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Decarbonization of Liquid Iron–Carbon Alloys[1]

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The decarbonization of iron–carbon alloys in argon–oxygen mixtures was studied at oxygen pressures from 10^{-4} to 10^{-2} atm., carbon contents from 2.0 to 4.5% and temperatures from 1290 to 1510°. The alloys were held in recrystallized alumina boats and crucibles of varying dimensions. The rate of evolution of $CO + CO_2$ could be represented by either of the expressions $d(CO + CO_2)/dt = kpO_2A_{gm}A_{cm}$ or $d(CO + CO_2)/dt = k'pO_2A_{gm}(A_{cm} + A_{gm})$, where A_{gm} and A_{cm} are the areas of the gas–melt and crucible–melt interfaces, respectively, and k and k' are constants the values of which are given by $k = 1.3 \times 10^{20}e^{-10,000\ (\pm 3,500)/RT}$ molecules/sec. atm. cm.^{4} and $k' = 9.6 \times 10^{19}e^{-10,000\ (\pm 3,500)/RT}$ molecules/sec. atm. cm.^{4}. The present results are not sufficiently extensive to distinguish between these possibilities. The results support the conclusion that elimination of carbon monoxide occurs solely at the crucible–melt interface, and a kinetic expression is derived which accounts in part for these observations.

Introduction

The oxidation of carbon dissolved in liquid iron has been the subject of numerous investigations. The results of early work have been summarized fully elsewhere.[2] The basis of present concepts regarding the mechanism is due largely to Darken[3] whose expression for the rate in terms of carbon monoxide evolution (molecules/sec.) under conditions favorable for nucleation in the open-hearth furnace may be written

$$dCO/dt = D_0A([O]_{se} - [O])/\Delta l \qquad (1)$$

where D_0 is the diffusion coefficient of oxygen in the metal, A is the area of the slag–metal interface and $([O]_{se} - [O])/\Delta l$ is the concentration gradient of oxygen across a postulated boundary layer of thickness Δl in the metal adjacent to the slag.

The importance of nucleation as a rate-determining step was emphasized by Larsen,[4] following the work of Körber and Oelsen.[5] This concept was further expanded by Richardson,[6] Sims[7] and Vallet.[8] Although it has been generally agreed, in the light of abundant experimental evidence, that such a process must play a significant role in determining the over-all rate, it has been generally recognized that nucleation alone cannot be rate-limiting under open-hearth conditions. Darken[3,9] has suggested that the over-all rate is governed simultaneously by the rates of the two processes of oxygen transfer from slag to metal and from the metal into expanding bubbles of carbon monoxide; these processes were regarded as being so closely coupled that the rate could be controlled by changing the conditions at either interface.

In spite of the success of this theory in accounting, at least semi-quantitatively, for the observed rates of decarbonization under industrial conditions, a detailed description of the mechanism has remained uncertain.[10] The present study was undertaken in an attempt to define more closely some of the factors which govern the rate under laboratory conditions. The decarbonization was studied in argon–oxygen mixtures at high flow rates and at partial pressures of oxygen in the range 10^{-2} to 10^{-4} atm. Rates were determined by measuring the rates of evolution of CO and CO_2.

Experimental

Apparatus.—The apparatus is illustrated in Fig. 1. "Welding" grade argon was dried by passage over magnesium perchlorate A and the last traces of oxygen were removed, when required, by passage through "pyrophoric" copper B at 200°.[11] Oxygen at known partial pressure was added to the metered argon stream by allowing the gas to pass downward through furnace D, 40 mm. in diameter, packed with cupric oxide wire. The temperature of this furnace, as indicated by a noble metal thermocouple located in the wire at the hottest zone, was varied between 600 and 1000°, depending on the desired pressure of oxygen. The temperature was uniform to within ± 5° over a length of 10 cm. in the hottest zone. The copper oxide was regenerated before each experiment by a stream of oxygen. This furnace served also to oxidize a trace of CO present as an impurity in the argon; CO_2 was removed in trap E cooled with liquid oxygen.

The reaction furnace G was wound with Pt–10% Rh wire and was equipped with a horizontal tube of recrystallized alumina of 35 to 40 mm. i.d. The argon–oxygen mixture was preheated by passage through a region P packed with alumina chips held in place by plugs of mullite wool. The alloy M was contained in a recrystallized alumina crucible[11a] supported on a sled of stabilized zirconia which, in turn, rested on rails of mullite tubing which served to protect the furnace tube from thermal shock. Temperatures were measured by a Pt–Pt/13% Rh thermocouple located inside one of the mullite rails, with its junction directly beneath the crucible. The temperature was uniform to within ± 1° over a length of 7 cm. and was automatically controlled to within 0.5° by a saturable core reactor in series with the furnace winding. The impedance of the reactor was varied by a controller which sensed the temperature of the furnace by means of the thermocouple and operated through a magnetic amplifier.

The gas which issued from the furnace was analysed chemically for CO and CO_2 in the apparatus shown in Fig. 2. CO_2 was removed in trap R which was cooled in liquid oxygen. Residual CO was oxidized by cupric oxide at 400° in furnace S and retained as CO_2 in trap T, also cooled with liquid oxygen. The remaining gas was vented *via* "Ascarite" in tube U. The CO_2 retained in either trap was de-

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[1] Issued as N.R.C. No. 7083.

