Thermodynamics of Carbon and Sulphur Solutions in Manganese Based Melts

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As a rule,there are some elements with different contents in manganese-based alloys. Interaction of solutes both each other and with solvent should be taken into account when describing physicochemical characteristics of the alloys. The parameters determined for manganese-based binary alloys can be characterized by substantially changed values for multi-component systems.There is a need to study these systems experimentally. For a number of cases, however, it is feasible to estimate the interaction in multi-component systems in advance, e.g. saturated solutions [1,2].

Carbon solubility in manganese-based melts with silicon has been studied by a number of authors [2-7]. However, these studies were performed for the fixed temperature. It doesn't allow someone to obtain a temperature dependence of silicon effect on carbon solubility in liquid manganese. The authors mentioned above interpreted the results obtained relatively to infinitely diluted solutions [3,6]. But it isn't conceptually correct because saturated solutions take place for this case. Parameters characterizing thermodynamics of saturated solutions were determined for Mn-Si-C_{sat} system in [2] and [7]. But results of these studies carried out for different temperatures are in a bad agreement.

Carbon solubility in liquid manganese and Mn-Si melts (as high as 8% Si) was studied within the 1673-1873 K. Electrolytic manganese (99.6%), crystalline silicon (99.99%) and spectrally pure graphite were used for the experiments. Figures 1 and 2 show results obtained. As seen, carbon solubility in liquid manganese rises with temperature. Silicon in melt results in the decrease of carbon solubility as compared with pure manganese because of weakening of carbon bonds.

The temperature dependence of carbon solubility in liquid manganese can be described by the following equation

$$\lg X_{C_{sat}} = - 314.61/T - 0.373. \quad (1)$$

The dependence obtained is in a good agreement with data published [2, 6-9].

For carbon solutions with third component i, effect of the latter on carbon can be described through activity coefficient:

$$\gamma_C^i = \frac{\gamma_{C(Mn,i)}}{\gamma_{C(Mn)}} = \frac{a_{C(Mn,i)} / X_{C(Mn,i)}}{a_{C(Mn)} / X_{C(Mn)}}, \quad (2)$$

where $\gamma_{C(Mn,i)}$, $a_{C(Mn,i)}$, $X_{C(Mn,i)}$ - activity coefficient, activity and mole portion of carbon in Mn-i melts, respectively; $\gamma_{C(Mn)}$, $a_{C(Mn)}$, $X_{C(Mn)}$ - activity coefficient, activity and mole portion of carbon in liquid manganese, respectively.

For equilibrium of solid carbon with binary and ternary solution saturated with carbon:

$$a_{C(Mn)} = a_{C(Mn,i)}, \quad (3)$$

therefore,

$$\gamma_C^i = X_{C(Mn)} / X_{C(Mn,i)}, \quad (4)$$

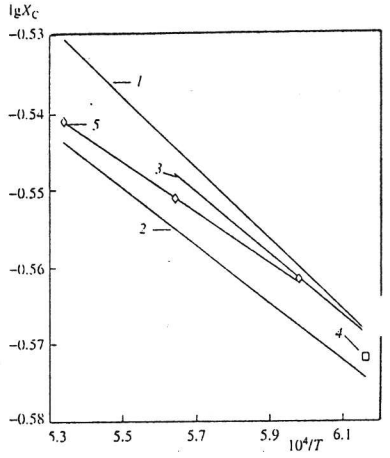

Fig. 1. Dependence of carbon solubility in liquid manganese on temperature: 1 - [8]; 2 - [2]; 3 - [7]; 4 - [9]; 5 - present data

