Thermochimica Acta, 34 (1979) 221—231

DIFFUSION OF MANGANESE IN LIQUID IRON SATURATED WITH CARBON IN THE SYSTEM FeC_{sat}— BLAST FURNACE TYPE SLAG

RYSZARD BENESCH, MAREK JAWORSKI, ROMAN KOPEĆ and ANDRZEJ SIMON

Akademia Gorniczo-Hutniczej, Aleja Mickiewicza 30, 30-059 Kracow (Poland)

(Received 26 January 1979)

ABSTRACT

Diffusion constants of manganese in liquid iron saturated with carbon at temperatures 1673—1723 K for the system FeC_{sat}—blast furnace slag were evaluated. The linear dependence of the manganese concentration in the surface layer at a metal—slag interface upon the time at constant temperature was found experimentally. The following dependence of the diffusion constant upon temperature was determined

$$D_{Mn,m}^{1673-1723} = 3.04 \times 10^{-7} \exp\left(-\frac{7260}{RT}\right) [m^2 s^{-1}]$$

INTRODUCTION

Determination of the velocity of metallurgical processes requires investigations into the kinetics of reactions, particularly the identification of a controlling step. For metal—slag systems, such a step is frequently diffusion of an element or a compound either in the slag or the metal.

Investigations into the kinetics and diffusion of manganese in liquid iron have gradually become active in recent years and have been used for developing a mathematical model of the blast furnace process [1—6]. Interpretation of the results is quite difficult as both phases, independently from reagents, may contain other components. For that reason, investigations are carried out for simple systems such as Fe—FeMn, FeC—FeCMn, FeC_{sat}—three- or four-component slag [7—14]. Authors of quoted papers have found values for the diffusion coefficients of manganese in liquid iron using several different methods. Results can hardly be compared as it seems they are dependent not only upon the physical-chemical state of the system but also the methodology of investigations and the apparatus used.

One should take into account that, in investigations into the transfer of manganese from $CaO—SiO_2—Al_2O_3—MgO—MnO$ slag to FeC_{sat} alloy carried out in a graphite crucible, the possibility of additional reactions with the carbon of the crucible as reductor cannot be eliminated As the authors decided to consider only the carbon from the alloy, it necessitated the introduction of isolating materials which did not take part in reaction.

The aim of the present work was an attempt to evaluate for the reaction

$$(MnO) + [C]_{sat} = [Mn] + \{CO\} \qquad (1)$$

the diffusion constants of manganese in metal $D_{\mathrm{Mn,m}}$ [$\mathrm{m^2 s^{-1}}$] and the activation energy of diffusion of manganese in metal $E_{D_{\mathrm{Mn,m}}}$ (J $\mathrm{mole^{-1}}$) at 1673 and 1723 K.

EXPERIMENTAL METHOD

Experiments were carried out in the graphite crucible shown in Fig. 1. Metal and slag were separated from the crucible walls by means of molybdenum foil and a tube of fused Al_2O_3, respectively.

FeC_{sat} alloy was obtained by saturation of hydrogen-reduced Fe (99.7%) produced by Byk-Mallincrod with 99.5% C electrode graphite powder. Analysis of the carbon content of the metal were in good agreement with the values given by Elliott [15] (Table 1).

Five-component, blast furnace-type slag was obtained by melting, at temperatures not higher than 1773 K, the following components: CaO, SiO_2, Al_2O_3, MgO, MnO_2; all of them were of high purity, pro analysis quality.

The same slag was used in all the runs and its mean chemical composition, determined on the basis of data from a blast furnace producing ferromanganese, was as follows: CaO 35.48%; SiO_2 37.20%; Al_2O_3 6.84%; MgO 4.50%; MnO 15.34%; CaO/SiO_2 0.97.