[2] P. T. Carter, *Iron and Steel*, **26**, 427 (1953).

[3] L. S. Darken in "Basic Open-Hearth Steelmaking," p. 592 (A.I.M.E., 1951).

[4] B. M. Larsen, *Trans. A.I.M.E.*, **145**, 67 (1941).

[5] F. Körber and W. Oelsen, *Mitt. Kaiser-Wilhelm Inst. für Eisenforschung*, **17**, 39 (1935).

[6] F. D. Richardson, *Disc. Faraday Soc.*, **4**, 335 (1948).

[7] C. E. Sims, *Trans. A.I.M.E.*, **172**, 176 (1947).

[8] P. Vallet, *Rev. Mét.*, **51**, 709 (1954); *Iron and Steel*, **28**, 463 (1955).

[9] L. S. Darken in "The Physical Chemistry of Steelmaking," ed. J. F. Elliott, Technology Press of M.I.T., Cambridge, Mass., 1958 p. 101.

[10] B. M. Larsen and L. O. Sordahl in "Physical Chemistry of Process Metallurgy," Vol. 8, Part 2, ed. G. R. St. Pierre, Interscience Publishers, Inc., New York, N. Y., 1961, p. 1141.

[11] F. R. Meyer and G. Ronge, *Angew. Chem.*, **52**, 637 (1939).

[11a] NOTE ADDED IN PROOF.—Morganite "Triangle RR" crucibles were employed. Several crucibles were subjected to porosity measurements in a mercury porosimeter at pressures up to 50,000 p.s.i. None showed any sign of porosity at this level of pressure, indicating that, if pores exist, they must be less than 17Å. in radius. The authors wish to thank Dr. D. S. Montgomery, Department of Mines and Technical Surveys, Ottawa, Ont., for kindly supplying these measurements.

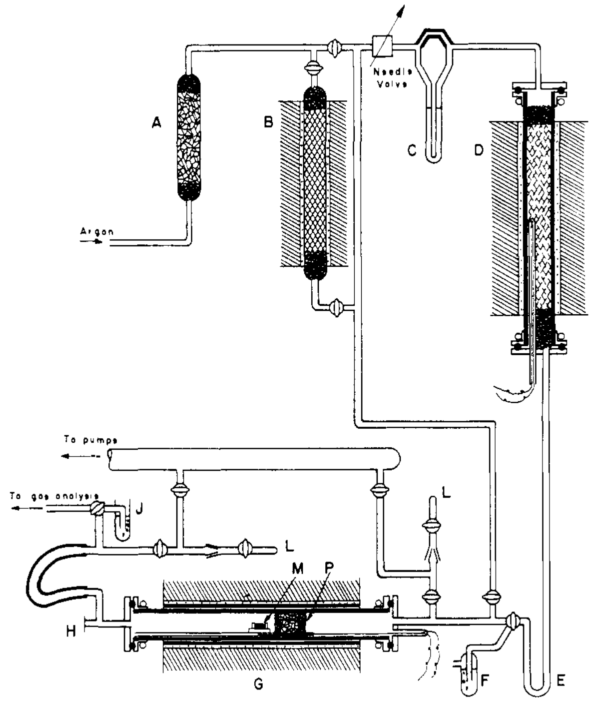

Fig. 1.—Apparatus: A, magnesium perchlorate; B, pyrophoric copper, 200°; C, flow meter; D, furnace packed with cupric oxide; E, liquid oxygen trap; F,J, dibutyl phthalate; G, reaction furnace; H, window; L,L, evacuated bulbs; M, alloy; P, alumina chips, mullite wool.

gassed, condensed in V, and measured with McLeod gage W in the calibrated volume between stopcocks X and Y.

In later experiments samples of gas both entering and leaving the reaction furnace were analysed mass spectrometrically for CO, CO_2 and O_2. The samples were withdrawn in previously evacuated bulbs L, Fig. 1. When this procedure was employed, the gas which issued from check value J was allowed to flush the annular space between the alumina tube and the refractory tube of the furnace.

Materials.—Alloys were prepared from iron sponge of high purity for which a typical analysis (p.p.m.), as supplied by the manufacturer, was Si, 8; Mn, 3; Mg and Na, 2; Ni, 1; Cu and Ag, each < 1; 43 other elements sought but not detected. This material was melted in argon with "spectroscopic" graphite powder in a graphite crucible also of "spectroscopic" grade. Before use the crucible was further purified by heating in a stream of H_2 until H_2S could no longer be detected in the effluent. "Pin" samples of liquid alloy were withdrawn in silica tubes and quenched in water. These were crushed, sieved and analysed for carbon as well as for possible contamination by silicon, which never was detected (Si < 0.001 %). Alloys of lower carbon content were prepared by mixing material prepared in this way with iron sponge.

Procedure.—Alloys were charged to or withdrawn from the furnace while it was flushed with argon, and a flow of argon was maintained until the required temperature was established. Zero time was taken as the time at which oxygen was introduced to the argon stream.

When analyses were performed chemically, decarbonization was allowed to proceed for a measured interval during which the products were collected continuously. The melt was then held in a slow stream of purified argon until the analysis was completed, whereupon decarbonization was continued for a further interval. This procedure avoided undue depletion of the melt in carbon during an analysis.