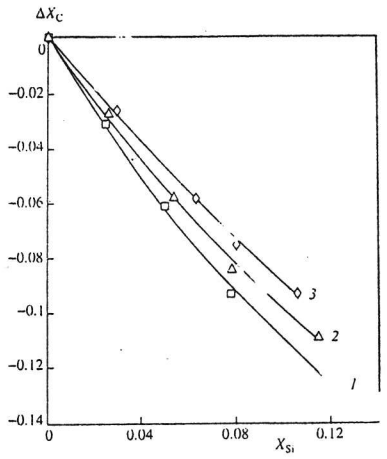

Fig. 2. Dependence of carbon solubility in Mn-Si melts on silicon content: T, K: 1 - 1673; 2 - 1773; 3 - 1873

i.e. activity coefficient γ_C^i is determined through ratio of carbon contents in binary and ternary solutions. Inasmuch

$$X_{C(Mn,i)} = X_{C(Mn)} + \Delta X_C^i, \quad (5)$$

we can imagine

$$\ln\gamma_C^i = \ln\frac{X_{C(Mn)}}{X_{C(Mn,i)}} = \ln\left[1 + \frac{\Delta X_C^i}{X_{C(Mn)}}\right]. \quad (6)$$

Taylor expansion, if limited with the second term, results in

$$\ln\left[1 + \frac{\Delta X_C^i}{X_{C(Mn)}}\right] = \frac{\Delta X_C^i}{X_{C(Mn)}} - \frac{1}{2}\left[\frac{\Delta X_C^i}{X_{C(Mn)}}\right]^2. \quad (7)$$

It is clear that $\Delta X_C^i \to 0$ if $X_i \to 0$. Let's assume that carbon content difference for binary and ternary solutions ΔX_C^i is proportional to content of i [7]

$$\Delta X^i = m X_i + S X_i^2, \quad (8)$$

where m and S - regression coefficients. The m-coefficient is called as a "solubility factor" in [2]. Substituting Eq. (8) into Eq. (7), we will obtain

$$\ln\left[1 + \frac{\Delta X_C^i}{X_{C(Mn)}}\right] = \frac{m}{X_{C(Mn)}} X_i + \left[\frac{S}{X_{C(Mn)}} - \frac{m^2}{2X_{C(Mn)}^2}\right] X_i^2, \quad (9)$$

then Eq. (6) can be imagined as follows

$$\ln\gamma_C^i = -\frac{m}{X_{C(Mn)}} X_i - \left[\frac{S}{X_{C(Mn)}} - \frac{m^2}{2X_{C(Mn)}^2}\right] X_i^2. \quad (10)$$

Values of

$$\omega_C^i = -\frac{m}{X_{C(Mn)}}; \quad \eta_C^i = -\frac{S}{X_{C(Mn)}} - \frac{m^2}{2X_{C(Mn)}^2}, \quad (11)$$

are called as "interaction parameters" of the first and second order, respectively, at constant carbon activity. Then Equation (10) can be imagined as

$$\ln\gamma_C^i = \omega_C^i X_i + \eta_C^i X_i^2. \quad (12)$$

Equations (8) and (10) show that interaction parameters ω_C^i and η_C^i can be directly obtained if we determine a shift of carbon saturated content in manganese due to the third component.

Figure 2 shows the effect of silicon on carbon solubility in liquid manganese as a dependence of ΔX_C^{Si} on silicon content in melt. Basing on results obtained, values of ω_C^{Si}, η_C^{Si} and m were calculated for Mn-Si-C_{sut} melts (Table 1). The calculation was performed by Eqs. (8) and (12). Table 2 show mean values. As seen, ω_C^{Si} decreases with temperature rising. It demonstrates a weakening of silicon effect on carbon solubility.

Temperature dependence of interaction parameter ω_C^{Si} can be imagined as follows

$$\omega_C^{Si} = 27584.58/T - 11.214. \quad (13)$$

A plot of dependence of interaction parameter ω_C^i on atomic number of the element i in the Periodic Table is a promising method to forecast the effect of different elements on carbon solubility in manganese-based melts [2, 10, 11]. The value of interaction parameter ω_C^i for elements of second and third periods was estimated basing on assumption ofthis parameter periodical dependence on the atomic number i. Table 3 shows the interaction parameters obtained. Figure 3 shows dependence of ω_C^i on atomic number for 1673 K which is plotted basing on results obtained. The zeroth line passes through inert gases insoluble in manganese.

