Diffusion in interstitial compounds with thermal and stoichiometric defects

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The ordinary flux equation for diffusion, which considers the composition gradient as the driving force, is seldom of much use in studying closely stoichiometric phases. Depending on the defect structure it would instead be profitable to use an appropriate function of the activity. Such functions will now be derived and it will be shown how the operating defect mechanism of diffusion can be identified from information on the variation of the activity inside a phase during diffusion. However, it is usually very difficult to measure the activity profile inside a phase. It will be shown how it can be obtained by combining results from several experiments. The method will be used to analyze experimental information on the formation of surface layers of Fe_4N and Fe_3C. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1999833]

I. INTRODUCTION

Many compounds have a very narrow range of composition and are often treated as stoichiometric. However, such compounds may form as a surface layer on a metallic material in a reactive atmosphere and the thickening of the layer occurs by diffusion through the compound itself in spite of the small composition gradient. It is then a problem how to analyze such information on diffusion. This problem will now be discussed with particular reference to interstitial compounds where the nonmetallic atoms do not dissolve in the main lattice but in lattice sites that are regarded as interstitial sites although their sublattice may be almost completely filled. It may even happen that there is an excess of nonmetallic atoms that are dissolved in a new interstitial sublattice. The hypostoichiometric case may be represented by the formula $A_m(B,Va)_1$ and the hyperstoichiometric case by $A_mB_1(Va,B)_n$. Diffusion of the nonmetal occurs by means of defects, in the first case by vacancies in the first interstitial sublattice and in the second case by an excess of the nonmetal being dissolved in the new interstitial sublattice. It will be demonstrated that information on the diffusivity can give information on the defect structure, which may otherwise be difficult to study. The diffusion of the metallic component will be neglected.

If there is only one kind of defects then their number is directly related to the deviation from the ideal stoichiometric composition and they may be regarded as stoichiometric defects. If two kinds are present, they can exist even at the stoichiometric composition and their numbers will vary with the temperature. They may be called thermal defects. It will be shown that such considerations are important for the method of analyzing data.

Diffusion in oxides has been studied extensively and the theoretical basis was outlined by Wagner.[1] There have not been as many attempts to evaluate diffusion coefficients from the growth of surface layers of carbides and nitrides although such information should be easier to analyze than informa-

tion on oxides because they are usually assumed not to be ionized. In an early study of cementite, which has the ideal composition Fe_3C, it was simply assumed that the diffusional flux should be proportional to the activity difference.[2] In a later study one instead used the logarithm of activity[3] by reference to a study of Fe_4N.[4] However, in the latter study other alternatives were also discussed. Typical of these experimental studies is that the activity on the inner side of the surface layer is controlled by a two-phase equilibrium and is thus constant for a binary system at any given temperature. The only experimental variable is the activity in the surrounding atmosphere. These activities will be denoted as a_B^0 and a_B^{atm} in the following.

II. FLUX EQUATIONS

Diffusion of B in a binary *A-B* solution usually occurs by a vacancy mechanism and it is common to apply the following type of flux equation for one-dimensional diffusion:

$$J_B = -y_B y_{Va}\frac{M_{BVa}}{V_m}\frac{d(\mu_B-\mu_{Va})}{d\xi} = -y_B y_{Va}\frac{M_{BVa}RT}{V_m}\frac{d\ln a_B}{d\xi},$$

(1)

where M_{BVa} is the mobility, y_i represents the site fractions in the sublattice where diffusion takes place, ξ is the length coordinate in the direction of diffusion, and V_m is the volume containing one mole of sites on that sublattice. For a simple substitutional solution y_i is identical to the ordinary mole fraction. Finally, a_B is the activity of B. It should be noted that the activity has here been introduced by considering the potential of vacancies as zero in the case of thermal vacancies, which is based on the assumption that their number is determined by equilibrium with a surrounding vacuum, sometimes called thermal equilibrium. In the case of stoichiometric vacancies, the B activity is defined from the difference in chemical potentials and the result for Eq. (1) will be the same. However, the final result will be quite different. (It should also be noticed that the flux must be constant

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everywhere in a completely stoichiometric phase because otherwise the composition would change.)

