Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. M. Samarin and R. A. Karasev

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Fig. 1.

Figure 1: Fig. 1.

Abstract

Full Text

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On the Deoxidizing Ability of Carbon in Vacuum

The interaction of carbon with oxygen in liquid iron, described by the formulas

$$[\mathrm{C}] + x[\mathrm{O}] = \mathrm{CO}_{x(\mathrm{g})} \tag{1}$$

$$k = \frac{P_{\mathrm{CO}x}}{[a_C][a_O]^x}, \tag{1a}$$

is the principal reaction of steelmaking.

The coefficient x in equation (1) determines the ratio between CO and CO_2 in the reaction products. When the composition of the reaction products changes from pure carbon monoxide to pure carbon dioxide, the value of x increases from 1 to 2 (^{1}).

In determining the equilibrium constant of the reaction it was established that the deoxidizing ability of carbon, determined by the value of the product $[\%C] \cdot [\%O]$, depends on the pressure and, at a pressure equal to 1 atm, can be represented by curve I in Fig. 1 (^{2}). Since in reaction (1) the change in the number of moles of gaseous substances is equal to unity, the equilibrium constant is a single-valued function of temperature. Consequently, the deoxidizing ability of carbon is inversely proportional to the pressure of the gas phase; i.e., lowering the pressure from 1 atm to 0.1 or 0.01 atm should be accompanied by an increase in the deoxidizing ability of carbon by factors of 10 and 100, respectively (curves II and III in Fig. 1). On the basis of such a mechanism of interaction, the supposition was expressed that, with the present capabilities of vacuum technology, the deoxidizing ability of carbon can be raised to values exceeding the deoxidizing ability of such strong deoxidizers as aluminum and zirconium ($^{3-6}$).

Fig. 1. I –pressure 1 atm; II –0.1 atm; III –0.01 atm. a –rarefaction $(1—5) \cdot 10^{-2}$ mm Hg; b –rarefaction $(5—7) \cdot 10^{-6}$ mm Hg.

Experience with the vacuum melting of iron-carbon alloys contradicts these statements, since at a gas-phase pressure below 1 mm Hg the deoxidizing ability of carbon becomes practically independent of pressure.

To establish the dependence of the deoxidizing ability of carbon

of the pressure was carried out by a series of experimental heats, in which liquid iron with various carbon concentrations was held at a given temperature in a high vacuum until equilibrium was established between the carbon and oxygen dissolved in the liquid iron.

The experimental procedure adopted was based on the assumption that, when equilibrium is reached on the oxidation side, the composition of the gas phase above the liquid metal does not have a noticeable effect on the state of equilibrium. This assumption was checked in heats carried out in an argon atmosphere at a pressure of 1 atm. The results of these preliminary heats are shown in Fig. 1. As is seen from comparison with curve I, corresponding to equilibrium with a gas phase consisting of CO and CO_2, the results obtained on the oxidation side in an argon atmosphere confirm the correctness of the assumption stated above.

Experimental heats under a pressure of $(5—7) \cdot 10^{-6}$ mm Hg were carried out in a resistance furnace equipped with a BA-0.5-1 pumping unit. The heating element was a molybdenum spiral, mounted in special beryllia ceramics. Heats under a pressure of $(1—5) \cdot 10^{-2}$ mm Hg were carried out in a high-frequency furnace operated from a generator with a power of 15 kW. In both cases the temperature was measured with a Pt–PtRh thermocouple. The accuracy of temperature measurement in the resistance furnace was $\pm 5^\circ$, and in the high-frequency furnace $\pm 15^\circ$.

In the investigation, crucibles made of MgO, Al_2O_3, ThO_2, ZrO_2, and BeO were tested. Spectral analysis of the metal established the presence of interaction between the liquid metal and the crucible material, and thus it proved impossible to determine the true deoxidizing ability of carbon in liquid iron. However, in studying the interaction between liquid iron and a corundum crucible it was observed that, if the same crucible is used, the aluminum content in the metal of subsequent heats decreases sharply. After 3-4 heats in the same crucible, the crucible material becomes practically inert with respect to liquid iron containing up to 0.8-1.0% C.

Taking this circumstance into account, all heats whose results are given in Table 1 were carried out in corundum crucibles that had undergone such treatment. In heats Nos. 15, 17, 19, 114, 115, 118, 119, 212, 214, 218, and 219, the presence of aluminum was checked; as a result of spectral analysis, small amounts of aluminum were found only in heats Nos. 114, 115, 118, and 218.

As follows from the results given in Table 1, the experimentally found deoxidizing ability of carbon at 1590° proves to be considerably lower than the deoxidizing ability calculated from the value of the equilibrium constant of the reaction. Moreover, the position of the experimental points in Fig. 1 shows that the results obtained at pressures of 10^{-2} and 10^{-6} mm Hg lie satisfactorily on one and the same curve. In other words, a change in the pressure of the gas phase by a factor of 10^4 in this range has no effect on the deoxidizing ability of carbon in liquid iron. It is important to note another fact as well: namely, the effect of vacuum on increasing the deoxidizing ability of carbon is not the same at different concentrations of the latter in liquid iron.