Measurements were carried out in a vertical tube, resistance-heated Tamman's furnace; the diameter of the graphite tube was 5.0×10^{-2} m and the height of the constant temperature zone was 7.0×10^{-2} m. A two positional system of regulation with thermal feed-back coupling (two thermocouples Pt—Rh 10, Pt—Rh 18) ensured an accuracy of temperature measurements within ±5 degrees.

The crucible containing the alloy and slag placed above the metal was put into an airtight furnace into which N_2 was blown downward through Al_2O_3

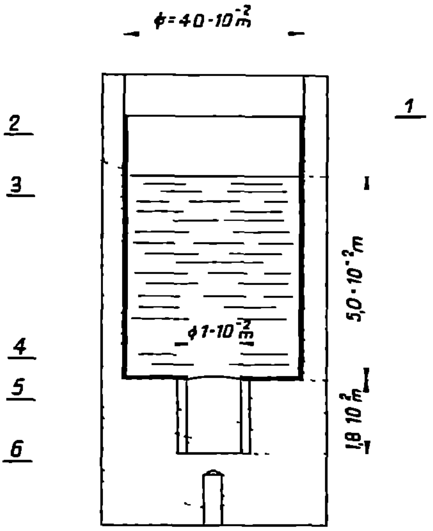


Fig 1. Graphite crucible. 1, Graphite; 2, molybdenum foil; 3, slag; 4, tube of fused Al_2O_3; 5, alloy FeC_{sat}; 6, thermocouple socket.

TABLE 1

Comparison of the carbon contents of the metal determined by Elliott [15] with those obtained in the present study

Temperature (K)	C_{sat} (%)	
	Elliott [15]	Present study
1673	4.896	4.80
1723	5.023	4 94

pipes. The masses of metal and slag were 11.0×10^{-3} kg and 15.0×10^{-2} kg, respectively. Measurements were carried out at temperatures of 1673 and 1723 K, the diffusion times being 3, 4, 5, 6, 7 and 9 h. At least three runs were made for each time and temperature. After completing an experiment, the crucible was taken out of the furnace and cooled in a water bath. Samples of metal were cut into layers 3×10^{-3} m high, parallel to the slag–metal interface, by means of an electroerosion machine. Each layer was then analysed for manganese and silicon contents.

Results

Chemical analyses for the manganese contents in each layer of metal (listed in Table 4) were made assuming that the mean manganese content equalled that at the center of a layer. Samples were cut into six layers; the metal–bottom of crucible interface was considered as distance $x = 0$ and the metal–slag interface as distance $x = l = 1.8 \times 10^{-2}$ m. Layers are identified in Table 2.

In Tables 3 and 4, the concentration of manganese in weight percent is given as well as the molar concentration of manganese at a distance $x = C^{x}_{Mn,m}$ mole for each particular layer. Values of $C^{x}_{Mn,m}$ were calculated from the relation

$$C^{x}_{Mn,m} = \frac{(\pi d^2/4) h \rho_m [Mn]}{54.938 \times 100 \times 10^{-3}} \tag{2}$$

TABLE 2

Identification of sample layers

Layer no.	x (m)
6	0.150×10^{-2}
5	$0 450 \times 10^{-2}$
4	0.750×10^{-2}
3	1.050×10^{-2}
2	1.350×10^{-2}
1	1.650×10^{-2}

TABLE 3

Contents of manganese and diffusion coeeficients of manganese in particular layers of metal and reaction times at temperature 1673 K

