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A new method for the measurement of the diffusivity of carbon in alpha-iron using an electrochemical cell

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A new method has been employed to measure the diffusivity of carbon in alpha iron. The method involves the measurement of ionic current of a carbon concentration cell which employs an iron cylinder as the anode. The design of the cell is such that when a constant external potential is applied, the ionic current is determined by the concentration polarization of carbon in the two electrodes. From the values of ionic current, the diffusivity of carbon (D_c) is calculated by the application of Fick's law. The results in the temperature range 854–975 K have been fitted by regression analysis to obtain the expression:

$$D_c = 2.448 \times 10^{-5} \exp(-102900.7/RT)$$

with D_c in $m^2\,s^{-1}$ and R in $J\,K^{-1}\,mol^{-1}$. The results agree well with data in the literature.

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1. Introduction

High-temperature iron-base alloys invariably contain interstitial carbon for maintaining favourable mechanical properties. Driven by a chemical potential gradient, the diffusion of carbon occurs from high to low concentrations. An accurate knowledge of the diffusion coefficient of carbon is important to understand the rate of carbon transport. The diffusivity of carbon in iron has been measured as a first step towards similar measurements in other alloys. In our laboratory, an electrochemical carbon meter, which employs a thin-walled iron tube as the probe, has been successfully employed to measure the carbon activity of fast reactor materials (coolant, cladding and fuel) [1, 2]. In this context, data for carbon diffusivity are essential to optimize the design of such probes.

Several methods are reported in the literature to measure the diffusion coefficient of carbon in iron. Wert [3] employed a lattice relaxation method at temperatures in the range 223–623 K. Smith [4] used permeability data from a moving phase boundary experiment in conjunction with carbon solubility data in the range 773–1133 K. Homan [5] used a radioactive tracer method over 889–1117 K. In the present investigation, a potentiostatic method involving an electrochemical carbon concentration cell (with alpha-iron cylinder as the anode) has been employed. Such a method was successfully used by Ramanarayanan and Rapp [6] for the measurement of the diffusion coefficient of oxygen in molten metals. Periaswamy *et al.* [7] have used this method to measure the diffusion coefficient of hydrogen in nickel.

2. Theory

2.1. *Electrochemical carbon meter*

The electrochemical carbon meter was primarily developed for the measurement of the carbon activity of sodium. The same configuration has been used in the present investigation. The original anode (graphite in nickel capsule) was replaced by an alpha-iron rod with dissolved carbon. The electrochemical cell is represented by

$$\text{alpha-iron} \left\| \begin{matrix} Na_2CO_3 \\ Li_2CO_3 \end{matrix} \right\| \text{iron, } [C]_{Na}$$

where $[C]_{Na}$ represents carbon dissolved in sodium. A thin-walled outer iron cup, immersed in sodium, forms the cathode. At equilibrium, the cathode attains the same carbon activity as the sodium. The ionic conducting electrolyte is an eutectic solution of 50 mol % sodium carbonate and 50 mol % lithium carbonate in the molten state. The activity of carbon at the cathode may be brought to a desired constant value by applying an external potential (using a potentiostat) or by buffering the carbon activity of sodium.

The gross interfacial reaction responsible for the local equilibration of carbon with the carbonate melt is given by

$$C + 3O^{2-} \rightleftharpoons CO_3^{2-} + 4e^- \qquad (1)$$

When the two electrodes are brought to a constant potential difference, the carbonate ion (CO_3^{2-})

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migrates from the anode to the cathode. The resulting ionic current is proportional to the diffusion flux of carbon in the anode because the molten carbonate is not expected to develop any significant concentration polarization in the electrolyte at very low currents. This current may be measured using a microammeter, which is externally connected between the two electrodes.