In a phase where the occupancies only vary in a sublattice containing B atoms and vacancies, the B activity is primarily proportional to the site fraction of B and inversely proportional to the site fraction of vacancies. In a hypostoichiometric compound the predominant defects are the vacancies on the interstitial sublattice and the site fraction of B can be approximated by 1. The B activity is thus inversely proportional to the site fraction of vacancies and using an activity coefficient f'_B we write $a_B = f'_B/y'_{Va}$. The prime identifies quantities in this interstitial sublattice. Assuming that f'_B is constant we get $a_B y_{Va} = f'_B = a^0_B y'^0_{Va}$, where the superscript "0" identifies quantities on the inner side of the surface layer of the compound and they are fixed by the presence of the other phase. Insertion in Eq. (1), integration over the surface layer, and use of the fact that the flux is constant in the layer yield

$$J_B = -\frac{y'^0_{Va} a^0_B}{a_B}\frac{M'_{BVa}RT}{V'_m}\frac{d\ln a_B}{d\xi}$$

$$= -\frac{y'^0_{Va} a^0_B}{a_B}\frac{M'_{BVa}RT}{V'_m}\frac{da_B}{a_B d\xi}$$

$$= \frac{a^0_B K'_B}{lV'_m}\left(\frac{1}{a^0_B} - \frac{1}{a^{atm}_B}\right) = \frac{K'_B}{lV'_m}\left(1 - \frac{a^0_B}{a^{atm}_B}\right), \quad (2)$$

where l is the thickness of the surface layer and $K'_B = y'^0_{Va} M'_{BVa}RT$. In the hyperstoichiometric case the predominant defects are B atoms in a new interstitial sublattice. The site fraction of vacancies is there close to 1 and the B activity is proportional to the site fraction of B. Using a new activity coefficient through $a_B = f''_B y''_B$ and assuming that f''_B is also constant, we get $a_B/y''_B = f''_B = a^0_B/y''^0_B$. The double prime identifies quantities in the new interstitial sublattice. Insertion in Eq. (1) and integration over the surface layer yield

$$J_B = -\frac{y''^0_B a_B}{a^0_B}\frac{M''_{BVa}RT}{V''_m}\frac{d\ln a_B}{d\xi}$$

$$= -\frac{y''^0_B a^0_B}{a^0_B}\frac{M''_{BVa}RT}{V''_m}\frac{da_B}{a_B d\xi}$$

$$= \frac{K''_B}{lV''_m a^0_B}(a^{atm}_B - a^0_B) = \frac{K''_B}{lV''_m}\left(\frac{a^{atm}_B}{a^0_B} - 1\right), \quad (3)$$

where $K''_B = y''^0_B M''_{BVa}RT$. It should be noticed that V''_m will differ from V'_m if the two interstitial sublattices have different numbers of sites. If the new interstitial sublattice has n times as many sites as the first one, then $V''_m = V'_m/n$.

As already emphasized, if there are defects in a quite stoichiometric compound, there must be two balancing kinds and in the present case we get $y''_B = y'_{Va}/n$. Their numbers are determined by thermodynamic equilibrium and their site fractions will be identified with the superscript "th" for thermal. At sufficiently small deviations from stoichiometry the defects with a stoichiometric origin will be relatively few and the defects with a thermodynamic origin will predominate. The total number of vacancies on the first interstitial sublattice and of B atoms on the second interstitial sublattice

will then be rather independent of composition and the B activity. We here have to consider diffusion in both interstitial sublattices and the flux equation will be the sum of the contributions from the two. By approximating y_B and y_{Va} as 1 we get by applying Eq. (1) twice,

$$J_B = -y'^{th}_{Va}\frac{M'_{BVa}}{V'_m}\frac{d(\mu_B - \mu_{Va})}{d\xi} - y''^{th}_B\frac{M''_{BVa}}{V''_m}\frac{d(\mu_B - \mu_{Va})}{d\xi}$$

