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A Data Treatment Method of Carbon Saturated Solubility in Fe-C-Cr Melt

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Abstract: Based on the current situation of studying the thermodynamic property of Fe-C-Cr melt using the carbon saturated solubility, an experimental data treatment method of the carbon saturated solubility was put forward. With this method a linear relationship expression of the carbon saturated solubility in Fe-C-Cr melt was obtained, which intercept is dependent on temperature and independent of third component [Cr], but which slope is dependent on third component [Cr] and independent of temperature. Through this expression activity interaction coefficients at different temperatures were calculated and the relationship between activity interaction coefficients and temperature is also obtained.

Key words: data treatment method; intercept; slope; carbon-saturated solubility; Fe-C-Cr melt

1 Introduction

The linear relationship expression of the carbon saturated solubility is widely used in the study of metallurgical thermodynamics to calculate the thermodynamic properties of components in metallic melt. Although lots of researchers ever reported their linear relationship expressions of the carbon saturated solubility and their results of the thermodynamic properties at the same temperature for the same system, there are great differences among these obtained results due to the lack of effective method for treating data. Also, because these thermodynamic property data are obtained at fixed temperatures, it is inconvenient and incorrect to use these thermodynamic parameters to analyze practical problems.

In this article, a method for treating the data of the carbon saturated solubility in Fe-C-Cr melt is proposed. With this method we can obtain the relationship among the carbon saturated solubility, temperature and third component [Cr], and the relationship between the activity interaction coefficient of components and temperature, which can be used to improve the calculation precision of activity interaction coefficient of components in Fe-C-Cr melt.

2 Experiment

The carbon-saturated solubility in Fe-C-Cr melt was studied in this experiment. 10 g metal and graphite powder were compounded in established proportion and then were put into the holes of a porous graphite crucible. The experimental temperature, measured with Pt-Rh30 and Pt-Rh6 thermocouple and controlled by DWK702 automatic controller, was kept at 1 723±3 K.

After all of the metal in the crucible melt, the system was kept in equilibrium for 5 h in order to make sure the dissolution of carbon reach equilibrium. Then, the graphite crucible was taken out from the experimental furnace, and after the water-cooling process, the metal was broken into powder for analysis. The carbon was analyzed by burning method and Cr was analyzed by potassium permanganate capacity method. The results of these analyses are listed in **table 1**.

Table 1 The carbon saturated solubility in Fe-C-Cr melt at 1 723 K

No.	[%Cr]	[%C]	Δ[%C]	x_{Cr}	x_C	Δx_C
1	0.00	5.04	0.00	0.000	0.198	0.000 0
2	2.21	5.11	0.07	0.020	0.200	0.002 0
3	5.38	5.46	0.42	0.048	0.211	0.013 1
4	8.10	5.53	0.49	0.072	0.213	0.015 0
5	10.81	5.82	0.78	0.095	0.222	0.023 8
6	12.97	6.12	1.08	0.113	0.231	0.032 9
7	13.31	6.10	1.06	0.116	0.230	0.032 2
8	15.04	6.33	1.29	0.130	0.237	0.039 0

For the purpose of dealing with data more conveniently in the following parts of this paper, the difference between the carbon saturated solubility in Fe-Cr-C melt and that in Fe-C melt is also given in the table 1, and the employed formula for calculating this difference is:

$$\Delta x_C = x_C - x_C^{Fe} \quad (1)$$

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$$\Delta[\%C] = [\%C] - [\%C]_{Fe} \quad (2)$$

where [%C], x_C, $[\%C]_{Fe}$ and x_C^{Fe} are the carbon saturated solubility in mass fraction and molar fraction respectively in Fe-Cr-C and Fe-C melt at different temperatures.

3 Conventional Method for Data Treatment

The conventional method for data treatment is:

(1) Based on these data of the carbon saturated solubility x_C (or [%C]) and the third component x_j (or [%j]) in ferroalloy melt at some fixed temperatures, a linear regressive relationship is obtained as following:

$$x_C = x_C' + k' x_j \quad (3)$$

$$[\%C] = [\%C]' + m'[\%j] \quad (4)$$

where x_C' and $[\%C]'$ are the interception of the linear relationship expression about the carbon saturated solubility, k' and m' are the slopes of the linear relationship about the carbon saturated solubility in molar fraction and mass fraction respectively, and the slope shows the extent of the effect of third component Cr on the carbon saturated solubility.

