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Thermodynamic Properties of Carbon and Manganese in Mn-C and Mn-Fe-C Melts

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Abstract: Carbon solubility in Mn-Fe melts ($x_{Mn}=0.083-0.706$, $x_{Fe}=0.034-0.715$) was measured experimentally at various temperatures. By thermodynamic derivation and calculation, the relationship between activity coefficient of carbon in infinite dilute solution of manganese in Mn-C system and temperature was obtained. Using Gibbs-Duhem relationship, the experimental results of this study, and experimental data obtained by strict thermodynamic derivation and calculation in references, the relationships between other thermodynamic properties (ε_{CC}, ε_{CCC}, ε_{CFe}, ε_{CCFe}, and ε_{CFeFe}) in Mn-Fe-C system and temperature were obtained.

Key words: Mn-Fe-C melt; activity interaction parameter; thermodynamic property; carbon; manganese

Symbol List

a_i——Activity of component i;
e_i^j——Interaction parameter of component j to i (standard state of $w_i=0.01$);
I——Integral constant;
M_j——Molar mass of component j;
M_1——Molar mass of solvent 1;
Q——Effect of the second-order and above second-order terms in Wagner formula;
r——Interrelation coefficient;
T——Absolute temperature;
w_i——Mass percent of component i;
x_i——Molar fraction of component i;
ε_i^j——Interaction parameter of j to i (standard state of pure i);
ρ_C^C——Second-order interaction parameter of C to C with standard state of graphite;
$\rho_C^{C,C}$——Third-order interaction parameter of C to C with standard state of graphite;
γ°_i——Activity coefficient of component i (standard state of pure i and $x_i\to 0$);
γ_i——Activity coefficient of component i (standard state of pure i);
γ'_C——Calculated activity coefficient of carbon.

The study on the thermodynamic properties in Mn-C and Mn-Fe-C systems is very important for improving current processes of making Mn-Fe and high-manganese alloys. During the decarburization, desiliconization or dephosohorization for ferromanganese melt, the oxidation of manganese occurs concurrently. To establish an optimum process without an excessive oxidation loss of manganese, it is important to know the thermodynamic behavior of carbon and manganese in liquid ferromanganese alloys. There have been certain experimental and theoretical studies on activities of carbon and manganese in Mn-C and Mn-Fe-C liquid alloys[1-5]. However, the data from various experimental techniques or model calculations are inconsistent[1-3]. In this article, the carbon solubility in Mn-Fe melts ($x_{Mn}=0.083-0.706$, $x_{Fe}=0.034-0.715$) was measured experimentally. Combining with the results reported in Ref. [1, 3-8], by strict thermodynamic derivation and calculation, the relationship equations with high correlation between the thermodynamic properties in Mn-C and Mn-Fe-C systems and temperature were

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obtained by linear regression analysis.

1 Experiment and Results

The equilibrium experiments on carbon solubility in melts were performed in a resistance furnace by $MoSi_2$ elements under nitrogen gas. The charge of 8 g with a definite amount of electrolytic manganese ($w_{Mn}>99.97\%$) and pure iron ($w_{Fe}>99.97\%$) was put in a four-hole graphite crucible. The temperature was measured by a Pt-Rh-Pt thermocouple. The temperature was controlled by a controller with high intelligence. The experiments were carried out at 1 623 K, 1 698 K, 1 723 K, 1 773 K, and 1 823 K for 5 h (from the melting point of metal charge). The temperature fluctuation is less than ±1 K. The metal samples were ground, cleaned, and crushed for analysis. The experimental results at different temperatures are listed in Table 1.