$$= \frac{K^{ln}_B}{lV'_m}\ln\frac{a^{atm}_B}{a^0_B}, \quad (4a)$$

$$K^{ln}_B = y'^{th}_{Va}M'_{BVa}RT + y''^{th}_B M''_{BVa}RTV'_m/V''_m$$

$$= y'^{th}_{Va}(M'_{BVa} + M''_{BVa})RT, \quad (4b)$$

where K^{ln}_B is often regarded as the self-diffusion coefficient[3,6,8] but it should be emphasized that this name is not justified for K'_B in Eq. (2) or K''_B in Eq. (3) which can be illustrated by the fact that they contain y'^0_{Va} or y''^0_B which are not only functions of the properties of the compound itself but also of the other phase in the two-phase equilibrium. That feature could be removed by instead introducing a fixed state of reference for the activity of B but that would be an arbitrary choice and affect the value of K^{ln}_B. In contrast, y'^{th}_{Va} in Eq. (4b) only depends on the properties of the compound itself.

For larger deviations from stoichiometry there will be a transition on each side of the ideal composition. Starting from hypostoichiometric compositions, one should first consider the gradient in $-1/a_B$ obtained from Eq. (2), then a transition to $\ln a_B$ from Eq. (4) and finally a transition to a_B from Eq. (3). At what compositions the transitions occur depend on the activation energy of the thermal defects. It would thus seem possible to obtain some information on that activation energy by studying where the transitions occur.

When studying the formation of an Fe_4N layer by treating iron specimens in a nitriding atmosphere, Schwerdtfeger et al.[4] used the gradient of $\ln a_B$ as the driving force with reference to Wagner.[1] However, in a final section, and evidently inspired by Darken, they discussed $-1/a_B$ and a_B, which appear in Eqs. (2) and (3), and they proposed that there should be a transition region where one should consider diffusion in both interstitial sublattices. In principle, they simply added the results of Eqs. (2) and (3) obtaining

$$J_B \cdot V'_m l = -k_1(a^{atm}_B - a^0_B) - k_2\left(\frac{1}{a^0_B} - \frac{1}{a^{atm}_B}\right). \quad (5)$$

They did not realize that the result would be quite different in the middle of the transition, i.e., close to the stoichiometric composition, where Eq. (4) applies. Of course, it is still possible that their equation could be of practical use. To test that possibility, Eq. (5) was applied to various values of k_1 and k_2 and compared with Eq. (4). It should be realized that we only wanted to compare the shapes of curves. The absolute values of k_1 and k_2 are thus of no importance and it was sufficient to vary their ratio. This was accomplished with a parameter F obtained by expressing the ratio as $F/(1-F)$, see Fig. 1. It is evident that there is no F value, which would yield a shape similar to the curve for thermal defects accord-
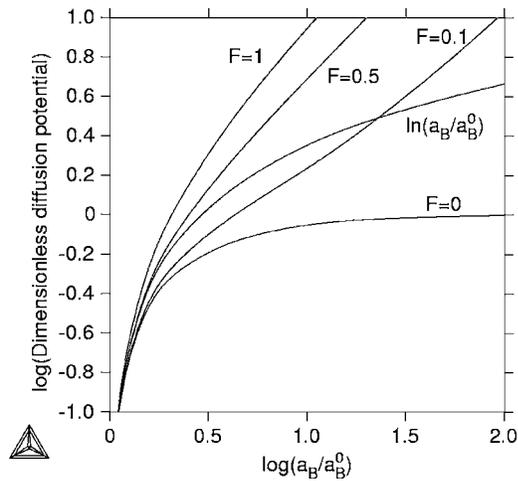
FIG. 1. Comparison of the dimensionless diffusion potential $F(a_B^{atm}-a_B^0)$ $+(1-F)(1-a_B^0/a_B^{atm})$ according to Eq. (5) with various F values and a dimensionless diffusion potential of $\ln(a_B^{atm}/a_B^0)$ according to Eq. (4).

FIG. 2. Different dimensionless diffusion potentials in Fe_4N calculated from the experimental N activity in the atmosphere at 781 K by Schwerdtfeger *et al.* (see Ref. 4) and plotted vs the rate constant reported. The curves where drawn manually to reasonable representation of the data for each kind of potential.

ing to Eq. (4), marked $\ln(a_B/a_B^0)$ in Fig. 1. Furthermore, Schwerdtfeger *et al.* proposed that the term with the largest k value would represent the dominating diffusion mechanism. However, they neglected to consider the effect of the choice of reference for the activity. The ratio of k_1 and k_2 will change dramatically if the reference is changed and it is thus evident that Eq. (5) has no physical meaning. In comparison, it should be noted that the results of Eqs. (2)–(4) are independent of the choice of reference.