(2) According to the definition of activity interaction coefficient, the obtained interception and slope of the linear relationship expression are used to calculate the activity interaction coefficient of components in multicomponent metallic melt at some known experimental temperatures.

Because of the differences of the concentration ranges employed in those studies, with regarding to experiment error and analysis error, different researchers have come up with different varying tendencies of the slope of the linear relationship expression of the carbon saturated solubility. These results differ greatly. For example, some researchers showed that the slope increased when the temperature was increased, while some others showed the opposite result.

For this research, the linear relationship expression of x_C and x_{Cr}, [%C] and [%Cr] is:

$$x_C = 0.195\,3 + 0.301\,2\,x_{Cr} \quad (5)$$

$$[\%C] = 4.958\,8 + 0.086\,1\,[\%Cr] \quad (6)$$

The slopes of the linear relationship between the carbon saturated solubility x_C and x_{Cr} in Fe-C-Cr melts obtained by different researchers are shown in **figure 1** (straight lines are drown according to the linear relationship expression and the concentration range from references). Among these six lines three intersect each other. Moreover, the line from reference [3] at higher temperature (1 873 k) is lower than that from reference [2] at lower temperature (1 823 k).

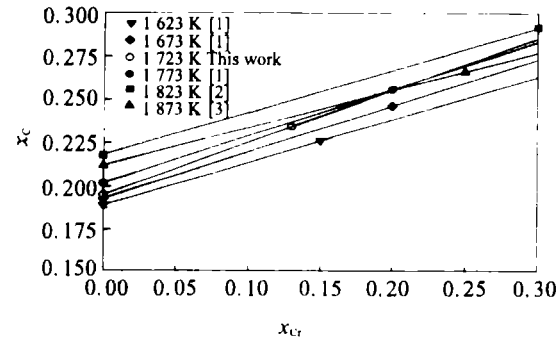

Figure 1 The carbon saturated solubility in Fe-C-Cr melts at different temperatures

When using x_C', k', $[\%C]'$, m' based on the definition of activity interaction coefficient, the obtained thermodynamics parameters of Fe-C-Cr melt diverge greatly. **Table 2** shows these activity coefficients and activity interaction coefficients about Cr and C in Fe-C-Cr melt. It can be seen that the difference among ε_C^{Cr} and different references is more than two times and the difference among ρ_C^{Cr} and different references is greater. Because in these studies the activity interaction coefficients were studied only at some fixed temperatures and no explicit relationship among them was proposed, it is difficult to get parameters at any temperature.

Table 2 Activity interaction coefficients of components in Fe-C-Cr melt from different references

No.	$\ln y_{Cr}^0$	ε_C^{Cr}	ρ_C^{Cr}	T / K	References
1	−0.218	−5.41	4.59	1 673	[1]
2	−0.321	−4.93	4.26	1 773	[1]
3	—	−3.81	—	1 823	[2]
4	−0.350	−7.60	−1.00	1 873	[3]
5	—	−3.15	—	1 873	[4]
6	—	−3.60	19.35	1 873	[5]
7	−0.030	−5.10	−0.07	1 873	[6]

4 Relationship of the Carbon Saturated Solubility and [Cr]

By analyzing a great deal of data of the carbon saturated solubility in Fe-Cr-C melts obtained from experiment and references, it is found that there is an apparent linear relationship between the difference Δx_C ($= x_C - x_C^{Fe}$) and x_{Cr}, as shown in **figure 2**.

$$\Delta x_C = x_C - x_C^{Fe} = k \cdot x_{Cr} = 0.254\,4\,x_{Cr} \quad (7)$$

where the unit of x is molar fraction.

