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Magnetic effect on diffusion of carbon and nitrogen in iron

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Abstract

Based on available experimental data on diffusion of carbon and nitrogen in b.c.c. iron, the temperature dependence of their diffusion coefficients is investigated by means of a model which takes the influence of the magnetic transformation in α -iron into account. The diffusion coefficients of carbon and nitrogen in α -iron can be expressed by

$$D = 2.72 \times 10^{-7} \exp[-59.6 \text{ kJ mol}^{-1}(1 + 0.337s^2)/RT] \text{ m}^2 \text{ s}^{-1}$$

and

$$D = 2.42 \times 10^{-7} \exp[-59.7 \text{ kJ mol}^{-1}(1 + 0.266s^2)/RT] \text{ m}^2 \text{ s}^{-1}$$

respectively, where s is the ratio of the spontaneous magnetization in iron at T K to that at 0 K. For diffusion of carbon in α -iron, the increment of the activation energy due to the magnetic spin ordering is 20 kJ mol⁻¹ and that for the diffusion of nitrogen is 16 kJ mol⁻¹, about half of the corresponding value for self-diffusion in α -iron.

Keywords: Magnetic effect; Diffusion; Carbon; Nitrogen; Iron

1. Introduction

Information on the diffusivities of carbon and nitrogen in steels has been applied to various heat treatments of steels to raise their quality (the diffusivities of these elements determine the rate of many phase transformations in steels). It is thus important to know accurately the temperature dependence of diffusion coefficients of carbon and nitrogen in iron and steels.

In recent decades extensive work on diffusion of carbon and nitrogen in α -iron below the α - γ transition temperature $T_{\alpha-\gamma}$ (1184 K) has been carried out [1,2]. Owing to the interstitial character of carbon and nitrogen in α -iron, several direct and indirect methods have been applied to evaluate volume diffusion coefficients over a wide temperature range of more than 900 K. In the cases of both carbon and nitrogen, a combined Arrhenius plot of the diffusivities measured by direct and indirect methods clearly exhibits a positive deviation from linearity with increasing temperature [2]. To explain the curvature of the Arrhenius plots da Silva and McLellan [3] have dis-

cussed possible diffusion mechanisms. However, they have not determined which mechanism is dominant. According to Jönsson [4], the effect of the magnetic transformation upon the diffusivity of carbon in b.c.c. iron is quite pronounced, although the effect is not as strong as for substitutional elements, while the effect on the diffusivity of nitrogen in b.c.c. iron is not at all as evident as it is for carbon. However, a quantitative evaluation of the magnetic effect on the diffusion of these interstitials, especially nitrogen, has not been made.

The influence of the magnetic transformation on the self-diffusion and diffusion of substitutional solutes in iron is well known and understood [5,6]. The Arrhenius plot of the self-diffusion coefficients below the Curie temperature deviates downwards from the extrapolated Arrhenius relationship for the paramagnetic state, and the temperature dependence of the diffusion coefficient D across the Curie temperature can be expressed by [7]

$$D = D_0^p \exp[-Q^p(1 + \alpha s^2)/RT] \quad (1)$$

where D_0^P and Q^P are the pre-exponential factor and the activation energy respectively for diffusion in the paramagnetic state. The value of s , the ratio of the spontaneous magnetization at T K to that at 0 K, has been experimentally determined by Crangle and Goodman [8]. The constant α denotes the increase of the activation energy due to the transformation from the paramagnetic state to the ferromagnetic state. The diffusion parameters in the completely ordered ferromagnetic state ($s = 1$) can be defined by $Q^f = Q^P(1 + \alpha)$ and $D_0^f = D_0^P$ [7]. In the present work, available diffusion data on carbon and nitrogen in b.c.c. iron are fitted to Eq. (1), and the values of D_0 , Q and α are evaluated. Since $s = 0$ above the Curie temperature T_c (1043 K), the values of D_0^P and Q^P could be calculated using a simple Arrhenius equation derived from Eq. (1) if the plot showed good linearity. However, direct determination of D_0^P and Q^P for these elements cannot be made, because both the Arrhenius plots of the diffusion coefficients of carbon and nitrogen above T_c show some scatter [3,4]. In the present work, to elucidate the deviation from the simple Arrhenius relation due to the magnetic effect, another plot has been attempted. Eq. (1) can be rewritten as

