

Diffusion of Carbon and Nitrogen in B.C.C. Iron

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SUMMARY

It is well known that Arrhenius plots of the diffusivity of carbon in b.c.c. iron exhibit positive departures from linearity.

It has been demonstrated that such an effect is shown by nitrogen but the strength of the deviation is only about one half that found for carbon.

The theoretical models proposed to account for this effect have been discussed and it is tentatively concluded that there is a change in the intrinsic jump frequency of the diffusing species due to the change in that portion of the motion energy due to the magnetic exchange energy.

INTRODUCTION

In recent years, the behavior of the diffusivity, D , of carbon in b.c.c. iron as a function of temperature, T , has been the object of much controversy, and many models have been proposed to account for the positive deviation in Arrhenius plots of $\ln D$ vs. $1/T$, occurring at high temperatures. The purpose of the present short report is to re-examine the diffusion data for both C and N in b.c.c. iron in order to assess the plausibility of the various models which have been proposed.

EXPERIMENTAL DATA

(a) The Fe-C system

The plot of $\ln D$ vs. $1/T$ is seen in Fig. 1. The bulk of the experimental points was taken from the paper of Lord and Beshers [1], but other data are also included. It is to be noted that, in all cases, actual experimental data points were used and not points computed

from representational equations. The references, corresponding to the various symbols used in Fig. 1, are listed in Table 1. The letters adjacent to the symbols in Fig. 1 indicate, briefly, the method used to determine the diffusion coefficients according to the scheme: MF = mass flow, IF = internal friction, EAE = elastic after effect, PAE = permeability after effect, MAE = magnetic after effect.

The curvature, noticeable as T increases, has been analyzed using a least-squares fitting technique involving a parabolic representation. The 83 separate data points can be represented by

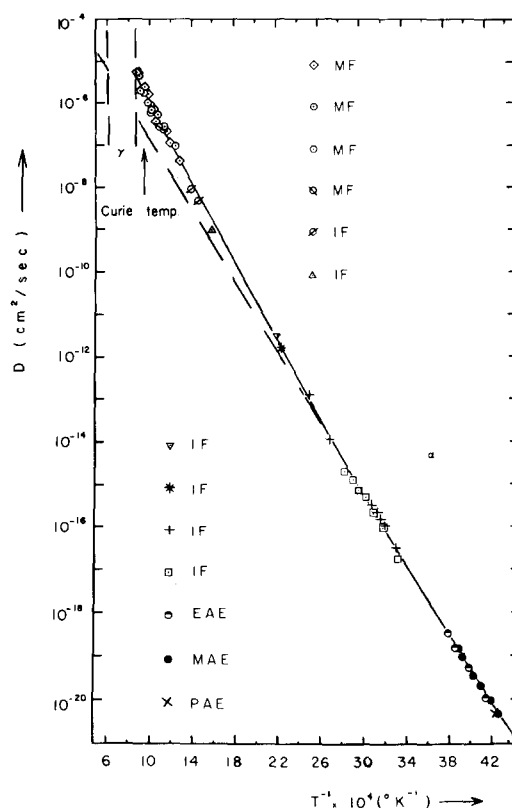


Fig. 1. Plot of $\ln D$ vs. $1/T$ for the Fe-C system.

TABLE 1

Authors	Ref.	Method	Temperature range (°C)	Symbols
Stanley	15	MF	514 - 786	⊙
Smith	16	MF	503 - 865	◇
Lord and Beshers	1	IF	353	△
Hasiguti and Kamoshita	17	IF	177.5	▽
Guillet and Hocheid	18	IF	187	*
Wert	19	IF	26.4 - 125	+
Wert	19	EAE	-35 to -10	●
Thomas and Leak	20	IF	23.7 - 74.2	□
Maringer	21	MAE	-38 to -17	●
Rathenau	22	PAE	-39	×
Ham	23	MF	648 - 702	⊖
Lord	24	IF	408 - 430	∅
Homan	2	MF	616 - 844	⊕

TABLE 2

Authors	Ref.	Method	Temperature range (°C)	Symbols
Grieverson and Turkdogan	25	MF	750 - 1470	△
Fast and Verrijp	26	MF	500 - 600	▽
Busby, Hart and Wells	27	MF	400 - 600	×
Podgurski and Gonzales	28	MF	322 - 398	∅
Lord and Beshers	1	IF	163	*
Hasiguti and Kamoshita	17	IF	163	◇
Guillet and Gence	29	IF	91 - 162	⊙
Guillet and Hocheid	18	IF	90 - 148	●
Thomas and Leak	20	IF	18.5 - 58.5	□
Wert	30	IF	-29 - 31	+
Fast and Verrijp	26	IF	10 - 21.5	▼
Wert and Keefer	31	EAE	-35 to -25	⊙
Bosman	32	PAE	-39	●
Maringer	33	MAE	-47 to -31.5	●

$$\ln D = -2.087 - 1.197 \chi + 0.0037 \chi^2 \quad (1)$$

where $\chi = (10^4/T)^\circ\text{K}^{-1}$. The mean-square deviation is 0.022. A separate representation of the low-temperature diffusivity was obtained by taking only points below 74 °C. These 23 points can be represented by,

$$\ln D = -6.395 - 0.9413 \chi \quad (2)$$

with a mean-square deviation of 0.023. The values of the diffusion parameters defined by

$$D = D_0 e^{-Q/kT}$$

corresponding to eqn. (2) are $D_0 = 1.670 \times 10^{-3} \text{ cm}^2/\text{s}$ and $Q = 18.65 \text{ kcal/mole}$.