$$\Delta[\%C] = [\%C] - [\%C]_{Fe} = m \cdot [\%Cr] = 0.076\,2[\%Cr] \quad (8)$$

where m is a constant independent from temperature, and the unit of [%j] is mass fraction. The relationship between the carbon saturated solubility in Fe-C melt x_C^{Fe} or $[\%C]_{Fe}$ and temperature is as following [8]:

$$x_C^{Fe} = 0.052 + 0.084\,8 \times 10^{-3} T \quad (9)$$

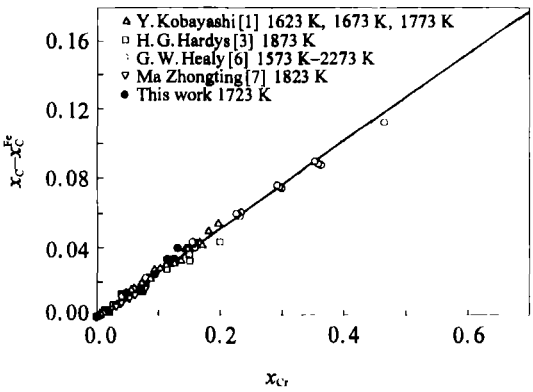

Figure 2 Effect of Cr on the carbon saturated solubility in Fe-C-Cr melt at different temperatures

$$[\%C]_{Fe} = 0.602\,1 + 2.578\,6\times10^{-3}T + 0.076\,2[\%Cr] \quad (10)$$

Substituting equations (9) and (10) into equations (7) and (8) respectively, it is obtained that:

$$x_C = 0.052\,0 + 0.084\,8\times10^{-3}T + 0.254\,4x_{Cr} \quad (11)$$

$$[\%C] = 0.602\,1 + 2.578\,6\times10^{-3}T + 0.076\,2[\%Cr] \quad (12)$$

where the intercept is dependent on temperature but independent of the third component [Cr]. The slope k = 0.254 4 or m = 0.076 2 is dependent on the third component [Cr] but independent of temperature.

5 Calculation of Activity Interaction Coefficient

Based on the definition of activity interaction coefficient at constant activity [9], in the case of carbon saturation, the first-order activity interaction coefficients of third component [Cr] upon [C] at constant activity are:

$$\dot{\varepsilon}_C^{Cr} = \left(\frac{-\partial \ln x_C}{\partial x_{Cr}}\right)_{\substack{a_C \\ x_{Cr}\to 0}} = -\frac{0.254\,4}{0.052\,0 + 0.084\,8\times10^{-3}T} \quad (13)$$

$$\dot{e}_C^{Cr} = \left(\frac{-\partial \lg[\%C]}{\partial[\%Cr]}\right)_{\substack{\%C \\ [\%Cr]\to 0}} = -\frac{1}{2.303}\times\frac{0.076\,2}{0.602\,1 + 2.578\,6\times10^{-3}T} \quad (14)$$

And the second-order activity interaction coefficients of third component [Cr] upon [C] at constant activity are:

$$\dot{\rho}_C^{Cr} = \frac{1}{2}\left(\frac{-\partial^2 \ln x_C}{\partial x_{Cr}^2}\right)_{\substack{a_C \\ x_{Cr}\to 0}} = \frac{1}{2}\left(\frac{0.254\,4}{0.052\,0 + 0.084\,8\times10^{-3}T}\right)^2 \quad (15)$$

$$\dot{r}_C^{Cr} = \frac{1}{2}\left(\frac{-\partial^2 \lg[\%C]}{\partial[\%Cr]^2}\right)_{\substack{\%C \\ [\%Cr]\to 0}} = \frac{1}{4.605}\left(\frac{0.076\,2}{0.602\,1 + 2.578\,6\times10^{-3}T}\right)^2 \quad (16)$$

while T = 1 573, 1 673, ···, 2 273 K, $\dot{\varepsilon}_C^{Cr}$, $\dot{e}_C^{Cr}$, $\dot{\rho}_C^{Cr}$ and $\dot{r}_C^{Cr}$ at different temperatures are shown in **table 3**, the relationship between $\dot{\varepsilon}_C^{Cr}$, $\dot{e}_C^{Cr}$, $\dot{\rho}_C^{Cr}$, $\dot{r}_C^{Cr}$ and temperature are:

Table 3 Activity interaction coefficient at constant activity $\dot{\varepsilon}_C^{Cr}$, $\dot{e}_C^{Cr}$, $\dot{\rho}_C^{Cr}$ and $\dot{r}_C^{Cr}$ at different temperatures (K)

Inter. coef.	1 573	1 673	1 773	1 873	1 973	2 073	2 173	2 273
$\dot{\varepsilon}_C^{Cr}$	−1.372	−1.312	−1.257	−1.207	−1.160	−1.117	−1.077	−1.039
$\dot{\rho}_C^{Cr}$	0.942	0.861	0.790	0.728	0.673	0.624	0.580	0.540
$\dot{e}_C^{Cr}\times10^2$	−0.710	−0.673	−0.639	−0.609	−0.582	−0.556	−0.533	−0.51₂
$\dot{r}_C^{Cr}\times10^4$	0.581	0.522	0.471	0.427	0.389	0.356	0.327	0.302

$$\dot{\varepsilon}_C^{Cr} = -0.296 - 0.170\times10^4 T^{-1},\ R = 0.999\,6 \quad (17)$$

$$\dot{\rho}_C^{Cr} = 0.365 + 0.205\times10^4 T^{-1},\ R = 0.999\,9 \quad (18)$$

$$\dot{e}_C^{Cr}\times100 = -0.068 - 0.101\times10^4 T^{-1},\ R = 0.999\,9 \quad (19)$$

$$\dot{r}_C^{Cr}\times10^4 = -0.331 + 0.143\times10^4 T^{-1},\ R = 0.999\,3 \quad (20)$$

Using the relationship between the activity interaction coefficient at constant activity and activity interaction coefficient at constant concentration [9], the results can be obtained as shown in **table 4**. The relationship between ε_C^{Cr}, ρ_C^{Cr}, $\rho_C^{C,Cr}$, ρ_{Cr}^{C} and temperature are:

$$\varepsilon_C^{Cr} = -0.467 - 4.426\times(10^4/T) + 0.099\times(10^4/T)^2 \quad (21)$$

$$\rho_C^{Cr} = 0.876 - 0.694\times(10^4/T) + 0.061\times(10^4/T)^2 \quad (22)$$

$$\rho_C^{C,Cr} = 1.407 + 0.571\times(10^4/T),\ R = 0.998\,4 \quad (23)$$

$$\rho_{Cr}^{C} = -0.568 - 1.119\times(10^4/T) + 0.077\times(10^4/T)^2 \quad (24)$$

Based on these thermodynamic parameters, the thermodynamic analysis was carried out for the process of the de-carbonization with blowing oxygen when medium and low carbon ferrochrome were smelted in converter practice, and the analytical results coincides with the data from industrial operation [10].

The above-mentioned new method for treating data can be successfully applied to the calculation of the thermodynamic parameters of components in other metallic melts. Because the calculating formula has been

Table 4 Activity interaction coefficient at constant concentration ε_C^{Cr}, ρ_C^{Cr}, $\rho_C^{C,Cr}$ and ρ_{Cr}^{C} at different temperatures (K)

Inter. coef.	1 573	1 673	1 773	1 873	1 973	2 073	2 173	2 273
ε_C^{Cr}	−5.548	−5.464	−5.369	−5.268	−5.162	−5.052	−4.941	−4.827
ρ_C^{Cr}	−1.059	−1.083	−1.089	−1.082	−1.067	−1.045	−1.045	−0.991
$\rho_C^{C,Cr}$	5.073	4.823	4.613	4.435	4.428	4.155	4.044	3.951
ρ_{Cr}^{C}	−4.556	−4.490	−4.416	−4.337	−4.254	−4.168	−4.080	−3.991

greatly simplified in this method, the thermodynamic property of metallic melt with carbon saturated solubility can be easily obtained.