Time (h)	No. of layer	Mn (wt %)	$C^{x}_{\mathrm{Mn,m}} \times 10^{4}$ (mole)	$D_{\mathrm{Mn,m}} \times 10^{8}$ ($\mathrm{m^2\,s^{-1}}$)	$D^{\mathrm{md,t}}_{\mathrm{Mw,m}} \times 10^{8}$ ($\mathrm{m^2\,s^{-1}}$)	$D^{\mathrm{md}}_{\mathrm{Mw,m}}$ ($\mathrm{m^2\,s^{-1}}$)
3	1	2.13	6.2694	4.259	3.838	$(3.421 \pm 0.387) \times 10^{-8}$
	2	1.90	5.5925	3.857		
	3	1.72	5.0626	4.159		
	4	1.45	4.2679	3.467		
	5	1.37	4.0325	3.578		
	6	1.35	3.9736	3.707		
4	1	2.85	8.3887	3.395	3.407	$(3.421 \pm 0.387) \times 10^{-8}$
	2	2.57	7.5645	3.134		
	3	2.37	6.9759	3.494		
	4	2.11	6.2106	3.111		
	5	2.14	6.2989	3.651		
	6	2.09	6.1517	3.657		
5	1	3.57	10.5079	2.822	2.836	$(3.421 \pm 0.387) \times 10^{-8}$
	2	3.24	9.5366	2.639		
	3	3.05	8.9774	3.139		
	4	2.84	8.3593	3.036		
	5	2.56	7.5351	2.641		
	6	2.53	7.4468	2.730		
6	1	4.37	12.8627	3.758	3.101	$(3.421 \pm 0.387) \times 10^{-8}$
	2	4.06	11.9502	3.033		
	3	3.73	10.9788	2.849		
	4	3.57	10.5079	2.964		
	5	3.44	10.1253	2.956		
	6	3.41	10.0370	3.046		
7	1	5.13	15.0996	3.970	3.720	$(3.421 \pm 0.387) \times 10^{-8}$
	2	4.85	14.2755	3.308		
	3	4.71	13.8634	4.016		
	4	4.52	13.3042	3.749		
	5	4.46	13.1276	3.937		
	6	4.26	12.5389	3.341		
9	1	6.66	19.6030	4.879	3.624	$(3.421 \pm 0.387) \times 10^{-8}$
	2	6.36	18.7200	3.351		
	3	6.08	17.8959	3.233		
	4	5.99	17.6310	3.583		
	5	5.81	17.1012	3.303		
	6	5.78	17.0129	3.393		

where d is the diameter of sample ($= 1.0 \times 10^{-2}$ m), h is the height of the layer ($h = 0.3 \times 10^{-2}$ m) ρ_{m} is the density of the $\mathrm{FeMnC_{sat}}$ alloy at a given temperature (kg $\mathrm{m^{-3}}$) and 54.938 is the atomic mass of Mn.

As density data for the $\mathrm{FeMnC_{sat}}$ alloy are not available in the literature, the data from Lucas' papers [17,18] for the density of the $\mathrm{FeC_{sat}}$ alloy for the same temperatures used in this work were used in calculations. This simplification, according to Patterson [16], is justified both by their close

TABLE 4

Contents of manganese and diffusion coeeficients of manganese in particular layers of metal and reaction times at temperature 1723 K