When analyses were performed mass spectrometrically, the rate of decarbonization at the time of sampling was determined directly from the flow rate and the composition of the effluent gas. Analysis of samples taken at the inlet allowed rates to be normalized for slight variations in the oxygen pressure and permitted a check on the percentage conversion of oxygen. This technique was employed in most of the experiments reported.

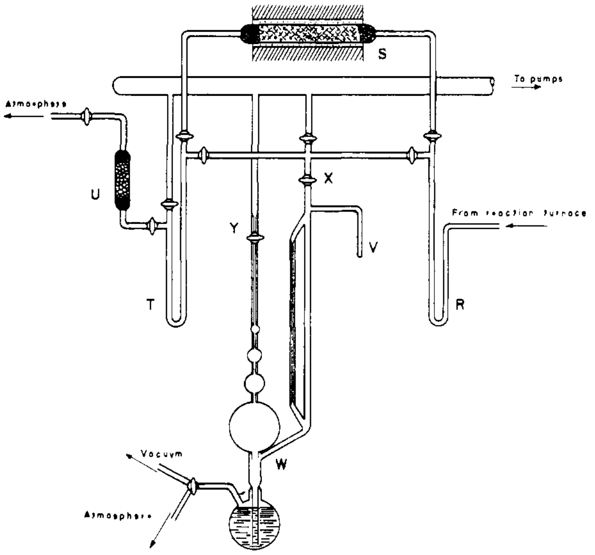

Fig. 2.—Analytical section: R,T, liquid oxygen traps; S, furnace packed with cupric oxide; U, "Ascarite"; V, cold finger; W, multiple-range McLeod gage; X,Y, calibrated volume.

At the end of a series of measurements the alloy was removed, quenched in water and analysed for carbon. The carbon content at any time during an experiment was estimated from the final carbon content and the measured rates.

Results

Figure 3 shows the results of experiments designed to check the accuracy with which argon–oxygen mixtures of known composition could be prepared. The gas from the copper oxide furnace D, Fig. 1, was passed through graphite at 1000° to convert the oxygen to carbon monoxide which subsequently was analysed chemically. The line in Fig. 3 corresponds to the data compiled by Coughlin[12] for the free energies of formation of Cu_2O and CuO. The present results are well within the limits of uncertainty of this line. The composition of the argon–oxygen mixtures was independent of flow rate up to 60 cm.^{3}/sec., the highest flow rate employed, and of the total volume of argon which passed through the furnace up to a maximum of 150 liters. Partial pressures of oxygen were reproducible to within 2.5%.

Blank experiments in which oxygen was omitted from the argon stream yielded rates of decarbonization of the order of 10^{-7} g. C/sec., or less than 1% of the lowest rates observed in the presence of oxygen. Allowing for differences in crucible–melt area, blank rates were of the same order as observed by Parlee, *et al.*[13] and were attributed mainly to reaction of the melt with alumina. These rates decreased rapidly with time at 1375–1500°, the deceleration being greater at the higher temperatures. This may be due to establishment of equilibrium between the melt and oxygen contained by the crucible or to inhibition of the crucible–

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(12) J. P. Coughlin, Bureau of Mines Bulletin 542, U. S. Government Printing Office, Washington, D. C., 1954.

(13) N. A. Parlee, S. R. Seagle and R. Schuhmann, Jr., *Trans. Met. Soc. A.I.M.E.*, **212**, 132 (1958).

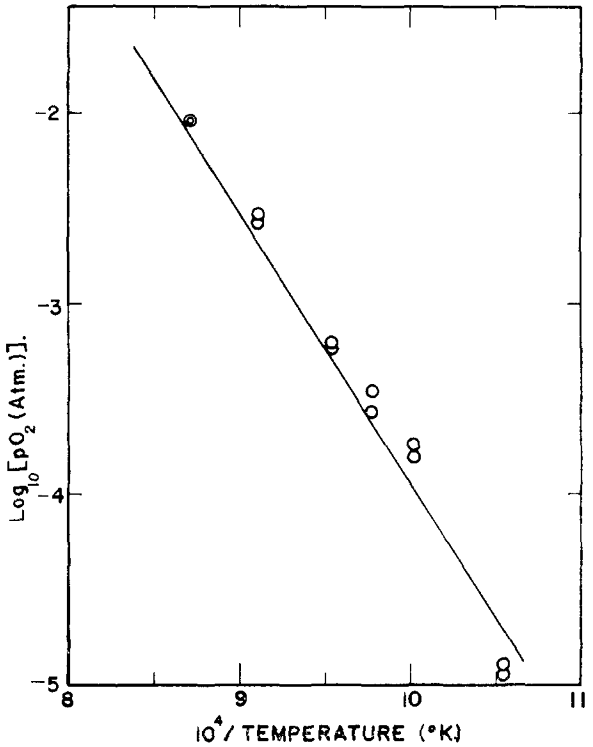

Fig. 3.—Log pO_2 in gas *vs.* $1/T$ for cupric oxide: O, experimental; ——, from compilation of Coughlin.[12]

melt reaction by formation of a solid product at the interface. Higher blank rates were observed when lime crucibles were used in place of alumina. This was attributed to a greater crucible–melt interfacial area due to the rough texture of the lime crucibles as compared with those of alumina.