2.2. *Diffusivity of carbon through iron*

The rate of change of concentration of carbon (the diffusing element) through a solid matrix is governed by Fick's second law which, for unidirectional flow with a D_c independent of concentration, is written as [8]

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C_c}{\partial x^2} \qquad (2)$$

where C_c represents the carbon concentration in the solid matrix, D_c, the diffusion coefficient and t, the time. For diffusion in a cylinder (of radius r), Fick's equation may be rewritten as,

$$\frac{\partial C_c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left(rD_c \frac{\partial C_c}{\partial r}\right) \qquad (3)$$

By solving Equation 3 for the boundary conditions,

$$C_c = C_c(1); \quad 0 \leqslant r \leqslant a; \quad t = 0$$

and

$$C_c = C_c(2); \quad r = a; \quad t > 0$$

the following equation for ionic current (I_{ion}) may be obtained [6]:

$$I_{ion} = 8\pi h F D_c [C_c(1) - C_c(2)] \times \exp -(2.405)^2 D_c t/a^2 \qquad (4)$$

where h is the height of the portion of the anode immersed in the electrolyte and F is the Faraday constant. Equation 4 may be written in simplified form as

$$\ln I_{ion} = \ln B - t/\tau \qquad (5)$$

where

$$B = 8\pi h F D_c [C_c(1) - C_c(2)]$$

and

$$\tau = a^2/D_c(2.405)^2$$

Thus a plot of $\ln I_{ion}$ against t should yield a straight line of slope given by $-D_c[(2.405)^2/a^2]$ from which D_c may be calculated.

The experimental procedure involves the measurement of ionic current between the two electrodes of the carbon meter after impressing a constant external potential.

3. Experimental details

The schematic of the electrochemical cell is given in Fig. 1. The central electrode (anode) was an alpha-iron cylinder (3 mm diam.) which was welded to a stainless steel rod. This electrode was immersed in the electrolyte which was contained in a thin-walled iron cup (18 mm o.d., 0.4 mm wall thickness and 70 mm long). The iron cup was immersed in distilled sodium (contained in a high-purity iron crucible) and formed the cathode.* The two electrodes were coupled through a conax fitting.

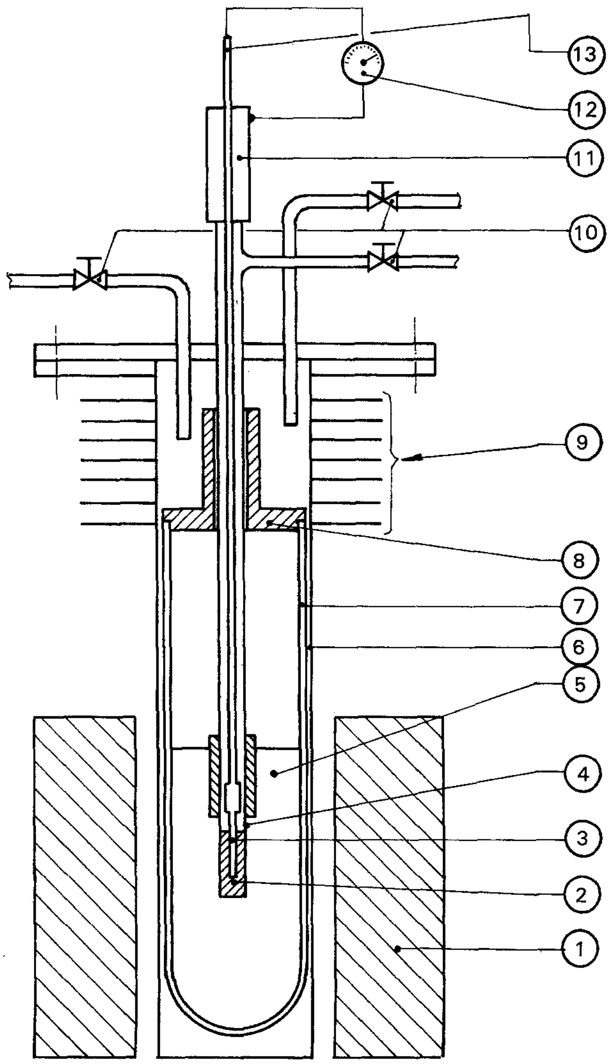

Fig. 1. Schematic of the electrochemical carbon meter. Key: (1) furnace, (2) electrolyte, (3) iron cylinder, (4) iron capsule, (5) sodium, (6) S.S. vessel, (7) iron crucible, (8) sodium vapour trap, (9) cooling fins, (10) diaphragm valve, (11) Conax fitting, (12) high impedance millivolt meter and (13) reference electrode.