The results obtained are entirely regular for a reaction proceeding in a liquid metallic solution with the formation of a new gaseous phase. The discrepancy between the calculated and experimental values of the deoxidizing ability of carbon in vacuum is caused only by an incorrect interpretation of the value of $P_{\mathrm{CO}x}$ in equation (1a). In the process of interaction of carbon with oxygen in the volume of the liquid metal, the value of P_{CO} is determined by three quantities: the barometric pressure above the metal; the pressure created by the column of liquid metal at the specified depth of the bath; and the pressure caused by the forces of surface ten-

on the surface of a gas bubble whose radius is equal to r:

$$P_{\mathrm{CO}x} = P_b + \gamma h + \frac{2\sigma}{r}. \tag{2}$$

Here P_b is the barometric pressure above the metal; γ is the density of the liquid metal; h is the depth of the metallic bath at the level of nucleation of the gas bubble; σ is the surface tension of the liquid metal; r is the radius of the gas-bubble nucleus.

Table 1

Effect of pressure on the equilibrium between carbon and oxygen dissolved in liquid iron (1590°)

Heat Nos.	Pressure, mm Hg	Holding time, min	[%C]	[% O] I	[% O] II	[% O] average
11 Ar	760 Ar	20	0.24	0.0113	0.0107	0.0110
12 Ar	760 Ar	30	0.03	0.0800	0.0780	0.079
13 Ar	760 Ar	40	0.07	0.0236	0.0252	0.0244
14 Ar	760 Ar	60	0.01	0.1272	0.1278	0.1275
15	$(5—7) \cdot 10^{-6}$	60	0.31	0.0012	0.0017	0.0015
16	$(5—7) \cdot 10^{-6}$	60	0.005	0.0860	0.0910	0.0880
28	$(1—5) \cdot 10^{-2}$	60	0.07	0.0017	0.0019	0.0018

Heat Nos.	Pressure, mm Hg	Holding time, min	[%C]	[% O] I	[% O] II	[% O] average
29	(1—5) · 10^{-2}	60	0.08	0.0018	0.0018	0.0018
210	(1—5) · 10^{-2}	20	0.006	0.0294	0.0286	0.0290
211	(1—5) · 10^{-2}	60	0.035	0.0021	0.0025	0.0023
212	(1—5) · 10^{-2}	60	0.30	0.0015	0.0017	0.0016
213	(1—5) · 10^{-2}	60	0.08	0.00017	0.0017	0.0017
214	(1—5) · 10^{-2}	60	0.12	0.0019	0.0020	0.0019
215	(1—5) · 10^{-2}	90	0.49	0.0014	0.0013	0.0014
218	(1—5) · 10^{-2}	60	2.95	0.0011	0.0011	0.0011
219	(1—5) · 10^{-2}	60	1.15	0.0010	0.0010	0.0010
17	(5—7) · 10^{-6}	60	0.008	0.0230	0.0230	0.0230
18	(5—7) · 10^{-6}	90	0.045	0.0020	0.0022	0.0021
19	(5—7) · 10^{-6}	90	0.45	0.0015	0.0018	0.0016
110	(5—7) · 10^{-6}	60	0.61	0.0008	0.0009	0.0008
111	(5—7) · 10^{-6}	60	0.37	0.0009	0.0009	0.0009
112	(5—7) · 10^{-6}	90	0.05	0.0024	0.0025	0.0024
113	(5—7) · 10^{-6}	60	0.072	0.0020	0.0028	0.0024
114	(5—7) · 10^{-6}	60	1.13	0.0009	0.0009	0.0009
115	(5—7) · 10^{-6}	60	3.43	0.0016	0.0016	0.0016
116	(5—7) · 10^{-6}	60	0.165	0.0014	0.0018	0.0016
118	(5—7) · 10^{-6}	60	1.75	0.0008	0.0010	0.0009
119	(5—7) · 10^{-6}	60	0.40	0.0019	0.0022	0.0020

It follows from equation (2) that when P_b and h tend to zero, $P_{\mathrm{CO}x}$ becomes equal to $2\sigma/r$, i.e., the deoxidizing capacity of carbon in vacuum is determined by the magnitude of the surface tension of the liquid metal and by the size of the gas nucleus forming in the liquid metal.

It also follows from equation (2) that the influence of vacuum on the deoxidizing capacity of carbon is determined by the ratio between the values of P_b and $\gamma h + 2\sigma/r$. When $\gamma h + 2\sigma/r \gg P_b$, a further reduction of the barometric pressure above the metal cannot change the value of $P_{\mathrm{CO}x}$ and therefore cannot influence any further increase in the deoxidizing capacity of carbon in the liquid metal. For the practice of deoxidizing steel with carbon in vacuum, it is of interest to determine the maximum rarefaction in the furnace at which a further increase in vacuum, from the standpoint of completeness of deoxidation, is no longer rational.

As follows from the data presented in Fig. 1, in the interval of carbon concentrations studied the minimum value of $[\%C] \cdot [\%O]$ lies in the region of 0.1 atm. Proceeding from this value of $P_{\mathrm{CO}x}$, it may be concluded that, for complete deoxidation of liquid iron by carbon dissolved in it, the pressure in the furnace should be 1–2 mm Hg, which is negligibly small in comparison with 0.1 atm.

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