In all experiments the main product of decarbonization was CO_2 while the content of CO in the products was usually less than 5%. Checks of the material balance in various experiments showed that the loss of carbon equalled to within 5% the total carbon evolved as gaseous oxides. Similarly, the oxygen in the products always corresponded within 3% to that consumed. This established that extraneous effects, such as the deposition of FeO in the furnace tube, were insignificant. Some alloys were analyzed colorimetrically[14] for aluminum at the end of an experiment. None was detected (Al < 0.001%).

Rates of decarbonization were independent of flow rate above 20 cm.^{3}/sec. under all conditions studied. In general, flow rates of 52 cm.^{3}/sec. were employed. Percentage conversions for oxygen were usually less than 20%. Exceptions were for melts of surface area greater than 5 cm.^{2}, when conversions as high as 40% were observed at flow rates of 52 cm.^{3}/sec. and oxygen pressures of 0.5×10^{-2} atm.

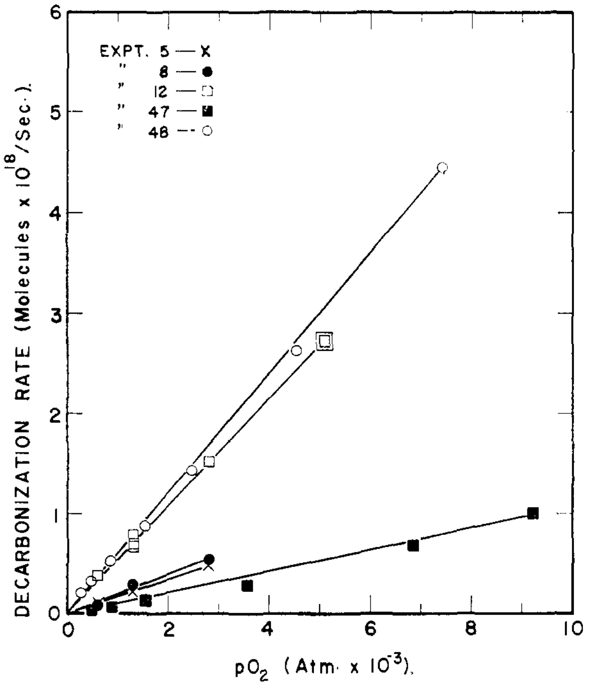

Fig. 4.—Rate *vs.* pO_2: X, boat, T = 1380°, $[C]_{initial}$ = 4.50%, $[C]_{final}$ = 3.77%; ●, boat, T = 1440°, $[C]_{initial}$ = 4.50%, $[C]_{final}$ = 3 72%; □, boat, T = 1381°, $[C]_{initial}$ = 4.34%, $[C]_{final}$ = 3.56%; ■, cylindrical crucible, T = 1381° $[C]_{initial}$ = 4.56%, $[C]_{final}$ = 4.42%, A_{gm} = 1.70 cm.^{2}, A_{cm} = 6.84 cm.^{2}; O, cylindrical crucible, T = 1381°, $[C]_{initial}$ = 4.15%, $[C]_{final}$ = 3.89%, A_{gm} = 7.55 cm.^{2}, A_{cm} = 13.09 cm.^{2}.

With other variables held constant, the rate of decarbonization was directly proportional to the oxygen pressure over the range 1×10^{-4} to 0.9×10^{-2} atm., as shown in Fig. 4. In some of these experiments (5, 8, 12) the alloys were held in argon between successive measurements while the temperature of the copper oxide furnace was adjusted. In other experiments (47, 48) the temperature of the copper oxide furnace decreased continuously during the experiment.

The effect of carbon concentration was studied over the range 2.0 to 4.5% C. Variation of the carbon content was accomplished by allowing decarbonization to proceed for measured intervals between successive determinations and its value at any time was calculated from the measured rates. Data therefore were obtained using the same initial alloy and in the absence of variations in the gas–melt and crucible–melt interfacial areas. Values of [C] are plotted against time for four experiments in Fig. 5.

The effect of temperature was studied over the range 1290–1510°. The same initial alloy was employed in each series of measurements, and rates were normalized for slight variations in oxygen partial pressure. Plots of log $[(-dC/dt)/pO_2]$ against the corresponding values of $1/T$ yielded a series of lines of approximately equal slope but with significantly different intercepts depending on the geometry of the melt.

Table I shows the results of experiments designed to establish the effect of gas–melt interfacial area. Shallow cylindrical crucibles of varying diameter were employed.

Discussion

The results have been interpreted on the basis that the primary product of the reaction is CO and

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(14) P. H. Scholes and D. V. Smith, *Analyst*, **83**, 615 (1958); *J. Iron Steel Inst.*, **195**, 190 (1960).