Table 2. Interaction Parameters for Mn-Si-C_{sut} System

T, K	ω_C^{Si}	η_C^{Si}	m
1673	5.296	0.289	-1.456
1773	4.298	-0.343	-1.271
1873	3.538	2.154	-1.019

Table 3. Interaction Parameter ω_C^i in Liquid Manganese (forecast)

Element i	ω_C^i		
	1673 K	1773 K	1873 K
B	3.972	3.233	2.653
C	5.296	4.298	3.538
N	6.620	5.372	4.422
Al	3.972	3.223	2.653
Si	5.296	4.298	3.533
P	6.620	5.372	4.422
S	7.944	6.447	5.307

Sulphur saturated solutions in liquid manganese and manganese-based melts were investigated by studying the equilibrium of manganese sulfide with liquid manganese both pure one and containing alloying component

$$MnS(s) = Mn(l) + [S]. \quad (14)$$

Manganese sulfide was synthesized by saturating liquid electrolytic manganese (99.8% Mn) with sulphur in helium atmosphere. Sulphur solubility in liquid manganese was studied within the 1573-1773 K. Sulphur solubility in liquid manganese is rather limited. The temperature dependence of sulphur saturated content can be described as follows

$$\lg X_S = -6036/T + 1.217. \quad (15)$$

Sulphur solubility in Mn-Fe (as high as 20 % Fe), Mn-Si (as high as 17% Si) and Mn-C (as high as 6% C) melts was studied at 1573 K.

Table 1. Results of Regression Analysis for Mn-Si-C_{sut} System

T, K	Results of regression analysis	ω_C^{Si}	η_C^{Si}	m
1673	1) 5.415 X_{Si} - 1.902 X_{Si}^2	5.415	-1.902	-1.489
	2) -1.424 X_{Si} + 3.005 X_{Si}^2	5.178	2.480	-1.424
1773	1) 4.596 X_{Si} - 1.974 X_{Si}^2	4.596	-1.974	-1.296
	2) -1.247 X_{Si} + 2.394 X_{Si}^2	4.000	1.288	-1.247
1873	1) 3.553 X_{Si} + 1.973 X_{Si}^2	3.553	1.973	-1.023
	2) -1.015 X_{Si} + 1.116 X_{Si}^2	3.524	2.335	-1.015

Notes: 1) calculation by Eq. (12); 2) calculation by Eq. (8)

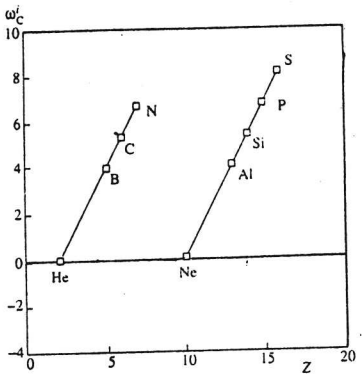

Fig. 3. Dependence of interaction parameter ω_C^i on atomic number (Z) of this element in the Periodic Table at 1673 K

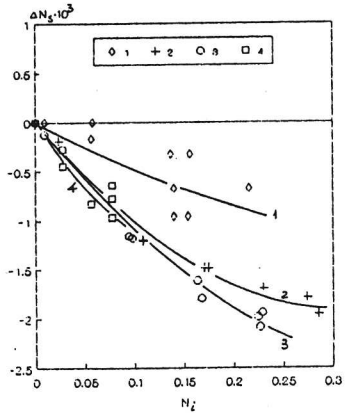

Fig. 4. Dependence of sulphur solubility in manganese-based melts on content of Fe (1), Si (2), C (3) и Cu (4): T, K: 1-3 - 1573; 4 - 1673

Sulphur solubility in Mn-Cu system (as high as 9% Cu) at 1673 K was studied as well. Silicon, carbon and copper in iron melt (within the concentration interval studied) result in decreasing of sulphur solubility as compared with pure liquid manganese (Fig. 4) because of sulphur bonds weakening in melt with these elements. So its activity rises.