It may be more realistic to use separate equations for the two transitions mentioned above. They would take the following forms where $0 \leq F \leq 1$:

$$J_B \cdot V_m' l = -K[(1-F)\ln(a^{atm}/a^0) + F(1-a^0/a^{atm})], \quad (6)$$

$$J_B \cdot V_m' l = -K[(1-F)\ln(a^{atm}/a^0) + F(a^{atm}/a^0 - 1)]. \quad (7)$$

At $F=0$ both equations will reduce to Eq. (4) for thermal defects and should hold sufficiently close to the stoichiometric composition. In Eq. (6) $F>0$ indicates that there is an effect of hypostoichiometric vacancies on the first interstitial sublattice and in Eq. (7) it indicates that there is an effect of hyperstoichiometric atoms on the new interstitial sublattice.

III. APPLICATION TO EXPERIMENTAL INFORMATION

When applying Eqs. (2)–(4) to the experimental data, we may regard $1-a_B^0/a_B$, $\ln(a_B/a_B^0)$, and a_B/a_B^0-1 as dimensionless diffusion potentials. The way these flux equations are formulated, the rate constant as obtained from the experiments should be proportional to the particular diffusion potential used in that flux equation, if the flux equation is based on the mechanism of diffusion that actually operates. In principle, the dominating diffusion mechanism could be identified by testing what potential varies most linearly through the growing layer of the compound because the flux must be almost constant if the composition of the layer is almost constant. However, as mentioned, it is not possible or at least extremely difficult to obtain information on the activity by
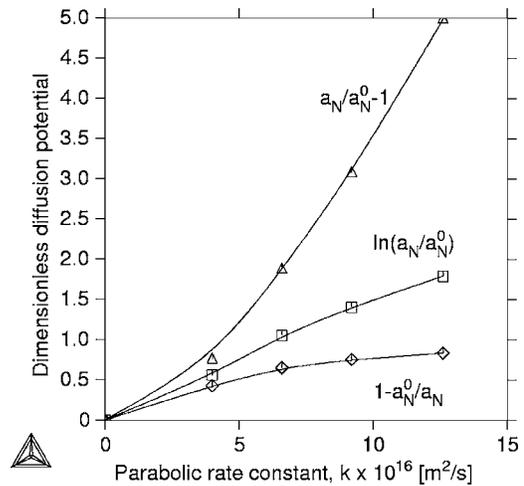
studying the situation inside the growing layer if the deviation from stoichiometry is very small. On the other hand, there is another experimental possibility.

Under the quasi-steady-state approximation one may treat the flux J_B as constant through the whole of the growing layer at any time. This approximation is particularly justified in the present case where the phase is almost stoichiometric and can hardly vary in composition. Furthermore, if the reaction is diffusion controlled, the growth is parabolic, $l^2=kt$, and J_B is proportional to k/l. Two experiments with different a_B^{atm}, say $(a_B^{atm})_1 > (a_B^{atm})_2$, would yield different rate constants, k_1 and k_2, respectively. One can then find two different times, t^* and t^{**}, where the thicknesses of the surface layers are related by $l_1^*/l_2^{**}=k_1/k_2$. As the flux J_B is proportional to k/l, it must be the same in both experiments. The activity as function of distance in the layer in the second experiment should then be identical to part of the corresponding activity profile in the first experiment because they both end at the same activity a_B^0 corresponding to the two-phase equilibrium at the temperature and they both have the same slope because the flux is the same. The results of both experiments could thus be represented by a single curve. The curve for the experiment with the largest a_B^{atm} would extend from that value and to a_B^0 at the phase interface. The same curve would apply to the other experiment but only from the lower value of a_B^{atm}. Furthermore, since $k_1/l_l^*=k_2/l_2^{**}$, when this comparison is made, one could represent l by k in this plot. Combining experiments with different values of a_B^{atm} one could thus study how the activity varies through the surface layer during the experiments. Of course, the same would apply to plots of any function of a_B. It is thus possible to test various functions of a_B. The function yielding a curve most similar to a straight line may be the operating diffusion potential. This method will now be used.