Table 1 Carbon solubility in Mn-Fe melts

No.	1 623 K			1 698 K			1 723 K			1 773 K			1 823 K		
	x_C	x_{Mn}	x_{Fe}	x_C	x_{Mn}	x_{Fe}	x_C	x_{Mn}	x_{Fe}	x_C	x_{Mn}	x_{Fe}	x_C	x_{Mn}	x_{Fe}
1	0.259	0.706	0.035	0.271	0.693	0.036	0.275	0.691	0.034	0.264	0.591	0.145	0.275	0.654	0.071
2	0.254	0.678	0.068	0.264	0.664	0.072	0.272	0.659	0.069	0.259	0.522	0.219	0.272	0.585	0.143
3	0.252	0.643	0.105	0.260	0.630	0.110	0.269	0.627	0.104	0.251	0.452	0.297	0.267	0.516	0.217
4	0.249	0.615	0.136	0.257	0.595	0.148	0.266	0.595	0.139	0.244	0.419	0.337	0.256	0.450	0.294
5	0.246	0.578	0.176	0.256	0.560	0.184	0.263	0.562	0.175	0.242	0.382	0.376	0.250	0.416	0.334
6	0.245	0.493	0.262	0.250	0.528	0.222	0.259	0.531	0.210	0.234	0.309	0.457	0.243	0.382	0.375
7	0.244	0.460	0.296	0.245	0.495	0.260	0.255	0.499	0.246	0.224	0.157	0.619	0.237	0.309	0.454
8	0.234	0.427	0.339	0.242	0.457	0.301	0.252	0.464	0.284	0.202	0.083	0.715			
9	0.230	0.381	0.389	0.244	0.419	0.337	0.249	0.430	0.321						
10	0.224	0.351	0.425	0.238	0.378	0.384	0.245	0.391	0.364						
11	0.215	0.314	0.471	0.232	0.349	0.419	0.242	0.362	0.396						
12	0.211	0.251	0.538	0.229	0.310	0.461	0.237	0.327	0.436						
13	0.207	0.190	0.603	0.222	0.274	0.504	0.234	0.290	0.476						
14	0.204	0.180	0.616	0.217	0.237	0.546	0.229	0.256	0.515						
15				0.215	0.198	0.587	0.225	0.220	0.555						
16				0.206	0.161	0.633	0.216	0.186	0.598						

2 Derivation and Calculation

2.1 Carbon solubility in Mn-Fe melts

From Table 1 and Ref. [6] (1 673 K), the linear regressions of the carbon solubility at different temperatures as the functions of x_{Mn} are as follows:

$$x_C=0.183\,2+0.110\,7x_{Mn} \quad (r=0.98,\ T=1\,623\ K) \tag{1}$$

$$x_C=0.188\,6+0.111\,9x_{Mn} \quad (r=0.914,\ T=1\,673\ K) \tag{2}$$

$$x_C=0.192\,7+0.111\,2x_{Mn} \quad (r=0.99,\ T=1\,698\ K) \tag{3}$$

$$x_C=0.200\,5+0.110\,1x_{Mn} \quad (r=0.99,\ T=1\,723\ K) \tag{4}$$

$$x_C=0.198\,8+0.113\,8x_{Mn} \quad (r=0.98,\ T=1\,773\ K) \tag{5}$$

$$x_C=0.200\,5+0.119\,9x_{Mn} \quad (r=0.98,\ T=1\,823\ K) \tag{6}$$

2.2 Thermodynamic properties of C and Mn in Fe-Mn-C system

Eqn. (7), Eqn. (8), and Eqn. (9) are the equations reported in Ref. [8], Ref. [9], and Ref. [10], respectively. When Q is used to represent the effect of the second-order and above second-order terms in Wagner formula for $\ln\gamma_C$ (here, $\ln\gamma_C=\ln x_C$) in Fe-Mn-C systems at corresponding temperature on $\ln\gamma_C$, Eqn. (10) to Eqn. (15) are obtained.

$$\ln\gamma^{\circ}_C(Fe)=-2.00+2\,718/T \tag{7}$$

$$e_C^C=158/T+0.058 \tag{8}$$

$$\varepsilon_i^j=230\frac{M_j}{M_1}e_i^j+\frac{M_1-M_j}{M_1} \tag{9}$$

$$-\ln x_C-8.462\,3x_C+0.325\,3=\varepsilon_C^{Mn}x_{Mn}+Q \tag{10}$$

$$-\ln x_C-8.318\,5x_C+0.374\,8=\varepsilon_C^{Mn}x_{Mn}+Q \tag{11}$$

$$-\ln x_C-8.249\,8x_C+0.399\,2=\varepsilon_C^{Mn}x_{Mn}+Q \tag{12}$$

$$-\ln x_C-8.183\,1x_C+0.422\,5=\varepsilon_C^{Mn}x_{Mn}+Q \tag{13}$$

$$-\ln x_C-8.054\,5x_C+0.467\,0=\varepsilon_C^{Mn}x_{Mn}+Q \tag{14}$$

$$-\ln x_C-7.934\,5x_C+0.509\,1=\varepsilon_C^{Mn}x_{Mn}+Q \tag{15}$$

It is assumed that y is equal to the left of Eqn. (10) to Eqn. (15). The linear regression Eqn. (16) to Eqn. (21) are obtained. The values of ε_C^{Mn} and Q are obtained. Wagner formulas Eqn. (28) to Eqn. (33) that can be used to calculate $\ln\gamma_C$ (here, $\ln\gamma_C=-\ln x_C$) in Fe-Mn-C systems ($x_{Mn}=0$, $x_{Mn}=1-x_C$) saturated with carbon can be obtained. The comparison between the calculated and experimental x_C shows that