Time (h)	No of layer	Mn (wt %)	$C^{x}_{\mathrm{Mn,m}} \times 10^4$ (mole)	$D_{\mathrm{Mn,m}} \times 10^8$ ($m^2\ s^{-1}$)	$D^{\mathrm{md,t}}_{\mathrm{Mw,m}} \times 10^8$ ($m^2\ s^{-1}$)	$D^{\mathrm{md}}_{\mathrm{Mw.m}}$ ($m^2\ s^{-1}$)
3	1	2.66	7.7842	2.983	3 287	(3 645 ± 0 454) × 10^{-8}
	2	2.32	6.7869	3 332		
	3	2.00	5 8508	3.233		
	4	1.86	5.4412	3 491		
	5	1 76	5.1487	3.589		
	6	1.50	4.3881	3.092		
4	1	3.68	10.7654	3.891	3 963	(3.645 ± 0.454) × 10^{-8}
	2	3.29	9.6245	3.347		
	3	3.13	9.1565	3.937		
	4	3.07	8.9809	4.555		
	5	2.85	8 3374	4.039		
	6	2 78	8.1326	4.000		
5	1	4.68	13 6908	4.835	3 911	(3.645 ± 0 454) × 10^{-8}
	2	4.25	12.4329	3 348		
	3	4.01	11.7308	3 546		
	4	3 89	11 3798	3 865		
	5	3.79	11.0872	3 934		
	6	3.71	10.8531	3 879		
6	1	5.62	16.4407	3 998	3.648	(0.3645 ± 0 454) × 10^{-8}
	2	5 26	15 3876	3 559		
	3	5 02	14 6855	3.738		
	4	4 80	14.0419	3.638		
	5	4 71	13.7786	3 774		
	6	4 43	12.9595	3.178		
7	1	6.56	19.1906	3 566	2 938	(3 645 ± 0.454) × 10^{-8}
	2	6.23	18.2252	3.678		
	3	5 69	16.6455	2 709		
	4	5 37	15 7093	2 598		
	5	5 14	15 0365	2 527		
	6	5.06	14.8025	2.550		
9	1	8 53	24 9536	4.488	4 124	(2.645 ± 0.454) × 10^{-8}
	2	8 19	23.9589	3 841		
	3	8 06	23.5786	4 584		
	4	7.81	22 8473	4.127		
	5	7.65	22.3792	3.938		
	6	7 54	22.0574	3 765		

proximity in the periodic table and the almost identical atomic mass of iron and manganese. Assumed values were (concentration of $C = 5\ 0\%$) 1673 K — $\rho_m = 6.863 \times 10^3$ and 1723 K — $\rho_m = 6.821 \times 10^3$ kg m^{-3}. Substitution of known values into eqn. (2) gives

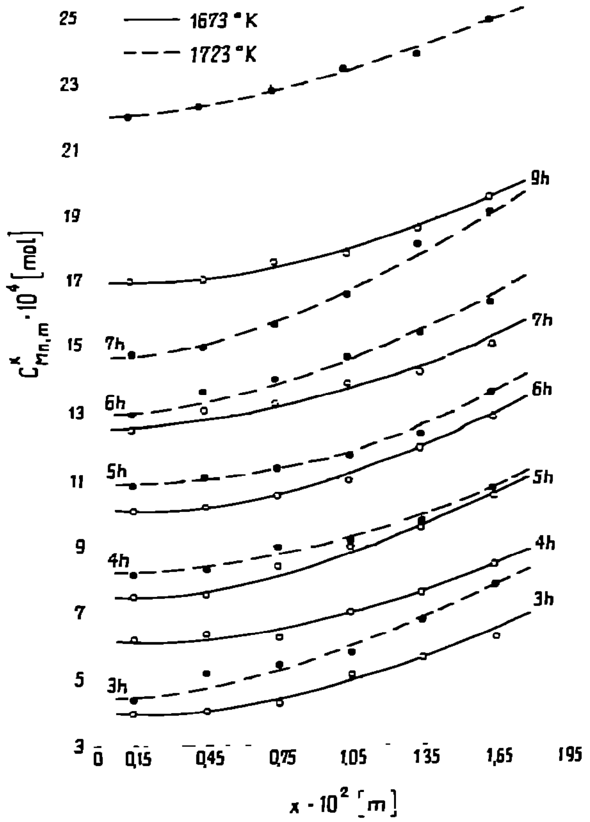
$$C^{x}_{\mathrm{Mn,m}} = 42.888 \times 10^{-9}\ \rho_m[\mathrm{Mn}] \qquad (2.1)$$

Values obtained for the concentration of Mn are plotted against distance in Fig. 2. It can be seen that, for different reaction times at constant temperature, curves display similar character and are approximately parallel. Furthermore, a linear dependence of the manganese concentration $C^{x}_{\mathrm{Mn,m}}$ in the alloy surface layer (for $x = 1.65 \times 10^{-2}$ m) upon the reaction time was found. Results, in the coordinate system $C^{x}_{\mathrm{Mn,m}}$ ($x = 1.65 \times 10^{-2}$ m) $= f(t)$, are shown in graphical form in Fig. 3. Values for the slope of the lines, corresponding to rate constants of manganese concentration changes in the surface layer, obtained as a result of correlation analysis by the method of least squares, are shown in Table 5.