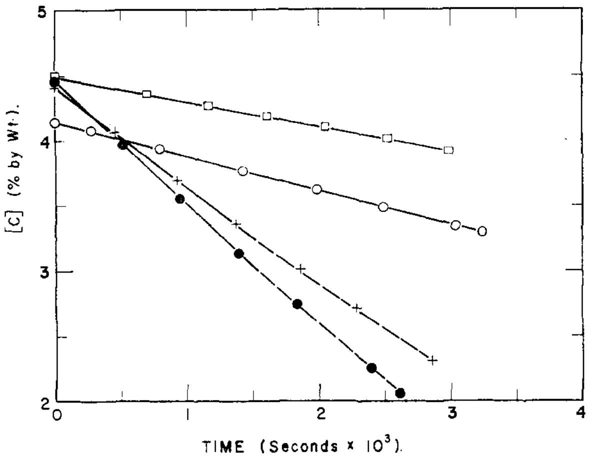

Fig. 5.—Carbon concentration *vs.* time for various experiments: □, cylindrical crucible, $T = 1380°$, $A_{gm} = 7.56$ cm.², $A_{cm} = 14.90$ cm.², $pO_2 = 6.30 \times 10^{-3}$ atm.; ○, cylindrical crucible, $T = 1380°$, $A_{gm} = 5.23$ cm.², $A_{cm} = 11.82$ cm.², $pO_2 = 1.03 \times 10^{-2}$ atm.; ●, boat, $T = 1454°$, $A_{gm} \approx 3.3$ cm.², $A_{cm} \approx 6.1$ cm.², $pO_2 = 1.67 \times 10^{-2}$ atm.; +, boat, $T = 1454°$, $A_{gm} \approx 3.5$ cm.², $A_{cm} \approx 6.5$ cm.², $pO_2 = 1.51 \times 10^{-2}$ atm.

that CO_2 arises almost exclusively by subsequent oxidation of CO as a homogeneous reaction in the gas phase. CO has been observed by Blyholder and Eyring[15] to be the primary product in the reaction of graphite with oxygen at high temperatures.

TABLE I

EFFECT OF ALLOY GEOMETRY AT 1380°

Expt.	Mean [C], %	A_{gm}, cm.²	Mass of alloy, g.	pO_2, atm. $\times 10^{-2}$	Rate of decarbonization, molecules $\times 10^{18}$/sec.
37	3.71	5.23	29.29	1.03	4.02
38	4.17	1.72	12.45	0.80	0.678
39	4.19	7.56	39.16	0.63	3.92
40	4.20	5.19	43.73	0.456	2.41
41	4.21	2.96	25.44	1.36	2.49
42	4.00	7.40	53.21	0.913	7.31
43	4.15	1.77	8.20	0.467	0.283
44	4.39	2.84	24.50	0.27	0.542
45	4.40	4.63	22.53	0.227	0.668
46	4.47	2.90	16.17	1.33	1.74
47	4.49	1.70	12.99	0.359	0.282
48	4.02	7.55	29.59	0.246	1.38

The most significant observation concerning the rate was derived from the data in Table I. The rate per unit pressure of oxygen was not a simple function of the gas–melt interfacial area, A_{gm}, as expected for a single surface reaction in which diffusion of reactants to this interface is rate-controlling. Inspection of the data revealed that the rate per unit pressure per unit gas–melt interfacial area was directly proportional to the crucible–melt interfacial area A_{cm} as shown in Fig. 6. Values of A_{cm} were estimated from the weight of the alloys assuming a value of 6.88 g./cm.³ for the density of liquid iron.

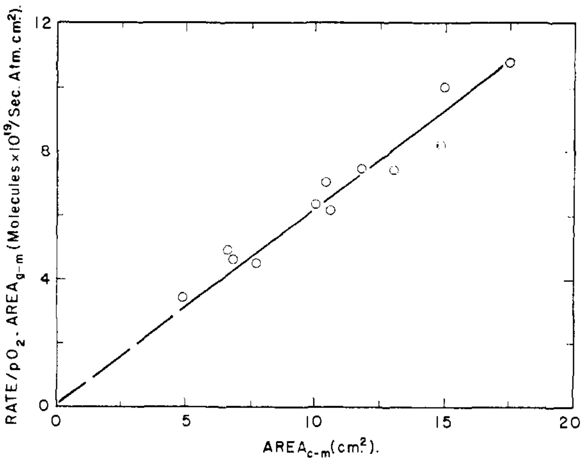

Fig. 6.—Rate/pO_2A_{gm} *vs.* A_{cm} at 1380°, from data in Table I.

The rate thus is given by the expression

$$d(CO + CO_2)/dt = kpO_2A_{gm}A_{cm} \quad (2)$$

where k is the slope of the line in Fig. 6.

A further expression which was also observed to fit the data within the limits of error is

$$d(CO + CO_2)/dt = k'pO_2A_{gm}(A_{cm} + A_{gm}) \quad (3)$$

as indicated by a linear plot of $\{d(CO + CO_2)/dt\}/A_{gm}pO_2$ against $(A_{gm} + A_{cm})$. The present data are not sufficiently extensive to distinguish between these possibilities as, fortuitously, the ratio $A_{cm}/(A_{gm} + A_{cm})$ was approximately constant in all experiments.

Values of log k for four experiments are plotted against $1/T$ in Fig. 7. A single point has been included for the data in Fig. 6. The value of k as a function of temperature is given approximately by

$$k = 1.3 \times 10^{20}e^{-10,000(\pm 3,500)/RT} \text{ molecules/sec. atm. cm.}^4$$

A similar plot yields for k'

$$k' = 9.6 \times 10^{19}e^{-10,000(\pm 3,500)/RT} \text{ molecules/sec. atm. cm.}^4$$

These plots do not eliminate slight variations in the temperature coefficient observed with different initial alloys, so that the over-all temperature coefficient appears to be complex.

