, this work: ● carbides observed, ○ carbides absent. Breaks in lines show limit of austenite field.

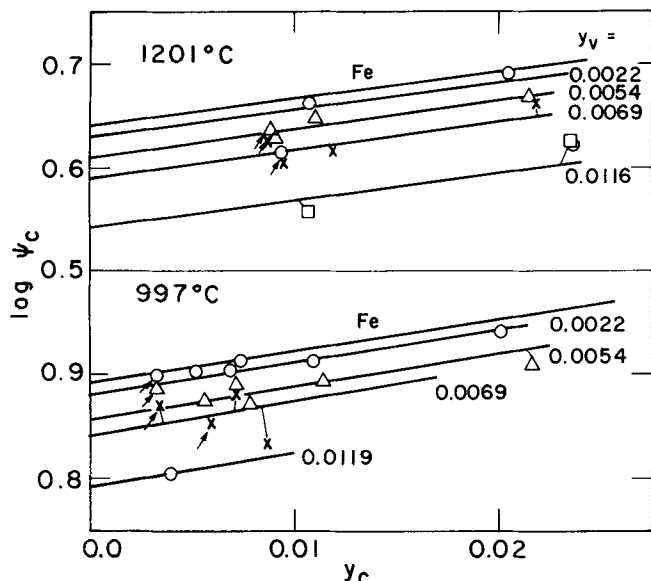


Fig. 10—Activity coefficient of carbon in Fe-V-C alloys at 997° and 1201°C.

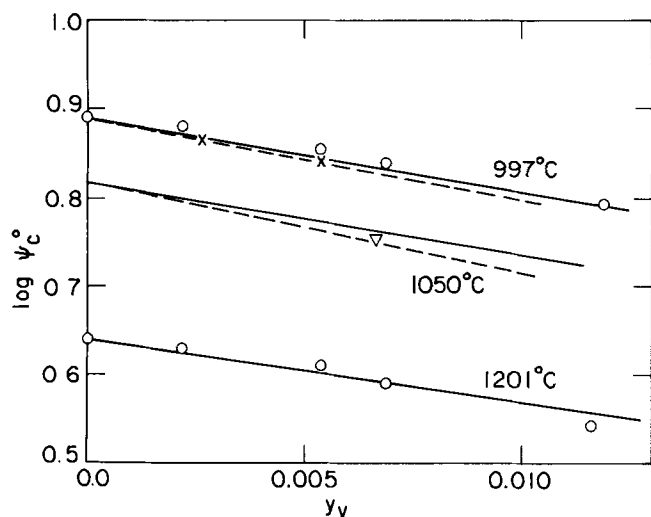


Fig. 11—Effect of vanadium on the activity coefficient of carbon at infinite dilution. Solid lines and circles, our data. Broken lines and triangle, Ebeling and Wever's data¹⁵ recalculated. Crosses, Zupp and Stevenson¹⁶ data at 1000°C.

tivity coefficient of vanadium, γ_V° , according to the results of Savostyanova and Shvartsman.¹⁹ However, Savostyanova and Shvartsman concluded by extrapolating the solubility of vanadium carbide in Fe-Mn-V-C alloy to zero manganese, that the solubility limit of carbide at 1000°C can be expressed by

$$(V)^4 \cdot (C)^3 = 0.224 \quad [9]$$

where (V) and (C) are atom percent of vanadium and carbon, respectively. This relation is in good agreement with the present results as shown in Fig. 12.

Ebeling and Wever¹⁵ determined the solubility of carbides from distribution of carbon in a diffusion couple and obtained results close to those of Flender and Wever.¹² This method is also not highly reliable, because of its kinetic character.

Narita and Koyama²⁰ proposed a formula for the solubility of vanadium carbide in austenite as

$$\log (\%V) \cdot (\%C) = -9500/T + 6.72 \quad [10]$$

This equation is a good approximation in the composition range up to about 0.5 pct V at 1000°C, but the departure becomes appreciable in the higher vanadium region.

The point $y_V = 0.0165$ and $y_C = 0.00512$, Table III, did not show any evidence of presence of α phase. The position of the $\gamma/\alpha + \gamma$ boundary in Fig. 12 is that estimated thermodynamically by West,²¹ which shows no inconsistency with the present work.