Diffusion constant of manganese in metal, $D_{\mathrm{Mn,m}}$

The present work has found a decrease in the manganese concentration along the height of a sample and a linear dependence between the manganese concentration in the alloy surface layer and time.

Preserved boundary conditions i.e. (a) the same initial concentration of manganese in metal = 0%, (b) a linear increase in manganese concentration in



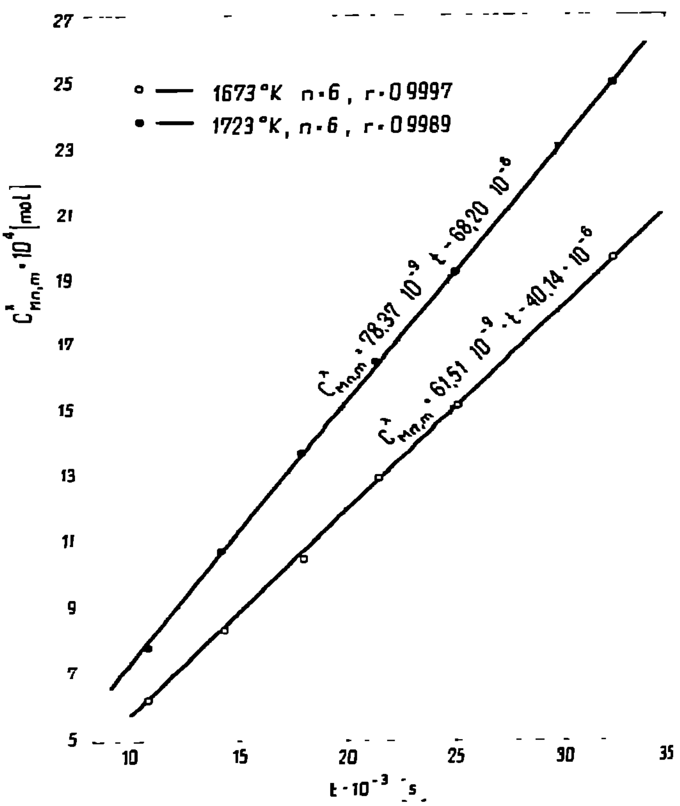


Fig 2. Gradient of manganese concentration in metal $C^{x}_{\mathrm{Mn,m}}$ (mole) at distance x (m) from metal—slag interface ($x = 1$), to metal—bottom of crucible interface ($x = 0$)

Fig. 3. Dependence of molar concentration of manganese in surface layer ($x = 1.65 \times 10^{-2}$ m) upon time of reaction

TABLE 5

Rate constant of Mn concentration changes with temperature in surface layer

Temperature (K)	Rate constant of Mn concentration changes in surface layer, k (mole s^{-1})
1673	61.51×10^{-9}
1723	78.37×10^{-9}

the surface layer with time, (c) constant temperature along the height of a sample during measurement are almost identical with those for which Williamson and Adams have given an approximated solution of Fick's second law. The solution should consequently be applicable to one-directional diffusion of manganese between the slag-metal and metal—bottom pf crucible interfaces.