$$T \ln D = [\ln D_0^P]T - Q^P(1 + \alpha s^2)/R \quad (2)$$

If the plot of $T \ln D$ vs. T shows linearity in the fully ferromagnetic range at low temperatures ($s^2 \approx 1$), the intercept and the slope of the line give the values of D_0^f and Q^f respectively. Using the value of D_0^f ($= D_0^P$) thus determined, the values of α and Q^P can be evaluated as follows. Eq. (1) can also be rewritten as

$$T \ln [D/D_0^P] = -Q^P/R - (\alpha Q^P/R)s^2 \quad (3)$$

Using the value of D_0^P obtained as above and the experimental values of s for pure iron [8], one can calculate $T \ln [D/D_0^P]$ as a function of s^2 . When the plot of $T \ln [D/D_0^P]$ vs. s^2 shows linearity, the values of α and Q^P can be obtained.

2. Diffusion of carbon in α -iron

Fig. 1 shows the plot of $T \ln D$ vs. T for all the available experimental points of the diffusion coefficients of carbon in α -iron. The sources of these data are summarized in Table 1. Stanley [9] and Ham [10] used the carburization method, Smith [11] used the decarburization method, Homan [12] and Budke et al. [13] used the radiotracer diffusion method. These methods are typical direct methods. The following authors used indirect methods: Wert [14] used the elastic after effect and the internal friction method; the latter method was also used by Hasiguti and Kamoshita [15], Thomas and Leak [16], Guillet and

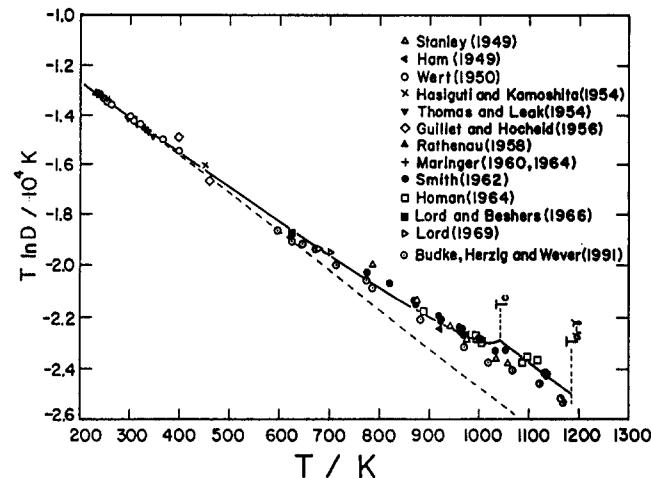


Fig. 1. Plot of $T \ln D$ vs. T for diffusion of carbon in α -iron.

