Inorganica Chimica Acta, 140 (1987) 183–186

Thermodynamics of Carbon Dissolved in Fe–Ce, Fe–Y, Fe–Ce–Sb and Fe–Ce–Bi Melts*

WANG CHANGZHEN†, WANG SHULAN and GUO WEI

Northeast University of Technology, Shenyang, China

Rare earth metals (RE) have been widely used in cast iron, but only a few investigations have been made on the effect of RE upon the behavior of carbon in iron [1–3]. The understanding of such effects is significant for directing the production of RE-containing iron and steel as well as cast iron. In this work, measurements of the solubility of carbon in iron–cerium and iron–yttrium alloys were made to determine the activity interaction coefficients of cerium and yttrium on carbon in iron melts.

Experimental

Materials

The materials used were as follows: Fe, 99.93%; Ce, 99.99%; Y, 99.9%. Graphite was spectrum purity.

In the preliminary test, it was found that the rate of reaching equilibrium was largely controlled by that of dissolution of carbon in molten iron. In order to shorten the duration of each experiment and to reduce the loss of cerium and yttrium from possible oxidation, mother alloys with different compositions were prepared by melting iron, graphite and RE in a carbon crucible under purified argon.

Apparatus

A furnace with $MoSi_2$ heating elements was used to obtain the desired temperature (1300–1515 ℃). The temperature was regulated through an automatic controller and kept constant for each experiment along a working zone of 6 cm within a variation of ±1 ℃. A PtRh6–PtRh30 thermocouple was used to measure the temperature. Argon was purified through silica gel, P_2O_5 and magnesium chips at 520–540 ℃. The working Al_2O_3 tube was sealed by water-cooled sleeves with rubber washers. In order to further reduce the oxygen potential in the tube, a certain amount of sponge titanium was put in the hot zone under the crucible. Two kinds of graphite crucibles were used in this work, one that is commonly used and another that is called a multicrucible. In this assembly, eight small crucibles covered with carbon lids were held together by a support, each crucible could be charged with 5 g of alloys.

Procedure

For the experiments using the common crucible, the crucible charged with about 100 g of alloy cut from the mother alloy was put into the furnace. The carbon content of the charge usually was 0.5% less than the expected value. The furnace was then evacuated and filled with purified argon. After this process was repeated three times, the oxygen pressure of the furnace was determined with a solid electrolyte cell probe; $P(O_2)$ was less than 10^{-17} atm. When the alloy was brought to the desired temperature, a small piece of RE which was wrapped in pure iron foil was added to the molten alloy through the quartz tube. Samples were also taken with a quartz tube that was filled with argon first. In about 4 h equilibrium conditions were reached. A certain amount of RE was added to the alloy following each sample. Samples were quenched in water and no measurable loss of carbon was found.

For the experiments using the crucible assembly, RE mother alloys were added. The gas replacing process was the same as that described above. The crucible assembly was hung at the top part of the working tube during the heating period, and was lowered down to the hot zone when the desired temperature was reached. After it had been kept at that temperature for 4 h, it was taken out and quenched in water. The analysis of the sample for carbon was carried out by a combustion method and for RE by a chemical method. The reproducibility of this method is ±0.01 wt.% C and ±0.005 wt.% RE, respectively.

Results

The Fe–C–Ce System

The experimental results for equilibrium time in the Fe–C–Ce system and the solubility of carbon in the Fe–Ce molten system are plotted in Fig. 1 and Fig. 2, respectively.

The least-squares line giving all points at three respective temperatures are expressed as follows:

$$N_C = 0.1850 + 2.81 N_{Ce} \quad \text{at } 1300\ ℃ \qquad (1)$$

$$N_C = 0.1937 + 2.74 N_{Ce} \quad \text{at } 1400\ ℃ \qquad (2)$$

$$N_C = 0.2032 + 2.56 N_{Ce} \quad \text{at } 1515\ ℃ \qquad (3)$$

These equations can be fitted into the following equation:

$$N_C = N_C^C + m N_{Ce}$$

or

$$N_C = 0.052 + 8.46 \times 10^{-5} T + (0.582 + 3550/T) N_{Ce} \qquad (4)$$

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987. This project was supported by NSFC.