Three different functions of the N activity are plotted versus the parabolic rate constant in Fig. 2. The data are from Schwerdtfeger *et al.*[4] who measured the rate constant for the formation of a surface layer of Fe_4N on iron specimens in an
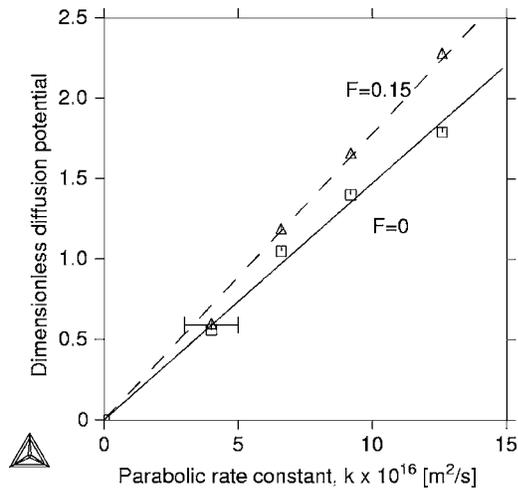
FIG. 3. Data from Fig. 2 plotted using Eq. (7) with two different F values.

FIG. 4. Different dimensionless diffusion potentials in Fe_3C calculated from the experimental C activity in the atmosphere at 723 K by Ozturk *et al.* (see Ref. 3 and 7) and plotted vs the rate constant reported. The curves where drawn manually to reasonable representation of the data for each kind of potential.

NH_3/H_2 atmosphere at 781 K. The N activity was defined as $P_{NH_3}/(P_{H_2})^{3/2}$ atm$^{-1/2}$ and the origin is a fixed point representing the equilibrium on the inner side of the layer where $a_N = a_N^0$. All the three potentials are thus zero at that point and an experiment with $a_N = a_N^0$ would yield a rate constant $k=0$ because no Fe_4N layer would form. The values of $\ln(a_N/a_N^0)$ show an almost linear dependence and a straight line would agree with all the experimental values within the uncertainty listed by the authors. This result would support the conclusion that the diffusion of N in Fe_4N occurs mainly by thermal vacancies. On the other hand, a closer examination reveals that the values may indicate a slightly negative curvature. An attempt was made to analyze this and Eq. (7) was applied because Fig. 2 demonstrates that the potential $a_N/a_N^0 - 1$ yields a positive curvature, which could be used for compensating a slightly negative curvature of $\ln(a_N/a_N^0)$. Various F values were tested and Fig. 3 shows that $F=0.15$ gives an almost perfect fit. Admittedly, the theoretical line (the straight dashed line) does not fall on the first experimental point to the left but it does fall within its range of uncertainty given by the authors and indicated in the diagram. It is thus tempting to accept this line and to propose that there are some hyperstoichiometric N atoms in a new interstitial sublattice in addition to the thermal vacancies. This is contrary to measurements of the composition by Wriedt[5] showing a N deficit in Fe_4N specimens and that was later supported by Simkovich.[6] We can offer no explanation for this discrepancy.

Simkovich[6] also analyzed kinetic data on the formation of Fe_4N in spherical carbonyl iron powder and could fit the data from 773 K with Eq. (5) when using $k_1 = 0.65$ and $k_2 = 2.16$, i.e., $k_1/k_2 = 0.3$. He concluded that the diffusion of N occurs in both interstitial sublattices. He made a similar analysis of data from 823 K but needed two straight lines and concluded that the diffusion primarily occurs on the first interstitial sublattice for low N contents but on both for higher contents. On the other hand, it could be argued that Eq. (5) was not capable of representing data for a transition from one case to the other with one straight line which was its purpose. Furthermore, as already explained, the ratio of k_1 to k_2 in Eq. (5) is very sensitive to the choice of reference for

the activity. In his paper he defined the N activity as $P_N^{1/2}$ but, when using Eq. (5), he introduced a "modified activity" which was lower by a factor of about 200. If the first kind of activity had been used in Eq. (5) the result for 773 K would have been $k_1/k_2 = 24\,000$ instead of 0.3. The conclusion would have been quite different.