Hocheid [17], Lord and Bessers [1] and Lord [18]; Rathenau [19] used the permeability after effect; Maringer [20] used the magnetoelastic after effect. As described in the previous section, direct determination of D_0^P and Q^P from the plot in Fig. 1 is impossible because of fairly large scatter in the points above the Curie temperature T_c . In contrast, at lower temperatures the plot shows good linearity. From the linear part below 398 K ($s^2 \geq 0.936$ [8]), where 25 points are plotted, the values of D_0^f ($= D_0^P$) and Q^f ($= Q^P(1 + \alpha)$) are calculated to be $(2.72 + 0.42/-0.36) \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and 79.3 kJ mol^{-1} respectively. The straight and broken lines in Fig. 1 show the temperature dependence of the diffusion coefficient of carbon in the hypothetically complete ferromagnetic state. Using 83 experimental points of D below T_c , and the value of D_0^P , $T \ln [D/D_0^P]$ was calculated as a function of s^2 and plotted in Fig. 2. The linearity of the plot is recognized, as expected by Eq. (3). From the least square fit of the plot, α and Q^P are determined to be 0.337 ± 0.008 and $59.6 \pm 0.3 \text{ kJ mol}^{-1}$ respectively. Thus the value of $Q^P(1 + \alpha)$ becomes 79.7 kJ mol^{-1} , which is consistent with the value 79.3 kJ mol^{-1} derived from the linear part below 398 K in Fig. 1. If we adopt another linear range in Fig. 1, we will obtain a somewhat different numerical set of diffusion parameters. Finally, minimizing the difference in the values of $Q^P(1 + \alpha)$ derived from Figs. 1 and 2, the above numerical set is found to be the best. Using the values of D_0^P ($= 2.72 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$), Q^P ($= 59.6 \text{ kJ mol}^{-1}$) and α ($= 0.337$), the solid line in Fig. 1 is drawn. The fitting of the line with the experimental points is excellent.

3. Diffusion of nitrogen in α -iron

Using all the available experimental data on diffusion of nitrogen in α -iron, the diffusion parameters

Table 1
Experimental data sources for diffusion of carbon in α -iron

Authors	Year	Method	Temperature range (K)	Datum points	Reference
Stanley	1949	C	787–1059	18	[9]
Ham	1949	C	921–975	2	[10]
Wert	1950	E. I	238–398	11	[14]
Hasiguti and Kamoshita	1954	I	450	1	[15]
Thomas and Leak	1954	I	297–347	7	[16]
Guillet and Hocheid	1956	I	398–460	2	[17]
Rathenau	1958	P	234	1	[19]
Maringer	1960, 1964	M	235–256	6	[20]
Smith	1962	D	776–1138	31	[11]
Homan	1964	R	994–1117	9	[12]
Lord and Beshers	1966	I	625	1	[1]
Lord	1969	I	681–703	2	[18]
Budke, Herzig and Wever	1991	R	596–1168	15	[13]

Methods: C, carburization; D, decarburization; E, elastic after effect; I, internal friction; M, magnetoelastic after effect; P, permeability after effect; R, radiotracer diffusion.

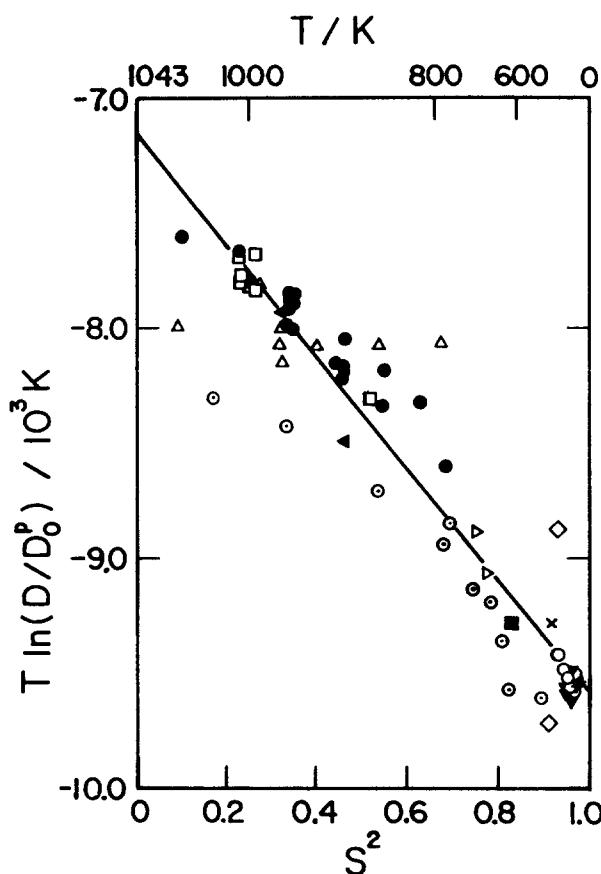


Fig. 2. Plot of $T \ln(D/D_0^P)$ vs. s^2 for diffusion of carbon in α -iron.