Since we only need to determine the carbon saturated solubility at some fixed temperatures and the slopes (k_j or m_j) of the expression of the carbon saturated solubility, it is also very easy to use this method to calculate activity interaction coefficient of components at constant activity at demanded temperature, and to calculate the activity interaction coefficient of components at constant concentration based on the relationship between activity interaction coefficient at constant activity and that at constant concentration.

6 Conclusions

(1) Based on experimental data of this work and some references, a new method for treating data is put forward. Using the method, the relationship expression of the carbon saturated solubility in Fe-Cr-C melt are obtained as follows:

$$x_C = 0.052\,0 + 0.084\,8\times10^{-3}\,T + 0.254\,4\,x_{Cr}$$

$$[\%C] = 0.602\,1 + 2.578\,6\times10^{-3}\,T + 0.076\,2[\%Cr]$$

where the intercept is dependent on temperature and independent of third component [Cr], slope $k = 0.254\,4$ or $m = 0.076\,2$ is a fixed value dependent on third component [Cr] and independent of temperature.

(2) Using the expression of carbon saturated solubility, activity interaction coefficient of components in metallic melt at demanded temperature can be calculated easily, and the relationship between the first-order or second-order activity interaction coefficient at constant activity or at constant concentration and temperature are:

$$\dot{\varepsilon}_C^{Cr} = -0.296 - 0.170\times(10^4/T),\quad R = 0.999\,6$$

$$\dot{\rho}_C^{Cr} = 0.365 + 0.205\times(10^4/T),\quad R = 0.999\,9$$

$$\dot{e}_C^{Cr}\times100 = -0.068 - 0.101\times(10^4/T),\quad R = 0.999\,9$$

$$\dot{r}_C^{Cr}\times10^4 = -0.331 + 0.143\times(10^4/T),\quad R = 0.999\,3$$

$$\varepsilon_C^{Cr} = -0.467 - 4.426\times(10^4/T) + 0.099\times(10^4/T)^2$$

$$\rho_C^{Cr} = 0.876 - 0.694\times(10^4/T) + 0.061\times(10^4/T)^2$$

$$\rho_C^{C,Cr} = 1.407 + 0.571\times(10^4/T),\ R = 0.998\,4$$

$$\rho_{Cr}^{C} = -0.568 - 1.119\times(10^4/T) + 0.077\times(10^4/T)^2$$

(3) The thermodynamic parameters of components in many metallic melts can be calculated with the data-treating method put forward in this work. There will not exist difficulty in studying the thermodynamic property of metallic melt with carbon saturated solubility, and therefore it is very easy to obtain the thermodynamic parameters because calculating formula has been greatly simplified.

Nomenclature

γ_{Cr}^{0}: Raoultian activity coefficient of solute Cr (infinitely dilute or 1% (mass fraction) solution standard);

ε_C^{Cr}: activity interaction coefficient of Cr upon C in Fe-C-Cr melt at constant concentration(pure substance and mole fraction basis);

ρ_C^{Cr}: 2nd order activity interaction coefficient of Cr upon C in Fe-C-Cr melt at constant concentration (pure substance and mole fraction basis);

$\dot{\varepsilon}_C^{Cr}$: activity interaction coefficient of Cr upon C in Fe-C-Cr melt at constant activity (pure substance and mole fraction basis);

$\dot{e}_C^{Cr}$: activity interaction coefficient of Cr upon C in Fe-C-Cr melt at constant activity(infinitely dilute or 1% solution standard and mass fraction basis).

$\dot{\rho}_C^{Cr}$: 2nd order activity interaction coefficient of Cr upon C in Fe-C-Cr melt at constant activity (pure substance and mole fraction basis);

$\dot{r}_C^{Cr}$: 2nd order activity interaction coefficient of Cr upon C in Fe-C-Cr melt at constant activity (infinitely dilute or 1% solution standard and mass fraction basis);

$\rho_C^{C,Cr}$: 2nd order cross activity interaction coefficient of C and Cr upon C in Fe-C-Cr melt at constant concentration (pure substance and mole fraction basis);

ρ_{Cr}^{C}: 2nd order activity interaction coefficient of C upon Cr in Fe-C-Cr melt at constant concentration (pure substance and mole fraction basis).

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