(b) The Fe-N system

The references taken for the diffusivity data are compiled in Table 2, and correspond

with the symbols, and in the plot of $\ln D$ vs. $1/T$, given in Fig. 2. This plot again shows a positive deviation from Arrhenius behavior as T increases, but the deviation is smaller than in the case of the Fe-C system.

The 52 data points were analyzed in the manner described for the Fe-C system with the result,

$$\ln D = -4.485 - 0.9979 \chi + 0.0014 \chi^2 \quad (3)$$

with a mean-square deviation of 0.030. The low-temperature range was taken to be less than 50 °C and these 24 data points can be represented by,

$$\ln D = -6.676 - 0.8858 \chi \quad (4)$$

with a mean-square error of 0.037. The corresponding diffusion parameters are

$D_0 = 1.26 \times 10^{-3} \text{ cm}^2/\text{s}$ and $Q = 17.54 \text{ kcal/mole}$.

The coefficient of the quadratic term in eqn. (1) (C) is about 2.5 times larger than that in eqn. (3) (N).

DISCUSSION

Three models which have been proposed to explain the diffusion anomaly in the Fe–C system will be discussed in terms of the facts revealed in Figs. (1) and (2).

(a) Interstitial–vacancy complexes

A model was proposed by Homan [2] in which the enhanced diffusivity at high temperatures is due to the greater mobility of C-atoms combined with vacant sites in the iron lattice in comparison with isolated solute atoms. This concept has been criticized by Beshers [3] in a recent review of interstitial diffusion, and also by McLellan, Rudee and Ishibachi [4], on the grounds that radiation damage studies indicate that C-vacancy pairs would not be stable at the temperatures where the diffusion anomaly is seen [5]. However, a persusal of Fig. 1 indicates that the internal friction measurements made at higher temperatures do not follow the extrapolated low-temperature internal-friction and MAE data, but are consistent with the diffusivities measured by mass-flow techniques. Since only a small fraction of the C-atoms are combined with lattice vacancies, the interstitial–vacancy theory would seem to predict that the higher temperature internal friction data should follow the dashed line in Fig. 1. Even in the case of N (Fig. 2), there is some indication that the higher temperature diffusivities determined by internal friction (*, \diamond , \bullet) are beginning to show a positive deviation from the dashed line which represents eqn. (4).

A further objection to the interstitial–vacancy model is that the diffusion anomaly occurs at temperatures where the vacancy concentration would seem to be much too low to account for the effects observed.

Neglecting a small vibrational entropy factor, the ratio of complexed to isolated solute atoms is,

$$f = \alpha C_v e^{B/kT} \quad (5)$$

where α is an orientation parameter depending on the vacancy–interstitial geometry, B is the binding energy, and C_v is the concentration of lattice vacancies. Mehl, Swanson and Pound [6] have given a value of 49.0 kcal/mole for the vacancy formation energy in iron. This estimate is in good agreement with that obtained by the elastic method of McLellan [4] and is about half the latent heat of sublimation. Using this value of the vacancy formation energy and the value of $B = 9.5 \text{ kcal/mole}$ proposed by Homan [2], eqn. (5) yields the value $f \approx 10^{-10}$ at 800 K and taking $\alpha = 6$. At this temperature, D for carbon in b.c.c. Fe is already $\sim 5 \times$ larger than the extrapolated low-temperature diffusivity. Even if a value of only 30 kcal/mole was taken for the vacancy formation energy in iron, the corresponding value of f of $\approx 10^{-5}$ would be difficult to reconcile with the observed behavior.

(b) Dual site occupancy

McLellan, Rudee and Ishibachi [4] proposed a model in which the enhanced diffusivity at high temperatures was due to the occupation of the energetically less-favorable tetrahedral sites by a fraction of the solute atoms. This fraction increases with temperature and, assuming that direct jumps between tetrahedral sites are characterized by a smaller activation energy than those between octahedral sites, leads to an enhanced diffusivity. A similar model has been considered by Condit and Beshers [8].

The weaker enhancement of diffusivity shown for N in Fig. 2, with regard to C, is qualitatively in agreement with the dual occupancy model. The thermodynamic data show that C is more tightly bound to the b.c.c. lattice than N. The partial enthalpies with regard to an atom at rest in a vacuum are $\bar{H}_C = -144.1 \text{ kcal/mole}$ and $\bar{H}_N = -74.3 \text{ kcal/mole}$ [9] and the partial molar volumes ($\bar{V}_N = 5.9 \text{ cm}^3$, $\bar{V}_C = 6.3 \text{ cm}^3$) are such that $\bar{V}_C > \bar{V}_N$ [10, 11]. Thus, it is reasonably safe to assume that the energy needed to transport a C-atom from an octahedral site in b.c.c. iron into a neighboring tetrahedral site would be less than the corresponding energy for an N atom. Thus the observed diffusion anomaly should be greater in the Fe–C system than in the Fe–N system.