D_0^P , Q^P and α are evaluated in the same way as above. Table 2 shows the sources of data on nitrogen diffusion in α -iron. Fig. 3 shows the plot of $T \ln D$ vs. T for the diffusion coefficients of nitrogen in α -iron. Fast and Verrijp [21] used the desorption method and the internal friction; the former method was also used by Podgurski and Gonzalez [22]; Busby et al. [23] used the absorption method; Grieveson and Turkdogan

[24] and Bohnenkamp [25] used both the absorption and the desorption methods. Owing to a lack of suitable radioisotopes of nitrogen, the radiotracer diffusion method could not be applied. The internal friction, i.e. a typical indirect method, was used by many authors (for example Wert [26], Hasiguti and Kamoshita [15], Thomas and Leak [16], Guillet and Hocheid [17], Guillet and Gence [27] and Lord and Beshers [1]). Bosman [28] used the permeability after effect; Maringer [29] used the magnetoelastic after effect; Keefer and Wert [30] used the elastic after effect.

Above T_c only several points have been obtained, but they are scattered. Thus, from the plot above T_c , calculation of D_0^P and Q^P cannot be made. In contrast, at low temperatures the plot shows good linearity, as in the case of carbon. From the linear part below 436 K ($s^2 \geq 0.923$ [8]), where 35 points are plotted, the values of D_0^f ($=D_0^P$) and Q^f ($=Q^P(1+\alpha)$) are calculated to be $(2.42 + 0.34/ - 0.30) \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and 75.2 kJ mol^{-1} respectively. The broken line in Fig. 3 shows the temperature dependence of the diffusion coefficients of nitrogen in the hypothetically complete ferromagnetic state. Next, in the same way as the analysis for the diffusion of carbon, $T \ln[D/D_0^P]$ is plotted vs. s^2 in Fig. 4. Neglecting two largely scattered points and fitting the plot of 55 points to Eq. (3) by the least-squares method, α and Q^P are determined to be 0.266 ± 0.009 and $59.7 \pm 0.4 \text{ kJ mol}^{-1}$ respectively. Thus, the value of $Q^P(1+\alpha)$ becomes 75.6 kJ mol^{-1} , which is consistent with the value 75.2 kJ mol^{-1} derived from the linear part below 436 K in Fig. 3. Under the conditions to minimize the difference in the values of $Q^P(1+\alpha)$ derived from Figs. 3 and 4, calculations of other numerical sets have been attempted. However, the above numerical set of D_0^P ($=2.42 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$), Q^P ($=59.7 \text{ kJ mol}^{-1}$) and α ($=0.266$) are found to be the best. Using these values,

Table 2
Experimental data sources for diffusion of nitrogen in α -iron

Authors	Year	Method	Temperature range (K)	Datum points	Reference
Wert	1950	I	244–304	5	[26]
Fast and Verrijp	1954	I	283–295	2	[21]
Fast and Verrijp	1954	Ds	773–873	2	[21]
Hasiguti and Kamoshita	1954	I	436	1	[15]
Thomas and Leak	1954	I	292–331	9	[16]
Guillet and Hochedl	1956	I	363–421	2	[17]
Busby, Hart and Wells	1956	A	673–873	4	[23]
Guillet and Gence	1957	I	364–435	6	[27]
Bosman	1960	P	234	1	[28]
Maringer	1961	M	226–242	8	[29]
Keefer and Wert	1963	E	238–248	2	[30]
Grieveson and Turkdogan	1964	A, Ds	1023–1146	3	[24]
Podgurski and Gonzalez	1966	Ds	595–671	3	[22]
Lord and Beskers	1966	I	599	1	[1]
Bohnenkamp	1967	A, Ds	763–1073	16	[25]

Methods: A, absorption; Ds, desorption; E, elastic after effect; M, magnetoelastic after effect; I, internal friction; P, permeability after effect.