Experimental data processing was performed by the method above. Values of the solubility factor and interaction parameter calculated on data obtained for sulphur solubility in manganese-based melts are below.

System	Mn-S-Fe	Mn-S-Si	Mn-S-C	Mn-S-Cu
T, K	1573	1573	1573	1673
m	-0.0031	-0.0130	-0.0145	-0.0140
ω_S^i	1.292	5.417	6.042	3.365

As above shown, the promising method to forecast the effect of different elements on sulphur solubility in manganese-based melts is plotting the dependence of interaction parameter ω_S^i on atomic number of i-element in the Periodic Table. Interaction parameters ω_S^i for elements of 2-d, 3-d and 4-th periods were estimated basing on assumption about the periodic dependence of this parameter on atomic number of i. Table 4 shows ω_S^i obtained. Figure 5 shows the dependence of ω_S^i on atomic number of i. The zeroth line passes through manganese and adjacent elements of VII-th group and inert gases as well.

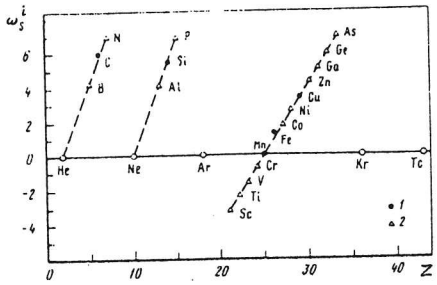

Fig. 5. Dependence of interaction parameter ω_C^i on atomic number (Z) of this element in the Periodic Table: 1 - present data; 2 - value forecasted

Table 4. Interaction Parameter ω_S^i in Liquid Manganese

Element	ω_S^i	Element	ω_S^i	Element	ω_S^i
Al	(4.293)*	Fe	1.292	Mn	0
Ar	0	Ga	(5.46)	P	(7.155)
As	(6.728)	Ge	(5.887)	Sc	(-3.364)
B	(4.293)	He	0	Si	5.417
C	6.042	Kr	0	Tc	0
Co	(1.682)	N	(7.155)	Ti	(-2.523)
Cr	(-0.841)	Ne	0	V	(-1.682)
Cu	3.365	Ni	(2.523)	Zn	(4.205)

*(...) — value forecasted.

REFERENCES

1. Katsnelson A.M., Dashevskii V.Ya., Kashin V.I. // DAN SSSR. 1992. V. 325, No 2. P. 983-986.

2. Schenck H., Frohberg M.G., Steinmetz E. // Archiv Eisenhuttenw. 1963. B. 34, H. 1. S. 37-42.

3. Petrushevskii M.S., Gel'd P.V. // Physicochemical Principles of Steelmaking Moscow : Izd. An SSSR. 1960. P. 50-60.

4. Tanaka A. // J. Jpn. Inst. Met. 1977. V. 41. P. 601-607.

5. Aida E., Joon M.D., Sano N. // J. Iron Steel Inst. Japan. 1988. V. 74, No 10. P. 43-50.

6. Ni R., Ma Z., Wei S. // Steel Research. 1990. V. 61, No 3. P. 113-116.

7. Ma Z., Ni R., Cheng W. // Steel Research. 1991. V. 62, No 11. P. 481-487.

8. Turkdogan E.T., Hancock R.A., Herlitz S.I. // J. Iron Steel Inst. 1956. V. 182. P. 274-277.

9. Katsnelson A., Tsukihashi F., Sano N. // ISIJ International. 1993. V. 33, No 10. P. 1045-1048.

10. Katsnelson A., Dashevskiy V.Ya., Kashin V.I. // Steel Research 1993. V. 64, No 4. P. 197-202.

11. Katsnelson A.M., Dashevskii V.Ya., Kashin V.I. // Izvestiya VUZ'ov Ferrous Metallurgy 1992. No 12. P. 7-15.