However, it is difficult to reconcile the dual occupancy model with the observation that

the D -values measured by internal friction agree with the mass-flow measurements. Notice particularly the points ($*$ + ∇ ϕ) in curve 1. It should be mentioned that the dual occupancy of different sites by interstitial atoms is a thermodynamic necessity because of the very large change in partial configurational entropy occurring when a second sub-assembly of sites begins to be occupied. The only factor in question is the magnitude of this effect. There is some evidence that this dual-site occupancy is reflected in the thermodynamic behavior of the Fe-H system where the energy needed to transfer an H atom from a tetrahedral site to an octahedral site may be quite small [12, 13].

(c) *The ferromagnetic model*

Wuttig [14] explained the diffusion anomaly in the Fe-C system by writing the free energy change accompanying the motion of an atom into a saddle point configuration in the form,

$$\Delta G^* = (1 - \delta) \Delta G_s^* + \delta \Delta G_{\text{mag}}^* \quad (6)$$

where ΔG_s^* is due to the elastic distortion, ΔG_{mag}^* is due to the magnetic exchange energy, and δ is a coefficient denoting that fraction of ΔG^* which is not an elastic energy. The activation entropy,

$$\Delta S^* = - \left[\frac{\partial \Delta G^*}{\partial T} \right]_P, \quad (7)$$

thus should vary with temperature since δ is given approximately by the saturation magnetization. This effect obviously leads to a positive deviation in the Arrhenius plot of $\ln D$ vs. $1/T$. Furthermore, the magnetic model is consistent with the fact that the diffusion anomaly is much smaller for N than for C because the pseudo dipolar interaction of N with the lattice atoms is only half as strong as that for C.

Figure 2 shows that the diffusivities obtained in the δ -iron region seem to be in excellent agreement with the linear extrapolation of the high-temperature data. Because of the small differences involved it is difficult to quantify such arguments, but the implication is that after the Curie temperature, T_c , is reached, no further enhancement of D occurs. This is in keeping with the magnetic model since $\Delta G^* \rightarrow \Delta G_s^*$ as $T \rightarrow T_c$. Unfortunately, no D -data exist for C in the δ -iron

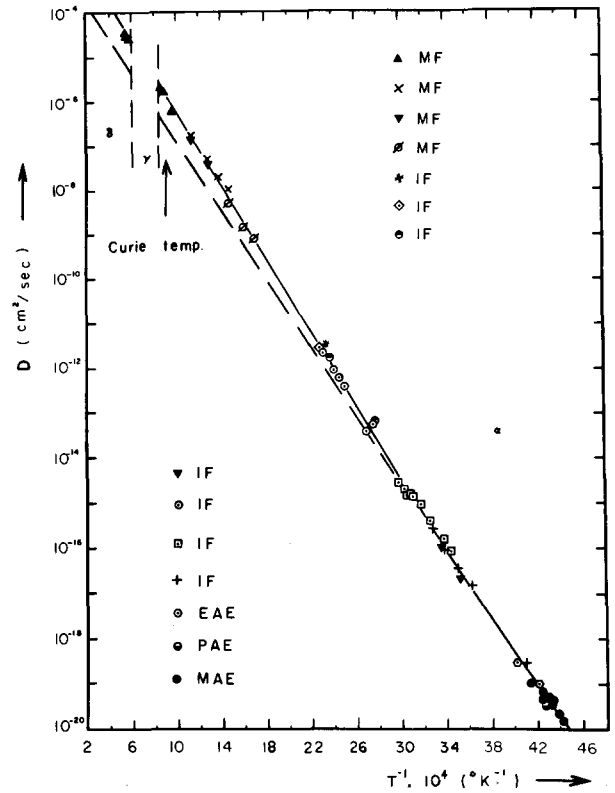


Fig. 2. Plot of $\ln D$ vs. $1/T$ for the Fe-N system.

range where the anomaly is much larger than in the case of N.

However, perhaps the strongest argument in favor of the magnetic model is that it provides for a single-stage diffusion mechanism where the diffusivities observed in mass-flow measurements should be in agreement with those determined from the internal friction data.

However, it is important to point out that the simple magnetic model may require some refinement. As Beshers [3] has pointed out, the strength of the pseudo dipolar interaction in N is only half as large as that for C, in keeping with the observed diffusion anomaly, but the effect does not seem to be large enough to account for the observations. Finally, the proposal of Borg [34] should be mentioned. Borg [34] pointed out the similarity in variations in elastic constants in iron close to the Curie temperature. The essence of Borg's suggestion is that the activation strain energy undergoes an anomaly in the region where the diffusion anomaly is observed. This suggestion is, of course, closely related to Wuttig's calculation and is in keeping with the fact that the curvature in the plots of $\ln D$ vs. $1/T$

are found for both the Fe-C and Fe-N systems.

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