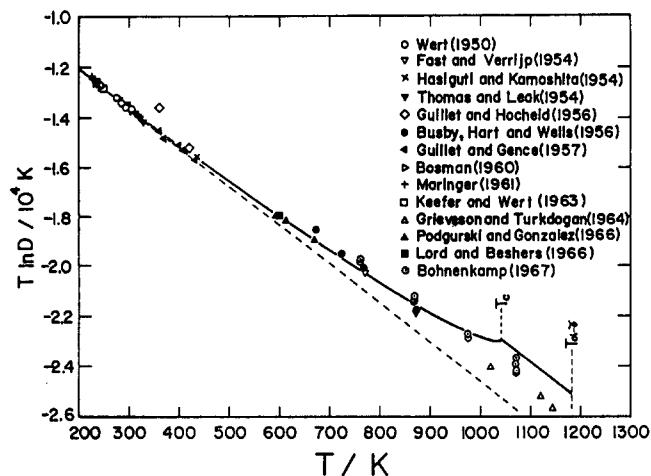


Fig. 3. Plot of $T \ln D$ vs. T for diffusion of nitrogen in α -iron.

the solid line in Fig. 3 is drawn. The fitting of the line with the experimental points below T_c is excellent, although the fitting above T_c is poor because of the small amount of experimental data.

Although the diffusion coefficient of carbon in δ -iron has not been obtained, only Grieveson and Turkdogan [24] have measured the diffusion coefficients of nitrogen in δ -iron. In Fig. 5 their experimental data are plotted in the temperature range between the γ - δ transition temperature $T_{\gamma-\delta}$ (1665 K) and the melting temperature T_m (1811 K), and they are fairly consistent with the solid line which is drawn by using the values of D_0^p and Q^p obtained as above. This consistency suggests that the values of these diffusion parameters are suitable over the whole temperature range of b.c.c. iron.