The simultaneous dependence of the rate on A_{gm} and A_{cm} must be interpreted to mean that the rate is defined by at least two steps, neither of which alone is rate-limiting under the conditions employed. This supports the conclusion of Darken[9] for the rate under open-hearth conditions. In line with the mechanism proposed by Darken it is assumed that the rate is governed by diffusion of oxygen atoms across boundary layers in the metal at the gas–melt and crucible–melt interfaces. It is also assumed that the rate at which oxygen reacts at the gas–melt interface is governed by the extent to which available sites are occupied.

For diffusion across boundary layers of thickness Δl_1 and Δl_2 at the gas–melt and crucible–melt interfaces, respectively

$$dCO/dt = D_0A_{gm}([O]_{gm} - [O])/\Delta l_1 \quad (4)$$

and

$$dCO/dt = D_0A_{cm}([O] - [O]_{cm})/\Delta l_2 \quad (5)$$

where $[O]_{gm}$, $[O]_{cm}$ and $[O]$ are, respectively, the steady-state concentrations of oxygen at the gas–

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[15] G. Blyholder and H. Eyring, *J. Phys. Chem.*, **61**, 682 (1957).

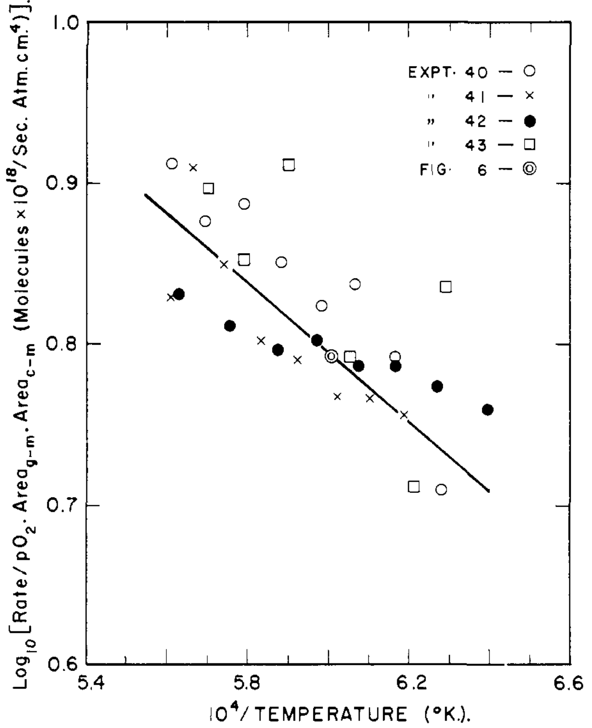

Fig. 7.—Log (rate/$pO_2A_{gm}A_{cm}$) *vs.* $1/T$: ○, A_{gm} = 5.19 cm.^{2}, A_{cm} = 15.08 cm.^{2}, $[C]_{initial}$ = 4.38%, $[C]_{final}$ = 3.93%; X, A_{gm} = 2.96 cm.^{2}, A_{cm} = 10.58 cm.^{2}, $[C]_{initial}$ = 4.47%, $[C]_{final}$ = 3.73%; ●, A_{gm} = 7.40 cm.^{2}, A_{cm} = 17.49 cm.^{2}, $[C]_{initial}$ = 4.60%, $[C]_{final}$ = 3.48%; □, A_{gm} = 1.77 cm.^{2}, A_{cm} = 4.94 cm.^{2}, $[C]_{initial}$ = 4.29%, $[C]_{final}$ = 4.05%.

melt and crucible–melt interfaces and in the bulk of the metal, and D_0 is the diffusion coefficient of oxygen. It is assumed that concentrations may be used in place of activities in the range under consideration. Elimination of [O] between equations (4) and (5) yields

$$\mathrm{dCO}/\mathrm{d}t = D_0A_{gm}A_{cm}([\mathrm{O}]_{gm} - [\mathrm{O}]_{cm})/(\Delta l_1A_{cm} + \Delta l_2A_{gm}) \quad (6)$$

The rate of evolution of CO at the crucible–melt interface is given by

$$\mathrm{dCO}/\mathrm{d}t = k_2[\mathrm{C}]_{cm}[\mathrm{O}]_{cm}\alpha A_{cm} - k_{-2}p\mathrm{CO}\alpha A_{cm} \quad (7)$$

or

$$\mathrm{dCO}/\mathrm{d}t = k_2\alpha A_{cm}([\mathrm{C}]_{cm}[\mathrm{O}]_{cm} - mp\mathrm{CO}) \quad (8)$$

where k_2 and k_{-2} are the specific rate constants for the formation and dissociation of CO at this interface, $[C]_{cm}$ is the interfacial concentration of carbon and α is the fraction of the measured crucible–melt area at which nucleation of CO occurs. Substitution of $[O]_{cm}$ from equation (8) in equation (6) yields

$$[\mathrm{O}]_{gm} = \frac{\mathrm{dCO}}{\mathrm{d}t}\left(\frac{\Delta l_1}{D_0A_{gm}} + \frac{\Delta l_2}{D_0A_{cm}} + \frac{1}{k_2\alpha A_{cm}[\mathrm{C}]_{cm}}\right) + \frac{mp\mathrm{CO}}{[\mathrm{C}]_{cm}} \quad (9)$$