THERMODYNAMIC PROPERTIES

The free energy change in the transfer of carbon from graphite into binary Fe-C austenite according to Eq. [1] is:

$$C(gr) = \underline{C}(\gamma); \Delta G_C = 10,520 - 4.21T \\ + 17,660y_C + RT \ln z_C$$

The heat of solution of graphite into the fcc phase for the binary system is

$$\Delta H_C^{(FeC)} = 10,520 + 17,660y_C \quad [11]$$

Correspondingly, the values for the three systems studied in this work as obtained from Eqs. [4], [6], and [8] are:

$$\Delta H_C^{(FeMoC)} = 10,520 + 17,660y_C - 43,500y_{Mo} \quad [12]$$

$$\Delta H_C^{(FeCrC)} = 10,520 + 17,660y_C - 43,500y_{Cr} \quad [13]$$

$$\Delta H_C^{(FeVC)} = 10,520 + 17,660y_C - 49,000y_V \quad [14]$$

The entropy of solution of graphite into the fcc phase for the same systems are

$$\Delta S_C^{(FeC)} = 4.21 - R \ln z_C \quad [15]$$

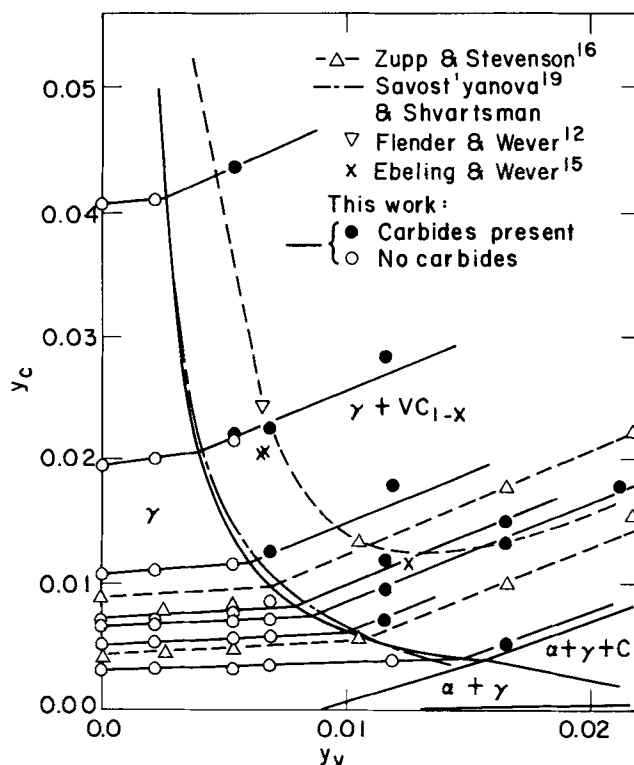


Fig. 12—Phase boundaries in Fe-V-C alloys at 1000°C. Our data support the solubility line of Savostyanova and Shvartsman.¹⁹

$$\Delta S_C^{(\text{FeMoC})} = 4.21 - 11.4y_{\text{Mo}} - R \ln z_C \quad [16]$$

$$\Delta S_C^{(\text{FeCrC})} = 4.21 + 14.0y_{\text{Cr}} - R \ln z_C \quad [17]$$

$$\Delta S_C^{(\text{FeVC})} = 4.21 - R \ln z_C \quad [18]$$

Eqs. [11] through [18] are applicable only over the ranges of composition where the fcc phase is stable, Figs. 4, 9, and 12.

Translation to Conventional Units

Equations in which the concentrations of carbon and alloying elements are expressed in weight percent are readily derived from Eqs. [4], [6], and [8]. In the following equations $f_C = a_C/[\%C]$ and graphite is the standard state for carbon. For a Henrian standard state based on infinite dilution the first two terms are omitted. For 0 to 4 pct Mo, 0 to 1.2 pct C

$$\log f_C = 2300/T - 2.24 + (182/T)\%C - (56/T - 0.015)\%Mo \quad [19]$$

For 0 to 12 pct Cr, 0 to 1 pct C

$$\log f_C = 2300/T - 2.24 + (179/T)\%C - (102/T - 0.033)\%Cr \quad [20]$$

For 0 to 2 pct V, 0 to 1 pct C

$$\log f_C = 2300/T - 2.24 + (179/T)\%C - (117/T)\%V \quad [21]$$

Within the specified experimental ranges these equations agree with Eqs. [4], [6], and [8] within less than 0.007 in $\log a_C$. They may be extended to somewhat higher alloy content without serious error.

SUMMARY

The effects of Mo, Cr, and V on the activity of carbon in austenite have been studied by equilibrating the alloys with methane-hydrogen mixtures in the temperature range from 848° to 1200°C. The activity of carbon was established from the carbon content of a binary Fe-C alloy equilibrated in the same experiment. The results have been compared with the experimental

measurements at 1000°C of a number of other investigators. In some cases the agreement is good, in others it is not. All of the alloying elements, Mo, Cr, and V, lower the activity coefficient of carbon and the decrease is found to be proportional to the carbon content.

The results also permit a further assessment of the solubility of the various carbides in alloyed austenite that have been published in the literature.

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