According to the symbols used in this paper Fick's second law can be written

$$\frac{\partial C^{x}_{\mathrm{Mn,m}}}{\partial t} = D_{\mathrm{Mn,m}} \frac{\partial^2 C_{\mathrm{Mn,m}}}{\partial x^2} \tag{3}$$

The function $C^{x}_{\mathrm{Mn,m}} = f(t, x)$ should be found which will satisfy eqn. (3) for the boundary conditions

$$C^{x}_{\mathrm{Mn,m}} = 0 \text{ for } 0 < x < 1 \text{ when } t = 0 \tag{4}$$

and

$$C^{x}_{\mathrm{Mn,m}} = kt \text{ for } x = l \text{ when } t > 0 \tag{5}$$

The solution of eqn. (3) satisfying conditions (4) and (5) has been given by Williamson and Adams [18]

$$C^{x}_{\mathrm{Mn,m}} = kt - \frac{k}{2D_{\mathrm{Mn,m}}}(l^2 - x^2) + \frac{2kl^2}{D_{\mathrm{Mn,m}}} \sum_{M=1}^{M=\infty} \frac{\cos \frac{(2M-1)\pi x}{2l}}{\left[\frac{(2M-1)\pi}{2}\right]^3 \cdot (-1)^{M+1}} \times \exp\left[-\frac{(2M-1)^2 \pi^3 t D_{\mathrm{Mn,m}}}{4l^2}\right] \tag{6}$$

where $D_{\mathrm{Mn,m}}$ is the diffusion constant of Mn in metal (m^{2}s^{-1}) and M is the number of terms in the sum of the series.

For long reaction times (the experiments were carried out for 3 h and more) the exponential factor in eqn. (6) approaches zero and, accordingly, the sum of the series in eqn. (6) was neglected in the first stage of calculations. Diffusion constants were calculated from the relation

$$C^{x}_{\mathrm{Mn,m}} = kt - \frac{k(l^2 - x^2)}{2D_{\mathrm{Mn,m}}} \tag{7}$$

In the coordinate system $C^{x}_{\mathrm{Mn,m}} = f[-(l^2 - x^2)]$, expression (7) is a line whose slope equals $k/2\,D_{\mathrm{Mn,m}}$ and the ordinate of the point of intersection of the $C^{x}_{\mathrm{Mn,m}}$ axis equals kt (Fig. 4). It can be seen from this figure that the slopes of the lines for different times at a constant temperature display small changes which do not have systematic character when the reaction time is increased. This fact therefore confirms the validity of the adopted assumption that the diffusion constant is either independent of concentration or that any change in $D_{\mathrm{Mn,m}}$ with composition is within experimental error.

Values of diffusion constants of manganese in liquid iron saturated with carbon, calculated as described above for particular times, layers and temperatures, are listed in Tables 3 and 4.

Mean values of $D_{\mathrm{Mn,m}}$ and relative error (δ) for particular temperatures are $D^{1673}_{\mathrm{Mn,m}} = (3.421 \pm 0.387) \times 10^{-8}$, $\delta = 11.3\%$; $D^{1723}_{\mathrm{Mn,m}} = (3.645 \pm 0.454) \times 10^{-8}$, $\delta = 12.5\%$.

The values obtained for the diffusion constants of manganese in the alloy $\mathrm{FeC_{sat}}$ [calculated from eqn. (7)] were substituted into eqn. (6) which, when solved with respect to $C^{x}_{\mathrm{Mn,m}}$, could determine the effect of the sum of terms of the series on experimentally obtained values of $C^{x}_{\mathrm{Mn,m}}$ at a distance x. Calculation showed that only the first term of the series has an influence on $C^{x}_{\mathrm{Mn,m}}$ [for $M = 1$ in eqn. (6)] and therefore only this term can affect the magnitude of the diffusion constant for manganese in metal. This influence