If it is assumed that oxygen is adsorbed as a molecular complex at the gas–melt interface prior to dissociation, the rates of condensation and removal of oxygen are given by

$$\mathrm{dO_2(ads.)}/\mathrm{d}t = k_1A_{gm}p\mathrm{O}_2(1 - \theta) \quad (10)$$

and

$$-\mathrm{dO_2(ads.)}/\mathrm{d}t = k_{-1}A_{gm}\theta + (^1/_2)\mathrm{dCO}/\mathrm{d}t \quad (11)$$

where k_1 and k_{-1} are the specific rate constants for adsorption and desorption, respectively, and θ is the fraction of the available surface which is covered. From (10) and (11), in the steady state

$$\mathrm{dCO}/\mathrm{d}t = 2k_1A_{gm}p\mathrm{O}_2(1 - \theta) - 2k_{-1}A_{gm}\theta \quad (12)$$

θ is related to $[O]_{gm}$ by the expression

$$\theta = [\mathrm{O}]_{gm}/b \quad (13)$$

where b is the value of $[O]_{gm}$ which corresponds to complete coverage of surface sites. Halden and Kingery[16] have shown that, for melts in alumina crucibles at 1570°, complete coverage corresponds approximately to a monolayer of FeO. The value of b therefore may be taken as the concentration of oxygen in FeO. Substituting the value of $[O]_{gm}$ from (9) in (13) and neglecting the small term $mp\mathrm{CO}/b[\mathrm{C}]_{cm}$ one obtains

$$\theta = \frac{\mathrm{dCO}}{\mathrm{d}t}\,\frac{1}{b}\left\{\frac{\Delta l_1}{D_0A_{gm}} + \frac{\Delta l_2}{D_0A_{cm}} + \frac{1}{k_2\alpha A_{cm}[\mathrm{C}]_{cm}}\right\} \quad (14)$$

Substituting for θ in (12) and simplifying yields for the over-all reaction

$$\frac{\mathrm{dCO}}{\mathrm{d}t} = \frac{2k_1A_{gm}A_{cm}p\mathrm{O}_2}{A_{cm} + \dfrac{2A_{gm}(k_1p\mathrm{O}_2 + k_{-1})}{b}\left\{\dfrac{1}{k_2\alpha[\mathrm{C}]_{cm}} + \dfrac{\Delta l_2}{D_0} + \dfrac{\Delta l_1A_{cm}}{D_0A_{gm}}\right\}} \quad (15)$$

Further resolution of equation (15) in terms of measurable parameters is possible by substituting for $[C]_{cm}$, using the relationship

$$\mathrm{dCO}/\mathrm{d}t = D_{\mathrm{C}}A_{cm}([\mathrm{C}] - [\mathrm{C}]_{cm})/\Delta l_2 \quad (16)$$

where D_C is the diffusion coefficient of carbon in the melt. This yields a quadratic expression for which a simple solution is not obtained except under limited conditions. It is readily shown, however, that $[C]_{cm}$ in equation (15) may be replaced by [C] when $D_CA_{cm}[C]/\Delta l_2 >> \mathrm{dCO}/\mathrm{d}t$. In the present study [C] was generally of the order of 10^{22} molecules/cc. and A_{cm} was of the order of 10 cm.^{2}. Using Morgan and Kitchener's[17] value of 5×10^{-5} cm.^{2}/sec. for D_C and assuming that Δl_2 does not differ greatly from the value of 0.003 cm. estimated by Darken for open-hearth conditions, the value of $D_CA_{cm}[C]/\Delta l_2$ is observed to be of the order of 1.7×10^{21} molecules/sec., which is significantly larger than the rates of 10^{17} to 10^{19} molecules/sec. which were generally observed. Replacement of $[C]_{cm}$ by [C] in equation (15) therefore appears justified under the present conditions.

Equation (15) yields the observed dependence of the rate on oxygen pressure if it is assumed that, at the low pressures employed, $k_1pO_2 << k_{-1}$. It is also intuitively of the form expected to yield the correct dependence of the rate on A_{gm}, A_{cm}, pO_2 and [C] under widely varying conditions. Thus, at sufficiently high values of A_{cm}, or correspondingly low values of A_{gm} and pO_2, equation (15) becomes, in the limit

$$\frac{\mathrm{dCO}}{\mathrm{d}t} \approx \frac{2k_1A_{gm}p\mathrm{O}_2bD_0}{bD_0 + 2\Delta l_1(k_1p\mathrm{O}_2 + k_{-1})} \quad (17)$$

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(16) F. A. Halden and W. D. Kingery, *J. Phys. Chem.*, **59**, 557 (1955).

(17) D. W. Morgan and J. A. Kitchener, *Trans. Faraday Soc.*, **50**, 51 (1954).