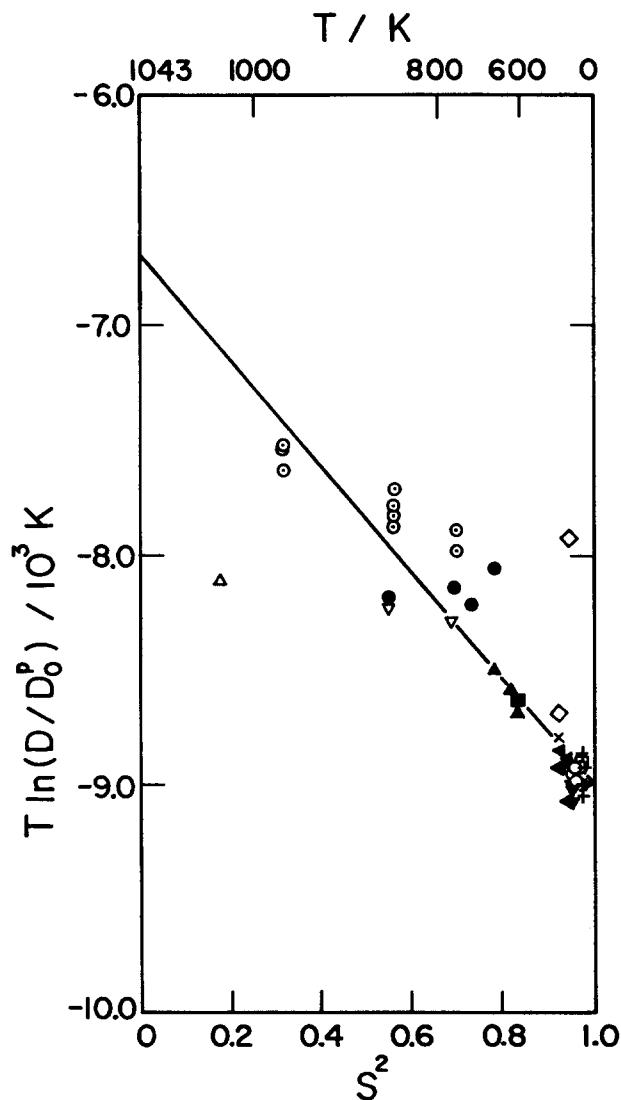


Fig. 4. Plot of $T \ln(D/D_0^p)$ vs. s^2 for diffusion of nitrogen in α -iron.

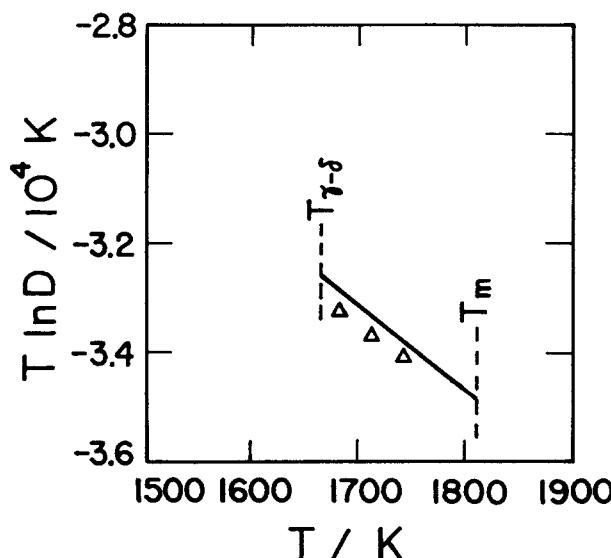


Fig. 5. Plot of $T \ln D$ vs. T for diffusion of nitrogen in δ -iron.

4. Discussion

So far, a negative interpretation for the magnetic effect on the diffusion of nitrogen in iron has been given [31]. Wasz and McLellan [32] have recently noted that the evaluation of the effect is difficult because of insufficient experimental data in the higher temperature range. Indeed, as shown in Fig. 3, the experimental points above T_c are insufficient. However, in the present method the values of D_0^f and Q^f have first been estimated from the points in the fully ferromagnetic range of low temperatures, and then the values of Q^p and α are calculated from all the experimental data below the Curie temperature T_c . Therefore, the scattered points above T_c , as shown in Fig. 3, do not influence the evaluation of the diffusion parameters. The value of α (0.266) for nitrogen is smaller than 0.337 for carbon, as predicted by Jönsson [4]. Recently, Budke et al. [13] have estimated α for carbon to be 0.25 by calculating D_0^p , Q^p and α simultaneously with a three-parameter fitting method. However, above T_c there is some discrepancy between the authors on the experimental data, as seen in Fig. 1. In the present analysis this is not serious because the experimental data above T_c are not used directly. For the self-diffusion in α -iron, the value of α has been determined to be 0.156, and the increment of the activation energy due to the magnetic spin ordering is 39 kJ mol^{-1} [5]. This is about twice those for the diffusion of carbon and nitrogen. Furthermore, since the diffusion coefficients determined by direct and indirect methods show a good agreement in Figs. 1 and 3, it may be noted that over the whole tempera-

ture range carbon and nitrogen atoms diffuse interstitially only via octahedral sites in b.c.c. iron.

5. Conclusion

The influence of the magnetic transformation on the diffusion of carbon and nitrogen in b.c.c. iron has been evaluated. The increment of the activation energy due to the magnetic spin ordering is 20 kJ mol^{-1} for carbon and 16 kJ mol^{-1} for nitrogen, values about half of that for self-diffusion in α -iron.

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