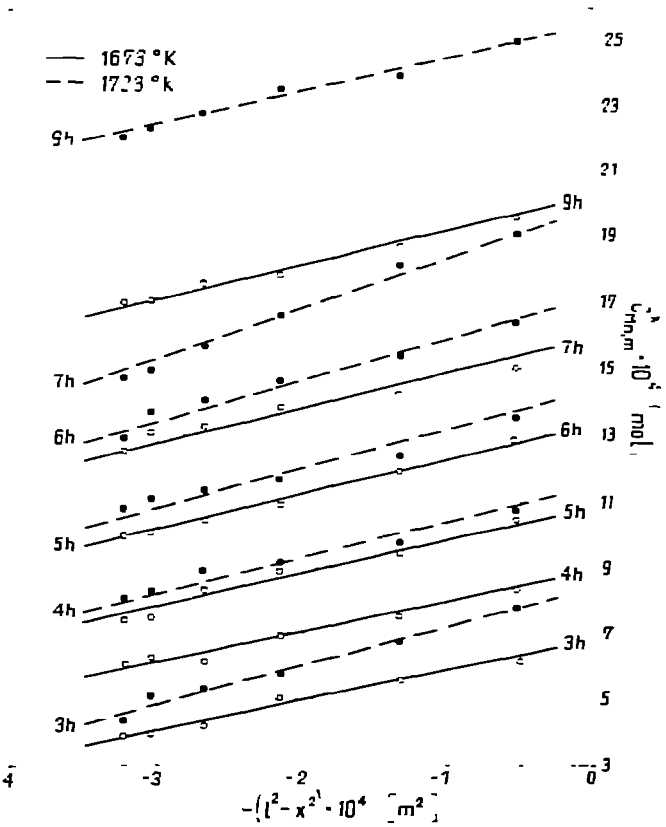


Fig. 4. Graphical representation of eqn (7) for particular temperatures and times of reaction.

TABLE 6

Comparison of obtained values of diffusion constants of manganese in iron saturated with carbon, $D_{Mn,m}$, and the activation energy of manganese diffusion, $E_{D_{Mn,m}}$, with results of other authors

Ref.	Temperature (K)	System	$D_{Mn,m} \times 10^8$ ($m^2 s^{-1}$)	$D_0 \times 10^8$ ($m^2 s^{-1}$)	$E_{D_{Mn,m}}$ (cal mole^{-1})
9	1673	FeMn—Fe (0—0.8% Mn)	0 0096	—	—
	1803		1.05		
	1843		1.01		
	1853		1.27		
	1873		2.20		
12	1573—1873	FeCMn—FeC (2 5% Mn)	0 30—0.41	1.93	5 800
10	1773	FeC—Mn	0 381	0.46	16 800
	1823		0 434		
14	1623—1823	FeC—Mn (Mn 13%)	0 39—0 45	—	—
13	1623—	FeC_{sat}—Mn	0.269	(0.385 ± 0.192)	16 600 ± 1700
	1823		0 465		
Present work	1673	FeC_{sat}—CaO + SiO_2 + Al_2O_3 + MgO + MnO (1 35 + 6.66% Mn)	3 421 ± 0.387	0.304	7 260 ± 750
	1723	as above (1.50 + 8.53% Mn)	3.645 ± 0.454		

is not great, however, and averages 3—5%. Values of [illegible]ner terms in the series have no material influence on the magnitude of $C^{x}_{Mn,m}$.

It has been assumed that values of diffusion constants calculated from eqn. (7) are sufficient for the evaluation of manganese diffusion in metal especially since the order of errors determined at constant temperatures for particular times is ±12%.

Taking advantage of the dependence of diffusion on temperature in the form of Arrhenius' equation

$$D = D_0 \exp(-E_D/RT) \tag{8}$$

values of D_0 and the activation energy of manganese diffusion in the alloy FeC_{sat} were calculated as well as the error E_D (error of the complex function taking into account errors in the diffusion constants) amounting to ±10%.

The mean values obtained for the diffusion constants of manganese in liquid iron saturated with carbon in the temperature range 1673—1723 K and the activation energy of diffusion are listed in Table 6, with the results of other authors given as a comparison. As can be seen there, values of $D_{Mn,m}$ obtained in this work are, on average, one order of magnitude higher than those given by other authors [10,12—14] but it should be emphasized that the system adopted, FeC_{sat}—blast furnace type slag, was completely different from the systems employed in the quoted papers.