Figures 4 and 5 show the data for the formation of Fe_3C as surface layers in fine iron powder from Ozturk *et al.*[3,7] and in pieces of iron from Schneider *et al.*[8] In Fig. 4 the results from Ozturk *et al.* are not easy to interpret due to experimental scatter. The data plotted as $a_C/a_C^0 - 1$ are represented by a straight line because the scatter makes it impossible to see whether to use a positive or negative curvature. This straight line would imply a predominance of hyperstoichiometric C defects. The data plotted as $\ln(a_C/a_C^0)$ indicate a slightly negative curvature and that could be taken as an indication that thermal defects predominate and hyperstoichiometric C
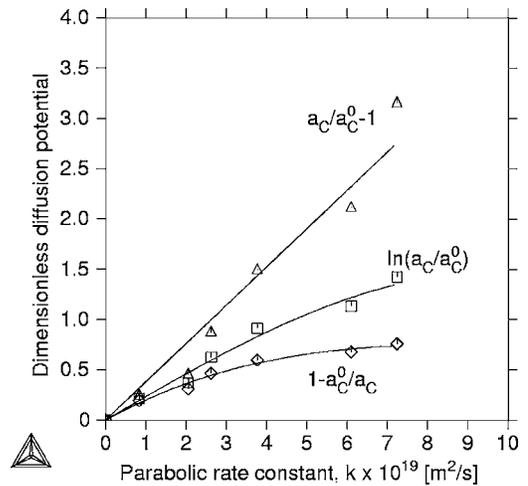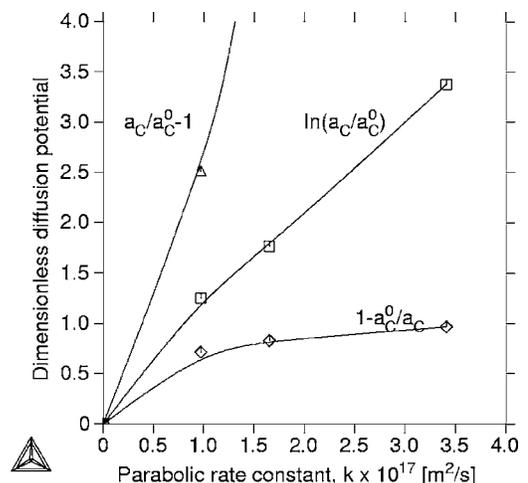

FIG. 5. Different dimensionless diffusion potentials in Fe_3C calculated from the experimental C activity in the atmosphere at 773 K by Ozturk *et al.* (see Ref. 8) and plotted vs the rate constant reported. The curves where drawn manually to reasonable representation of the data for each kind of potential.

TABLE I. Carbon self-diffusivity in Fe_3C according to different sources.

Source	Temp. (K)	D_C^* (m^2 s^{-1})
Ozturk et al.[a]	723	2.85×10^{-19}
Schneider et al.[b]	773	5.57×10^{-18}
Borgenstam et al.[c]	1138	1.2×10^{-14}

[a]Reference 3.
[b]Reference 8.
[c]Reference 9.

defects only play a minor role. However, it should be noted that for low values of a_C/a_C^0 all three equations predict a linear relationship and it is thus essential to use a sufficiently wide range of values of a_C^{atm}/a_C^0 in order to identify the predominant diffusion mechanism. The information from Ozturk et al. has a maximum of 20 for the C activity, which seems to give a range of activity that was too narrow. Schneider et al.[8] recently extended the range of C activity to 100 and Fig. 5 indicates that only $\ln(a_C/a_C^0)$ does not yield a strong curvature. The last point for a_C/a_C^0-1 fell well above the diagram but actually showed a very strong positive curvature. It may be concluded that diffusion by thermal defects predominate in Fe_3C.