The cell was assembled in an inert atmosphere glove box. It was removed from the box and heated to the desired experimental temperature using a resistance furnace whose temperature was maintained at the appropriate value (within ±1 K) by using a proportional controller (M/s Indotherm, model 301, Bombay, India). A more comprehensive description of the carbon meter and the associated experimental assembly may be found in an earlier publication [9].

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* For this cell geometry the carbon flux through the thin iron annulus can support the diffusion flux with negligible concentration polarization.

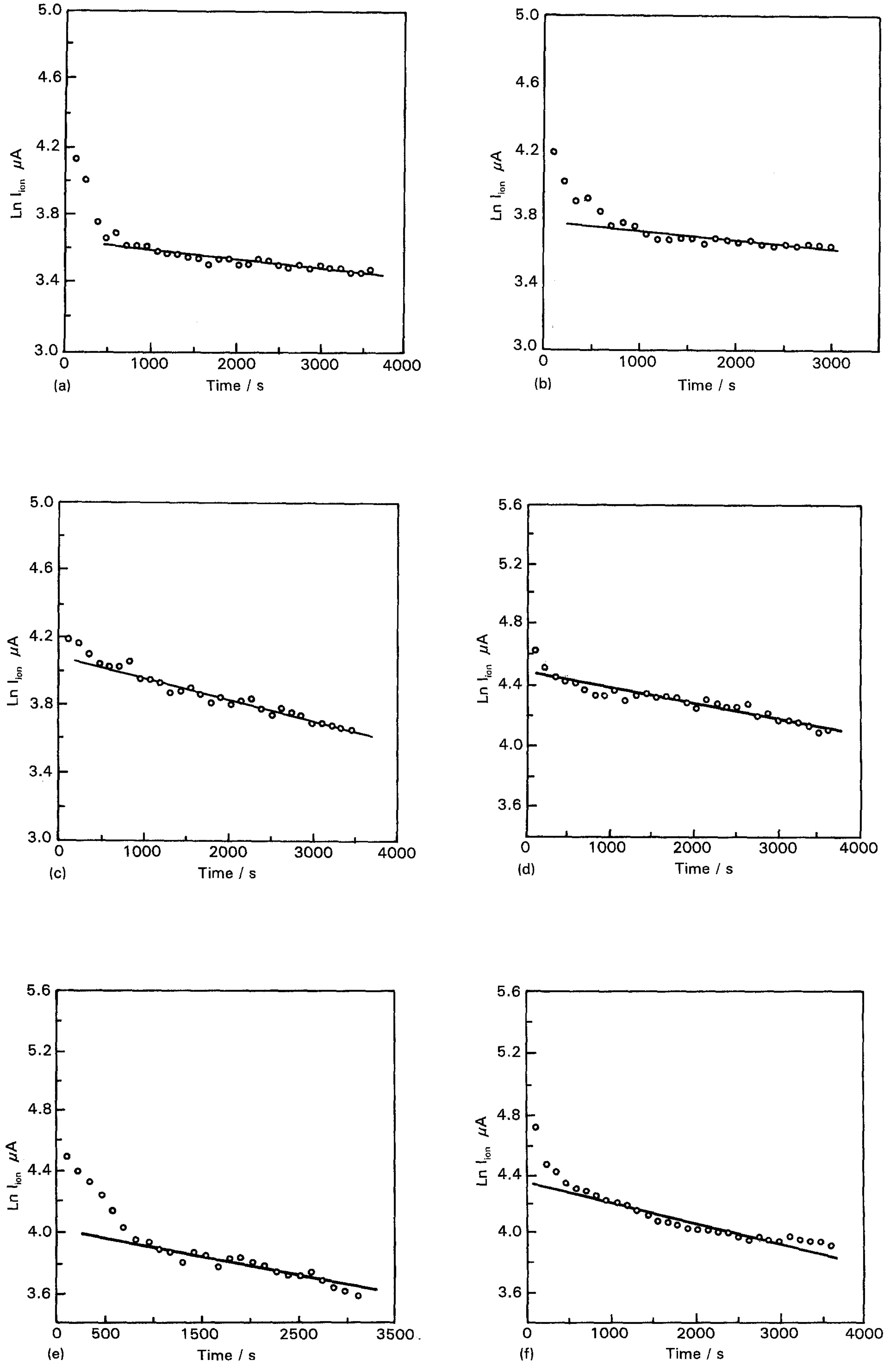
(a)
Ln I_{ion} μA
5.0
4.6
4.2
3.8
3.4
3.0
0
1000
2000
3000
4000
Time / s
(b)
Ln I_{ion} μA
5.0
4.6
4.2
3.8
3.4
3.0
0
1000
2000
3000
Time / s
(c)
Ln I_{ion} μA
5.0
4.6
4.2
3.8
3.4
3.0
0
1000
2000
3000
4000
Time / s
(d)
Ln I_{ion} μA
5.6
5.2
4.8
4.4
4.0
3.6
0
1000
2000
3000
4000
Time / s
(e)
Ln I_{ion} μA
5.6
5.2
4.8
4.4
4.0
3.6
0
500
1500
2500
3500
Time / s
(f)
Ln I_{ion} μA
5.6
5.2
4.8
4.4
4.0
3.6
0
1000
2000
3000
4000
Time / s

