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A. A. ZHUKOV

1964

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Abstract

Full Text

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SOME REGULARITIES OF THE GEOMETRIC THERMODYNAMICS OF BINARY AND TERNARY IRON-CARBON ALLOYS

(Presented by Academician A. A. Bochvar, 15 V 1964)

In papers ([1]-[3]), questions of the geometry of the line $JE'E$ of the constitution diagram of iron-carbon alloys were considered by superposing on it lines of isoactivity of carbon. In particular, in paper ([1]) it was shown that the line $JE'E$ is rectilinear in the coordinates temperature–wt.% C. In Fig. 1, constructed in the coordinates temperature–atomic fractions of carbon, this line turned out to be slightly curved.

As early as 1955 M. Hillert proposed a method for the thermodynamic calculation of the position of the lines of the right-hand part of the iron-carbon diagram relative to the eutectic point on the basis of data on the position of the lines of the left-hand part ([4]). In particular, by this method M. Hillert determined the position of the line CD, the experimental construction of which is extremely difficult, if not impossible (owing to the rapid decomposition of cementite at high temperatures).

These data are now given in handbooks ([5], [6]) and were used by the author ([2], [3]) in calculations of the thermodynamic activity of carbon in the ternary phosphide eutectic γFe—Fe_3C—Fe_3P at its solidification temperature (950°). The magnitude of the activity was then found to be $a_C^{\phi.e} = 0.78 \div 0.80$. However, subsequent investigations ([7]) showed that these figures are apparently underestimated. In Fig. 2 the point L_1 of the ternary eutectic lies to the right of the dashed curve $a_C = 1.0$, drawn from the point d_1' (see Fig. 1) and corresponding to the solubility of graphite in supercooled melts Fe–C–P at 950° (the position of the point L_1 is taken according to ([8]), and the slope of the graphite-solubility lines according to ([9])). This means that $a_C^{\phi.e} > 1$.

In this connection, and in view of the new data on the position of the line JE ([1]), it was necessary to revise the results of paper ([4]) and to refine the position of the line CD. The values a_C^{γ} in austenite (including supersaturated austenite) were calculated from the Darken and Gurry equation ([10]). Calculation along the 950° isotherm showed that, at the point e_1 of intersection of the isotherm with the line JE, the value $a_C^{\gamma-}$ is equal to 4.95. This figure was adopted by us as the base value a_C^0 in calculations of $a_C^{\phi.e}$ by the Hillert equation ([11]).

Figure 2 shows the tie-line triangle $E_1L_1F_1$ of the three-phase equilibrium liquid

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Fig. 1. Corrected phase diagram of iron-carbon alloys with carbon isoactivity lines plotted on it

Figure 1: Fig. 1. Corrected phase diagram of iron-carbon alloys with carbon isoactivity lines plotted on it

ternary eutectic–austenite–cementite in the Fe–C–P system at 950°. We carry out the calculation at the point L_1 of the tie line E_1L_1:

$$a_C^{\phi.\mathrm{e}} = a_C^0 \exp\left[-n\left(1 - \frac{c_C + c_C^0}{2}\right) - c_P\right] =$$

$$= 4.95 \exp\left[-1.67\left(1 - \frac{0.107 + 0.234}{2}\right)\right] - 0.106 = 1.12, \qquad (1)$$

where c_C and c_P are the coordinates of the point L_1; c_C^0 is the abscissa of the point l_1; n is the tangent of the angle of inclination of the tie line E_1L_1.

After complete solidification of the ternary phosphide eutectic at 950°, the point L_1 disappears and the tie-line triangle $E_1L_1F_1$ is replaced by the triangle $E_1R_1F_1$, the vertex R_1 of which corresponds to phosphide Fe_3P at 950°. This triangle is also the geometric locus of the representative points $a_C = \mathrm{const}$. We carry out the calculation of the value a_C at the point E_1 of the tie line E_1F_1 equal–

pro-eutectic austenite–cementite. The base tie-line in this case is the straight line s_1f_1 (see Fig. 1).

The base value a_C^0 in this case is equal to 1.06 (see Fig. 1, where the line ES intersects the 950° isotherm at point s_1, lying on the isoactivity line $a_C^\gamma = 1.06$). The calculation gives

$$a_C^{E_1} = 1.06 \exp\left[0.09\left(1 - \frac{0.053 + 0.063}{2}\right) - 0.017\right] = 1.13. \qquad (2)$$

It is quite obvious that the quantities $a_C^{E_1}$ and $a_C^{\phi.e}$ must be identical, since crystallization of the ternary eutectic in the ternary system proceeds isothermally. This is in fact the case.

Fig. 1. Corrected phase diagram of iron–carbon alloys with carbon isoactivity lines plotted on it

The data obtained make it possible to recalculate the position of the curve CD (see Fig. 1) by a somewhat modified Hillert method ([4]).