IV. EVALUATION OF SELF-DIFFUSION COEFFICIENT

The above inspection of the experimental data indicates that the experimental information is rarely accurate enough and rarely covers a sufficiently wide range of activities to allow the diffusion mechanism to be identified with any certainty. It would thus seem that for practical purposes one could often apply any one of the three alternative flux equations. It seems reasonable to select one of them for general use and Eq. (4) will now be recommended and, as discussed in connection with Eq. (4), it has the advantaged that its rate constant K_B^{ln} can be regarded as the self-diffusion coefficient, D_B^*. This was done in the cited works on Fe_4N and Fe_3C, where the self-diffusion coefficient was calculated from the parabolic rate constant in $l^2=kt$ by using the material balance at the inner side of the growing layer of the compound. Neglecting the diffusion into the metallic interior of the specimens, which may be justified in the case of bcc Fe with a very low solubility of N and C, we get

$$\frac{dl}{dt} \cdot \frac{1}{V_m'} = J_B. \tag{8}$$

It should be emphasized that with its definition V_m' is the volume containing one mole of B for a stoichiometric compound. Insertion of the parabolic growth law and Eq. (4a) into Eq. (8) yield

$$\frac{k}{2lV_m'} = \frac{K_B^{ln} \ln(a_B^{atm}/a_B^0)}{lV_m'}, \tag{9}$$

$$K_B^{ln} = 0.5k/\ln(a_B^{atm}/a_B^0). \tag{10}$$

The results on Fe_3C reported in the literature are summarized in Table I. Very similar values can be obtained by evaluating $k/\ln(a_B^{atm}/a_B^0)$ from the slope of a straight line through the data, including the origin, in Fig. 4 or 5. However, as already
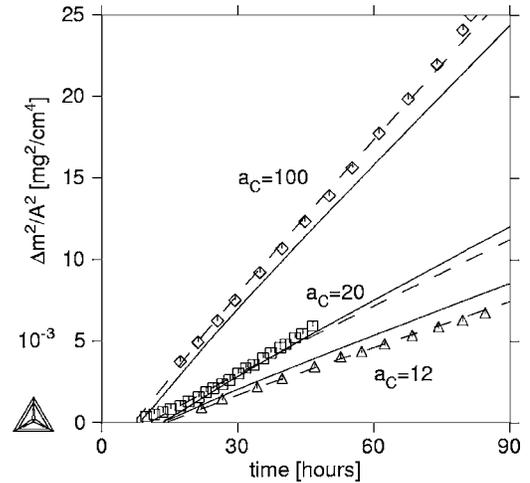

FIG. 6. The growth of Fe_3C as (mass-gain/surface area) (see Ref. 2) according to Schneider et al. (see Ref. 8) plotted as function of time for three different C activities in the atmosphere at 773 K. The solid lines are calculated from Eq. (4) for diffusion by thermal defects. The dashed lines were obtained from Eq. (7) and indicate some contribution from hyperstoichiometric C atoms.

mentioned, Eq. (10) is based on the neglect of the diffusion into the metallic interior of the specimens. That may be a rather good approximation in the present case because the interior consists of bcc Fe and the solubilities of N and C in bcc Fe are low. Nevertheless, a numerical procedure was now applied in order to take that diffusion into account using the DICTRA software package[9] in combination with the simulation software package MATLAB (Ref. 10) by means of a developed programing interface.[11] Then it was also possible to simultaneously optimize D_C^* and the individual incubation times for each set of experiments in a single optimization procedure. The experimental information indicates that there was an incubation time before the growth of the present Fe_3C layer started. That was accepted in the previous assessments as well as in the new one. The incubation time may be related to the finite rate of surface reactions as well as the time for spreading of Fe_3C over the metal surface to form a homogeneous layer. In any case, through the application of Eq. (4) it was assumed that the growth is parabolic once it gets started.

The assessment yielded $D_C^*=4.43 \times 10^{-18}$ m^2 s^{-1} at 773 K which was just a little lower than the value given by Schneider et al. The fit to the experimental data is shown by the full lines in Fig. 6. There is a discrepancy of less than 15%, which is not serious for a diffusion coefficient. The reason will soon be discussed. In order to test that the diffusion into the bcc Fe phase in the interior is not important, the optimization was repeated with the diffusivity of C in bcc Fe set to zero. Practically the same result was obtained.