Fig. 2(a)–(f).

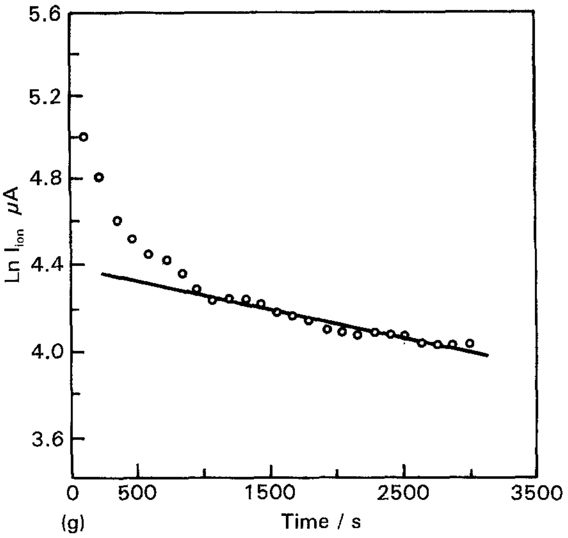

Fig. 2. Plot of ln I_{ion} against time. Temperatures: (a) 854, (b) 873, (c) 894, (d) 915, (e) 941, (f) 956 and (g) 975 K. Key: (o) experimental data; (——) fitted line.

Initially, due to the presence of dissolved carbon in sodium, the e.m.f. was in the range 30–40 mV. However, the desired initial e.m.f. value was in the range 80–100 mV. This desired value was discerned from trial experiments and was determined by the generation of a measurable (50 to 100 μA) ionic current in the subsequent measurement. The initial e.m.f. was obtained by employing the same method as reported in [6]. Carbon was pumped from the cathode to the anode by means of an external reverse biased voltage source (−100 mV). In the present case, a high-impedance potentiostat was connected between the two electrodes (for 6–8 h) so that carbon diffused out of the cathode and reached the anode and subsequently dissolved in it. The completion of this process (attainment of equilibrium) was indicated by a low ionic current, which was measured simultaneously. Subsequently a constant potential of +30 mV was impressed between the two electrodes. By this process, carbon was made to diffuse from the anode and reach the cathode through the molten electrolyte. The transient current generated due to this imposed voltage was monitored using a micro-ammeter (M/s Schlumberger Technologies, UK, Model 7150 plus). Under steady-state conditions, the ionic current was proportional to the instantaneous diffusion flux of carbon in the anode. From the ionic current data the diffusivity of carbon was calculated by using the method described above. However, the diffusivity values obtained this way were very high, probably due to the segregation of carbon on the anode surface (without dissolving) while applying the reverse potential. In other words, the kinetics of dissolution of carbon were slower than the rate at which it was pumped into the anode. Obviously, the release behaviour of graphite which was segregated on the surface of iron did not depend on diffusion.

Subsequently, the desired initial e.m.f. value was obtained by a gettering procedure without resorting to the application of any external reverse voltage. This could be achieved easily because the cathode was dipped into a medium (sodium) that is a known agent for carbon transport. By this method, annealed S.S 304 foils were immersed in sodium, for 10–12 days, which gettered the carbon. Obviously, this procedure did not result in the segregation of carbon in the anode.