Let x be the abscissa of the point d_1 where the curve dCD intersects the 950° isotherm. Hillert' s equation, as applied to point L_1 of the tie-line L_1F_1, gives

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Fig. 2

Figure 2: Fig. 2

$$a_C^0 \exp\left[0.70\left(1-\frac{0.107+x}{2}\right)-0.106\right]=1.13. \quad (3)$$

Since the quantities a_C^0 and x are interdependent, we perform the calculation by the method of successive approximations and first choose some approximate value for x, for example 0.118 ([2]). The first approximation gives $a_C^0 = 0.674$. The isoactivity line $a_C^x = 0.674$ intersects the 950° isotherm at $x = 0.136$. Substitution of this value of x into calculation (3) gives $a_C^0 = 0.679$. Further approximations do not change the values of x and a_C^0 in the third digit ($x = 0.136$ and $a_C^0 = 0.680$).

An analogous calculation was carried out at 1050° and made it possible to establish the position of point d_2 (see Fig. 1). The line Cd was thus constructed from three points d_1, d_2, and C. Its extrapolation to point D was carried out as follows.

It was established that the temperature dependence of the quantity $a_C^{\gamma-\ell}$ is logarithmic (in Fig. 3 the line $JE'Ee$, constructed in semilogarithmic···

on a logarithmic scale, turned out to be practically straight). This approximately corresponds to the known linear dependence of the logarithm of the thermodynamic activity on the reciprocal of the absolute temperature. On this basis the curve CD in Fig. 3 was constructed by extending the line Cd to the left of point C.

The curve dCD in Fig. 1 corresponds to a greater slope than in Hillert' s work ([4]), who also used the Fe–C–P system for calculations. In that work Hillert also pointed out that the slope of the line dCD obtained by him was too small and that the actual curve must be steeper.

Fig. 2. Tie-line triangles corresponding to the three-phase equilibrium austenite–cementite–liquid eutectic in the ternary Fe–C–P system at 950 and 1050°, and lines of carbon isoactivity in supercooled Fe–C–P melts

Of particular interest is the fact that the positions of the lines JEe and dCD, corrected in ([1]) and in the present study, correspond to linear temperature dependences of the quantities $\ln a_C^{\gamma-l}$ and $\ln a_C^{l-\mathrm{cem}}$. This made it possible to establish a quantitative relation between the temperature of the ledeburite transformation of ternary Fe–C–Me alloys (where Me is the third component) and the angle β at the vertex of the eutectic tie-line triangle corresponding to the liquid eutectic. The possibility of the existence of such a dependence was discussed earlier ([12,13]).

According to Hillert' s equation ([11])

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Fig. 3

Figure 3: Fig. 3

$$\ln a_C^{\mathrm{l}} - \ln a_{C_I}^0 = -n_I \left(1 - \frac{c_C^{\mathrm{l}} + c_{C_I}^0}{2}\right) - c_{\mathrm{Me}}, \tag{4}$$

$$\ln a_C^{\mathrm{l}} - \ln a_{C_{II}}^0 = -n_{II} \left(1 - \frac{c_C^{\mathrm{l}} + c_{C_{II}}^0}{2}\right) - c_{\mathrm{Me}}, \tag{5}$$

where a_C^{l} is the thermodynamic activity of carbon in the liquid eutectic (having the same value in equations (4) and (5)); I and II are indices corresponding to the equilibria austenite–liquid eutectic and cementite–liquid eutectic.

In alloys with a low content of the third component Me, the values $c_{C_I}^0$ and $c_{C_{II}}^0$ are close to the value c_C, equal to 0.174 (the abscissa of point C in Fig. 1). Consequently:

$$\ln a_{C_I}^0 - \ln a_{C_{II}}^0 = 0.826\,(n_I - n_{II}). \tag{6}$$

From the data of Fig. 3 we have

$$\ln a_{C_I}^0 - \ln a_{C_{II}}^0 = -0.0106\,(t_{\mathrm{ledebur}} - 1147^\circ).$$

On the other hand, for small values of c_{Me} we have $n_I - n_{II} = \pi - \beta$ (in radians). Thus:

$$\beta \cong 0.0128\,(t_{\mathrm{ledebur}} - 1147^\circ) + \pi. \tag{7}$$

In this case it is assumed that when the vertex of the eutectic conode triangle corresponding to the liquid eutectic is directed upward, as shown in Fig. 2, we have $\beta < \pi$, and the eutectic ledeburite transformation of such alloys takes place at temperatures below 1147°. When the vertex is directed downward, we have $\beta > \pi$, and the interval of eutectic transformation of such alloys is above 1147°.

Fig. 3. Curves of the temperature dependence of the quantities $\ln a_C^{\gamma-}$ and $\ln a_C^{-}$, $\ln a_C^{\alpha-\gamma}$ and $\ln a_C^{\gamma-}$ in the system Fe–Fe_3C

An equation analogous to (7) was also obtained for the eutectoid pearlitic transformation of ternary iron-carbon alloys (on the basis of the data from the right-hand part of Fig. 3):

$$\beta \cong 0.018\,(t \quad - 727^\circ) + \pi. \tag{8}$$

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The results of calculations by equations (7) and (8) as applied to the systems Fe–C–Si, Fe–C–Cr, Fe–C–S, and Fe–C–As agree satisfactorily with the literature (experimental) data. In the case of the Fe–C–P system, the calculated and experimental data, naturally, coincide completely, since this system was used in compiling the reference dependences.

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Received
21 IV 1964

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