†Author to whom correspondence should be addressed.

0020-1693/87/$3.50

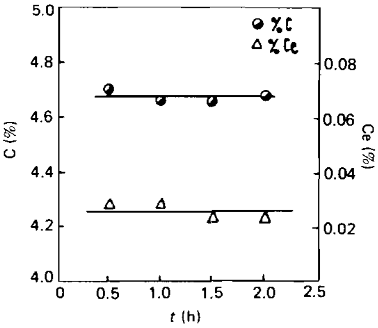

Fig. 1. Variation with time of % C and % Ce (by weight) in the Fe–C–Ce system at 1300 ℃.

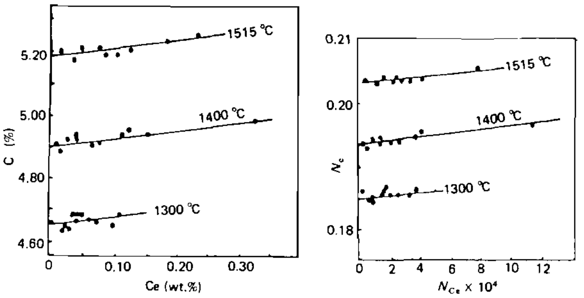

Fig. 2. Solubility of carbon in the Fe–Ce molten system (N_{Ce},N_C are the molar fractions of Ce and C, respectively).

Equation (4) expresses the relationship between the solubility of carbon and the temperature, as well as the cerium content. Its extrapolated results, the solubility of carbon when $N_{Ce} = 0$ are in good agreement with the work of Chipman *et al.* [4].

$$N_C^S = 0.052 + 8.46 \times 10^{-5} T$$

If the concentrations of components are expressed as the lattice ratio, that is,

$$Z_i = \frac{n_i}{(n_1 + \Sigma\gamma_j n_j)}$$

where n_1 is the mole fraction of solvent, n_i and n_j are the mole fractions of the solutes, γ_j is a parameter, and substitutional solutes $\gamma_j = -1/b$ for interstitial solutes, b is the interstitial sites per lattice atom [5]. It is found that $\ln \psi_C$ is a better linear function of Z_{Ce} than N_C, via N_{Ce} at the three different temperatures (see Fig. 3). Here, $a_C = 1$, $a_C = \psi_C Z_C$, ψ_C is an activity coefficient of carbon. The lines in Fig. 3 can be expressed by the following equations:

$$\ln \psi_C = 1.225 - 15.52 Z_{Ce} \quad \text{at } 1300\,℃ \qquad (5)$$

$$\ln \psi_C = 1.151 - 13.86 Z_{Ce} \quad \text{at } 1400\,℃ \qquad (6)$$

$$\ln \psi_C = 1.072 - 12.12 Z_{Ce} \quad \text{at } 1515\,℃ \qquad (7)$$

The relationship of $\ln \psi_C$ with Z_{Ce} and temperature is

$$\ln \psi_C = -0.147 + 2170/T + (15.09 - 48410/T) Z_{Ce} \qquad (8)$$

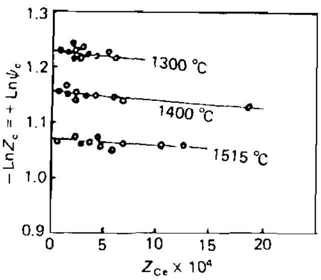

Fig. 3. ln ψ_C as a function of lattice ratio Z_{Ce}.

In the experiments on iron–cerium alloys, those with a cerium content higher than 0.23% were not successful, because of the formation of Ce_xC_y compounds that have not been identified yet.

The Fe–C–Y System

The same treatments as for the iron–cerium–carbon system were used for the iron–carbon–yttrium system. The following results were obtained. The solubility of carbon in the Fe–Y molten system are plotted in Fig. 4 using the following equation.

$$N_C = 0.074 + 7.20 \times 10^{-5}/T + (-5.60 + 13000/T) N_Y \quad \text{at } 1300\text{–}1450\,℃ \qquad (9)$$

When the concentration of the components is expressed in a lattice ratio, the solubilities of carbon in Fe–Y alloys are:

$$\ln \psi_C = 1.177 - 12.69 Z_Y \quad \text{at } 1350\,℃ \qquad (10)$$

$$\ln \psi_C = 1.148 - 11.22 Z_Y \quad \text{at } 1400\,℃ \qquad (11)$$

$$\ln \psi_C = 1.111 - 9.83 Z_Y \quad \text{at } 1450\,℃ \qquad (12)$$

$$\text{or } \ln \psi_C = 0.0426 + 1842/T + (36.59 - 79976/T) Z_Y \qquad (13)$$

which are better linear functions than N_C via N_Y (see Fig. 5).