The external voltage was subsequently changed to 30 mV by means of a potentiostat and the transient current was measured. The measurement of ionic current was continued until the variation with time showed a steady trend, thereby indicating that the process of ionic migration was controlled by the diffusion of carbon through the anode. The measurements were carried out at temperatures of 854, 873, 894, 915, 941, 956 and 975 K.

4. Results and discussion

The logarithm of the ionic current was plotted against time, at each temperature; the plots are shown in Fig. 2(a)–(g). The data representing the linear region of these plots were fitted by regression analysis and the slopes were calculated. By employing Equation 4 and the graphical method described above, the diffusion coefficient of carbon was determined. The values, obtained at different temperatures, were fitted by regression analysis to obtain the relation:

$$D_c = 2.448 \times 10^{-5} \exp(-102900.7/RT)$$

with D_c in m^2 s^{-1} and R in J K^{-1} mol^{-1}. The correlation coefficient is 0.96.

The different methods and the corresponding expressions relating diffusion coefficient and temperature are summarized in Table 1. The different values of energies of activation and pre-exponential factors are found to agree to a considerable extent. The diffusion coefficient values are plotted against the reciprocal of absolute temperature in Fig. 3. Results

Table 1. Comparison of different data for the diffusion coefficient of carbon in iron

Method	*Temp. range*/K	*Equation*, D/m^2 s^{-1}	*Ref.*
Lattice relaxation	223–623	$2.07 \times 10^{-6} \exp(-85048.3/RT)$	[3]
Permeability	773–1133	$1.792 \times 10^{-5} \exp(-98421.5/RT)$	[4]
Radioactive tracer	889–1117	$2.19 \times 10^{-4} \exp(-122555.5/RT)$	[5]
Potentiostatic	854–975	$2.448 \times 10^{-5} \exp(-102900.7)/RT)$	*

* Present method.

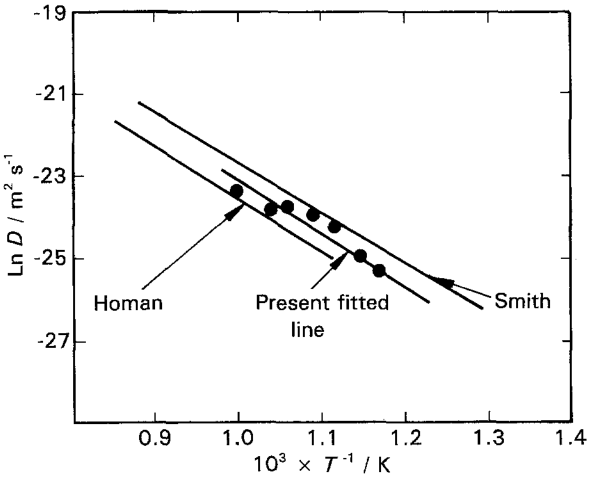

Fig. 3. Diffusion coefficient of carbon in alpha iron. Comparison of present results with literature data.

of two other investigations [4, 5] (at temperatures in the range of the present study) are also included in this figure. The good agreement in the data obtained by different methods suggests the validity of this relatively simple potentiostatic method for determining the diffusion coefficient of nonmetals in metals.

One important consideration for employing this method is that the cell design should ensure that the ionic current passes only as a consequence of concentration (diffusion) polarization between the two electrodes. The large ratio of surface area of cathode when compared to the anode (40:1) and the presence of a sink for carbon (S.S 304 foil immersed into sodium) at the cathode have ensured that diffusion of carbon in the anode is the rate limiting step.

In Fig. 2, a relatively high ionic current was observed for the initial period. This may be attributed to the current associated with the release of impurities adsorbed on the anode. Similar high initial values of ionic current were obtained by Ramanarayanan and Rapp [6] even though the exact reason was not quantitatively explained.

5. Conclusion

The diffusivity of carbon in iron has been measured using a simple potentiostatic method This procedure may be employed for other alloys containing carbon. The data, thus generated, are useful in predicting the kinetics of carburization–decarburization phenomena at high temperature. From a knowledge of the kinetics of carbon transfer it is possible to predict the carbon profile and service life of components in a system.

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