Under the same conditions, combining equations (12) and (14)

$$\theta \approx \frac{2\Delta l_1 k_1 pO_2}{bD_0 + 2\Delta l_1(k_1 pO_2 + k_{-1})} \qquad (18)$$

Equation (17) therefore reduces to

$$dCO/dt \approx D_0 A_{gm} b\theta/\Delta l_1 \qquad (19)$$

which has the form of a single diffusion step at the gas–melt interface when the oxygen content of the melt is negligible in comparison with that at the interface. Similarly, at sufficiently high values of A_{gm}, [C] and pO_2, equation (15) reduces to

$$dCO/dt \approx D_0 A_{cm} b/\Delta l_2 \qquad (20)$$

which is the flux of oxygen to the crucible–melt interface when the iron is oxidized completely to FeO. A condition approaching this extreme case was recently observed by Larsen[10] under laboratory conditions. Further limiting cases of interest are readily derived from equation (15).

Equation (15) predicts that, at sufficiently high values of $[C]_{cm}$ the rate will become independent of [C]. At low values of $[C]_{cm}$, on the other hand, equations (15) and (16) yield

$$\frac{dCO}{dt} \approx \frac{bk_2\alpha A_{cm}[C]}{1 + \dfrac{k_{-1}}{k_1 pO_2} + \dfrac{bk_2\alpha\Delta l_2}{D_C}} \qquad (21)$$

i.e., in the limit, the rate becomes first-order with respect to [C]. A simple dependence of the rate on carbon concentration over the entire range is not, therefore, expected. This may account for various apparently contradictory reports in the literature regarding the influence of this variable. In the present study the rate was independent of [C] at concentrations above about 3%, as shown by linearity of the plots in Fig. 5 in this range. At lower carbon concentrations, however, departures from linearity were observed in a manner predicted qualitatively by equation (15).

To account for the simultaneous first-power dependence of the rate on A_{gm} and A_{cm} observed in this work, it must be postulated that the denominator of equation (15) does not vary with small changes in these variables. Alternatively, an extra term in the denominator is required which is insensitive to small changes in A_{gm} and A_{cm} and which is large compared with the existing terms under the conditions employed. A_{cm} was not, however, varied extensively in the present study and further work over a wider range is required to test the general validity of equation (15).

In the derivation of equation (15) the effect of surface activity of oxygen was not considered. It has been shown by several investigators that oxygen in liquid iron is surface active. The recent work of Halden and Kingery indicates that the excess surface concentration is approximately proportional to the oxygen content of the melt up to 0.04%, when saturation of surface sites occurs. Strictly, equations (4) and (5) should be replaced by (22) and (23), respectively

$$dCO/dt = D_0 A_{gm}([O]_{gm} - [O]_{gm}^*)/\Delta l_1 \qquad (22)$$

and

$$dCO/dt = D_0 A_{cm}([O]_{cm}^* - [O]_{cm})/\Delta l_2 \qquad (23)$$

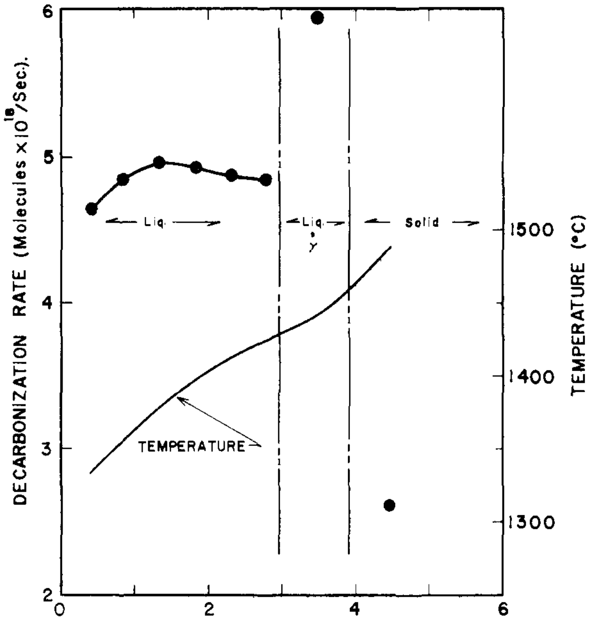

Fig. 8.—Effect of solidification: $[C]_{final} = 0.162\%$.

where $[O]_{gm}^*$ and $[O]_{cm}^*$ are the interfacial concentrations of oxygen which would be in equilibrium with the steady-state concentration of oxygen in the melt. The use of these equations in place of (4) and (5) does not alter the final expression for the rate provided the excess surface concentrations at equilibrium for the two interfaces are identical. The results of Halden and Kingery, however, indicate that a complete layer of oxygen is formed at the alumina-melt interface at a somewhat lower concentration of oxygen in the bulk phase than for the gas–melt interface. The results are not, however, sufficiently extensive to warrant this refinement at present. The general form of equation (15) remains unchanged.

The significance of α deserves comment. The value of this coefficient undoubtedly depends on the nature of the surface at which nucleation occurs. This is suggested by the work of Körber and Oelsen[5] with glazed crucibles, as well as by numerous qualitative observations by various workers. Further support for this was obtained in the present study when incipient solidification of melts, due to depletion of carbon, occurred in some experiments. Coincident with the appearance of a second phase at which nucleation could occur, a marked increase in the rate of evolution of CO was observed, then a sharp decrease when solidification was complete. The effect, illustrated in Fig. 8 for an experiment in which the temperature was varied continuously, is, however, complicated by the abrupt change in solubility of oxygen at the melting point.

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