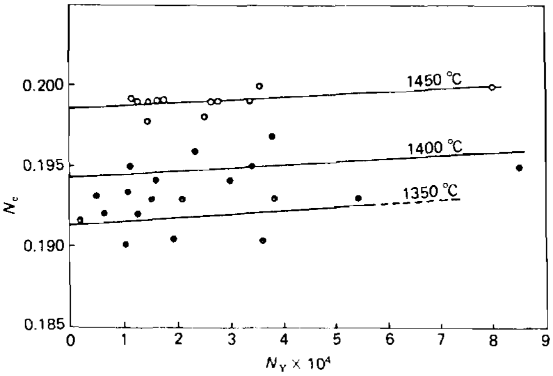

Fig. 4. Solubility of carbon in the Fe–Y molten system.

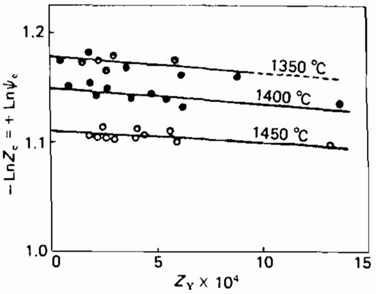

Fig. 5. ln ψ_C as a function of the lattice ratio Z_Y.

The Fe–C–Ce–Sb and Fe–C–Ce–Bi Systems

The solubility of carbon in molten Fe–C–Ce–Sb and Fe–C–Ce–Bi alloys at 1350 ℃ are expressed as

$$N_C = 0.1888 + 1.10 N_{Ce}\ (0.2\%\ \mathrm{Sb}),\ N_{Ce} < 7.0 \times 10^{-4}$$

$$N_C = 0.1887 + 1.26 N_{Ce}\ (0.2\%\ \mathrm{Bi}),\ N_{Ce} < 4.0 \times 10^{-4}.$$

Discussion

The definition of the activity interaction coefficient in carbon saturated iron base solution is [6]:

$$\epsilon_C^{*i} = \left(\frac{\partial \ln \gamma_C}{\partial N_i}\right)_{\substack{a_C = 1\\ N_i \to 0}} = -\left(\frac{\partial \ln N_C}{\partial N_i}\right)_{\substack{a_C = 1\\ N_i \to 0}} \tag{a}$$

the relationship between ϵ_C^{*i} and ϵ_C^i (the latter is the activity interaction coefficient in dilute solution) is

$$\epsilon_C^{*i} = (\epsilon_C^i + \rho_C^{i,C} N_C^*)/D \tag{b}$$

where

$$D = 1 + \epsilon_C^C N_C^* + 2\rho_C^C N_C^{*2}$$

N_C^* is the solubility of carbon in pure iron ρ_C^C and $\rho_C^{i,C}$ are the second-order and the cross-product second-order coefficients, respectively. If the term $\rho_C^{i,C} N_C^*$ is neglected, eqn. (b) gives:

$$\epsilon_C^i = \epsilon_C^{*i} D \tag{c}$$

For the Fe–Ce–C system, there is

$$\epsilon_C^{Ce} = \epsilon_C^{*Ce} D$$

Equation (b) can be used to calculate the activity interaction coefficient ϵ_C^{Ce} from the results of carbon saturated solution.

According to eqn. (b), ϵ_C^{*Ce} can be calculated and has

$$\epsilon_C^{*Ce} = -36700/T + 8.00 \text{ at } 1300\text{–}1515\ ℃ \tag{14}$$

From the literature [7, 8], can be obtained the following:

$$\epsilon_C^C = 7816/T + 3.67 \tag{15}$$

$$\rho_C^C = 15646/T + 5.23 \tag{16}$$

and then, if the eqns. (14), (15) and (16) are substituted into eqn. (b), and extrapolated to above the melting point of pure iron (1600 ℃), the ϵ_C^{Ce} and e_C^{Ce}, as well as e_{Ce}^C, at three different temperatures can be calculated and are listed in Table I.