One could judge, therefore, that the diffusion of manganese — obtained as a result of reaction (1) — proceeds faster in metals. It can hardly be stated at the moment whether this is true or not. Further investigations on this subject should bring the answer. It seems that the calculated value for the activation energy of diffusion corresponds relatively well to the respective values quoted in the literature [10,12—14].

SUMMARY

As a result of the experiments performed, the concentration gradient of manganese in metal was evaluated and the linear dependence of concentration changes of Mn on the surface of the metal was stated. In this way, it became possible to determine the diffusion constants of Mn in iron saturated with carbon in the temperature range 1673—1723 K and the activation energy of diffusion adopting quoted solution of Fick's second law. The results can be expressed by means of Arrhenius' equation whose detailed form is

$$D_{Mn,m}^{1673-1723} = 3.04 \times 10^{-7} \exp\left(-\frac{7260}{RT}\right) [\mathrm{m^2\,s^{-1}}] \tag{9}$$

Penetration of silicon was not identified in samples of metal.

Studies on the diffusion of elements in the liquid state are quite complicated. It is rather difficult to obtain accurate results because of errors arising in the course of experiments. It is worth saying that a number of unknown factors affecting deformation of results makes it difficult to determine the actual state as well as the lack of a sufficient theoretical basis. The reasons mentioned above and other objective difficulties caused some error in the results. For that reason the present work should be treated as a trial run for acquiring elementary information on manganese diffusion in iron saturated with carbon for the assumed system.

Continuation of investigations on manganese diffusion seems to be not only of theoretical but also practical importance for purposes of calculating zone heat balances of blast furnaces and developing a dynamic—kinetic mathematical model of the blast furnace process.

REFERENCES

1 L. von Bogdany, E. Förster, J. Rellermeyer, W. Schaefers and R Wartman, Proc. Int. Conf. Sci. Technol. Iron Steel., 1971, Part I, Iron and Steel Institute of Japan, p 131

2 P Fontana and G De Marchi, Boll. Tec Finsider, 353 (1976) 459.

3 Th. Kotz and E. Wilms, Thyssenforschung, 4 (1972) 91.

4 M. Kuwabara and I. Muchi, Trans. Iron Steel Inst. Jpn., 17 (1977) 271.

5 J. Szczeniowski, Centre D'Etudes Supérieures de la Sidérurgie, 13931/DL, 1974, p. 1.

6 R. Benesch et al , Hutnik, 12, (1969) 593.

7 S.K. Tarby and W.D Philbrook, Trans AIME, 239 (1967) 1005.

8 M Ashizuka, A Moribe and K Sawamura, Tetsu to Hagane, 61 (1975) 36.

9 M Paschke and A. Hauttmann, Arch. Eisenhuettenwes., 9 (1935) 305

10 A Majdič, D. Graf and H. Schenck, Arch. Eisenhuettenwes., 40 (1969) 1.

11 Y. Ono and S. Ishitobi, Trans. Iron Steel Inst. Jpn., 15 (1975) 262.

12 T Saito and K. Maruya, Sci. Rep Res. Inst Tohoku Univ. Ser A, 10 (1958) 259.

13 Y. Ono and T. Yagi, Trans Iron Steel Inst. Jpn., 11 (1971) 275.

14 B M. Liepinskich, A.W. Kajbicziew and J A. Sawieliew, The Diffusion of Elements in Liquid Metals of the Iron Group, Science, Moscow, 1974.

15 J F. Elliot, M. Gleiser and V. Ramakrishna, Thermochemistry for Steelmaking, Vol. II, Addison-Wesley, Reading, MA, 1963.

16 W. Patterson and W. Koppe, Giesserei Tech Wiss. Beih., 14 (1962) 213

17 L D Lucas, C.R. Acad. Sci., 250 (1960) 1850.

18 E D Williamson and L.H. Adams, Phys. Rev., Ser II, 14 (1919) 99.