The Arrhenius plot in Fig. 7 shows all the values of D_C^*. The open square represents the result of the optimization. A straight line through the points from Ozturk et al. and Schneider et al. would give a surprisingly high activation energy and frequency factor. It seems that both points should not be accepted. Rather than applying a least-squares fitting of a straight line to all the values, it was decided to trust the straight line between the value from experimental informa-
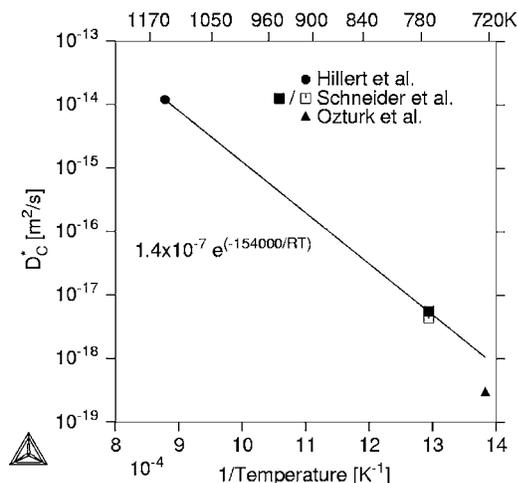
FIG. 7. Self-diffusivity of C in Fe_3C according to different sources. The filled symbols represent values from the literature. The open square is from new assessment.

tion from Schneider *et al.* at 773 K and Hillert and Sharp's value from 1138 K. It gave the result $D_C^* = 1.4 \times 10^{-7} \times \exp(-154\,000/RT)$ m² s⁻¹. The frequency factor seems reasonable because it should be in the order $\nu \delta^2$, ν being the phonon frequency (about 10^{13} s⁻¹) and δ being the jump distance (about 0.3–1 nm), which would yield a value of about 10^{-7} m² s⁻¹. An argument for trusting the information from Schneider *et al.* rather than from Ozturk *et al.* is that the latter workers used iron powder with less controlled shape and size and so fine that there would be complete carburization within rather short times.

In connection with Fig. 5 it was mentioned that the data from Schneider *et al.* give an indication that hyperstoichiometric C atoms contribute to the diffusivity. This is again indicated by Fig. 7 where the full line for $a_C^{atm} = 100$ falls below the data points and the full line for $a_C^{atm} = 12$ falls above those data points. In order to evaluate the possible role of hyperstoichiometric C atoms Eq. (7) was applied and F was used as a adjustable parameter together with all the previous ones. The result was $F = 0.03$ and the dashed lines in Fig. 6 demonstrate the excellent fit. This may be taken as a strong indication that hyperstoichiometric C atoms actually contribute to the diffusivity but their effect is relatively small.

V. SUMMARY

The purpose of the present study was to demonstrate the importance of various kinds of defects for the diffusivity in closely stoichiometric phases. Different defect structures yield different flux equations and the importance to distinguish between stoichiometric and thermal defects has been demonstrated. Three different cases have been considered

and they yield different functions of the activity as the driving force for diffusion. It is shown how the nature of the operating defect can be tested by examining what function of the activity shows the most linear variation through the growing surface layer of a stoichiometric phase.

Experimental measurements of an activity from inside a phase are rarely reported and for a stoichiometric phase it cannot be calculated from the composition profile measured after the experiment. It is now shown how information on the activity profile during diffusion through a surface layer can be obtained by combining information on the parabolic rate constant evaluated in a series of experiments using different activities in the surrounding atmosphere.

Such information is available for the formation of surface layers of Fe_4N and Fe_3C. That information has now been successfully analyzed and a previous analysis was criticized. It is demonstrated that a successful test requires rather accurate information from a sufficiently wide range of activities.

From a practical point of view it seems that the choice of mechanism may rarely be very important for the representation of the diffusivity. An equation based on thermal defects is recommended for more general use in less ambitious studies. It predicts that the flux is proportional to the gradient of $\ln a_B$ and the rate constant, evaluated with this model, can be identified with the self-diffusion coefficient. It was evaluated for Fe_3C using that model and the value was compared with previous evaluations. The temperature dependence was evaluated to $D_C^* = 1.4 \times 10^{-7} \exp(-154\,000/RT)$ m²/s.

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