TABLE I. Activity Interaction Coefficients

T (K)	ϵ_C^{Ce}	e_C^{Ce}	e_{Ce}^C
1823	−46.44	−0.078	−0.91
1848	−45.63	−0.076	−0.89
1873	−44.82	−0.075	−0.88

Their relationships with temperature are:

$$\epsilon_C^{Ce} = -110800/T + 14.33$$

$$e_C^{Ce} = -206/T + 0.035$$

$$e_{Ce}^C = -2055/T + 0.22 \text{ at } 1550\text{–}1600\ ℃.$$

If eqns. (a) and (c) are applied to the Fe–Y–Ce system, the following can be obtained:

$$\epsilon_C^{*Y} = -76350/T + 34.45$$

$$\epsilon_C^Y = -277600/T + 124.0$$

$$e_C^Y = -763/T + 0.343$$

$$e_Y^C = -564/T + 2.51 \text{ at } 1500\text{–}1600\ ℃$$

The above treatments for calculating activity interaction coefficients at 1600 ℃ have avoided the difficulties of experiments at temperatures higher than that of the melting point of pure iron and can be convenient for providing crucible material with graphite. This is because rare earth metal is active with ordinary oxide crucibles.

Conclusions

The solubility of carbon in molten Fe–Ce and Fe–Y alloys can be expressed respectively as:

$$N_C = 0.052 + 8.46 \times 10^{-5} T + (0.582 + 3550/T) N_{Ce} \quad \text{at } 1300\text{–}1515\ ℃$$

$$N_C = 0.0744 + 7.20 \times 10^{-5} T + (-5.60 + 13000/T) N_Y \quad \text{at } 1360\text{–}1450\ ℃$$

When the concentrations of components are expressed in lattice ratios, the solubilities of carbon are represented by:

$$-\ln Z_C = -0.147 + 2170/T + (15.09 - 48410/T) Z_{Ce}$$

$$-\ln Z_C = -0.0426 + 1842/T + (36.59 - 77976/T) Z_Y$$

The activity interaction coefficients in carbon saturated solution and in dilute solution are:

$\epsilon_{C}^{*Ce} = -36\,770/T + 8.00$ at 1300–1515 ℃

$\epsilon_{C}^{*Y} = -76\,350/T + 34.45$ at 1350–1450 ℃

and

$\epsilon_{C}^{Ce} = -110800/T + 14.33$

$e_{C}^{Ce} = -206/T + 0.04$ at 1550–1600 ℃

$e_{Ce}^{C} = -2055/T + 0.22$

$\epsilon_{C}^{Y} = -277610/T + 124.0$

$e_{C}^{Y} = -763/T + 0.34$

$e_{Y}^{C} = -564/T + 2.51$ at 1500–1600 ℃.

References

1 B. P. Bouleilef, B. B. Bacelef and E. M. Leibalkin, *J. Phys. Chem., 43,* 1907 (1969).

2 B. B. Bacelef and B. P. Bouleilef, *J. Phys. Chem., 45,* 2058 (1971).

3 A. Ejima, K. Suzecki, N. Marada and K. Sanbangi, *Trans. Iron Steel Inst. Jpn., 17,* 349 (1977).

4 J. Chipman, P. M. Alfred, L. W. Gott, R. B. Snall, D. W. Wilson, C. N. Thomson, D. L. Genernsey and J. C. Fulton, *Trans. S.S.M., 44,* 1215 (1952).

5 J. Chipman, *Trans. A.I.M.E., 239,* 2 (1969); *239,* 1332 (1969).

6 C. H. P. Lupis, *Acta Metall., 16,* 1365 (1968).

7 C. H. P. Lupis and J. F. Elliott, *Acta Metall., 14,* 529 (1966).

8 G. K. Sigworth and J. F. Elliott, *Met. Sci., 8,* 298 (1974).