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Determination of depths of multiple traps for interstitials and their influence on diffusion kinetics

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Abstract

Trapping of interstitial atoms by foreign substitutional atoms is a phenomenon that significantly influences the chemistry of the system as well as the diffusivity of the interstitial components. In their previous paper (Svoboda \textit{et al} 2013 \textit{Modelling Simul. Mater. Sci. Eng.} 21 065012), the present authors determined the trapping energy and the chemical diffusion coefficient of an interstitial component for a dilute system by assuming only one type of trap. This model is now generalized for non-dilute systems, and it accounts for the fact that each interstitial trap position can be influenced by several foreign atoms.

The model is applied to a non-dilute Fe–Cr–rather dilute C system neglecting interstitial–interstitial interactions. Fitting of the chemical potential of the interstitial component given by the model to that given by thermodynamic databases provides parameters allowing calculation of the depth of the trap depending on the number of foreign atoms surrounding the trap position. The results of fitting indicate that the model is physically sound. Based on an established concept, subsequently, the chemical diffusion coefficient of the interstitial is calculated for different chemical compositions.

Keywords: foreign atoms, trapping enthalpy, carbon diffusion, chemical potential, thermodynamic concept
1. Introduction

The influence of trapping on diffusion of interstitials in metals is now well understood based also on thermodynamic arguments; see, e.g. the recent papers by the present authors [1, 2] and references therein, offering an overview of the last five decades. In a first approximation, each interstitial position can be considered as an ordinary lattice position, where the interstitial atom is mobile and can diffuse, or as a trap position, where the interstitial atom becomes immobile. As already established, the traps are characterized by volumes $V_{Tk}$, $[V_{Tk}] = m^3 \text{mol}^{-1}$, corresponding to 1 mol of interstitial positions, which can trap interstitials, and by $\Delta E_k$, $[\Delta E_k] = J \text{mol}^{-1}$, corresponding to the decrease of the total energy of the system if 1 mol of interstitials is trapped in traps of type $k$ ($k = 1, \ldots, n$). The so-called equilibrium constant $K_k$ is directly related to the trapping energy $\Delta E_k$ by the relation $K_k = \exp\left(-\frac{\Delta E_k}{R_g T}\right)$, with $R_g$ being the gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ the temperature, $[T] = K$. The name ‘equilibrium constant’ points to the fact that in thermodynamic equilibrium, the site fraction, $y_{Tk}$, $[y_{Tk}] = 1$, of interstitials in the traps and the site fraction, $y_L$, $[y_L] = 1$, of interstitials in the lattice are related by an equation dependent only on $K_k$ (Oriani equation, see equation (11) below). The quantity $V_{Tk}$ depends on the density of traps represented, e.g. by dislocation cores or foreign substitutional atoms, and bears de facto information about the microstructure and chemical composition of the material (see, e.g. the corresponding comments in [1] and [2]). The quantity $\Delta E_k$ depends exclusively on the type of trap, and its determination has become a topic of research in atomistic (ab initio) modelling. As a relevant selection of the numerous papers having appeared in the last decade, the reader is referred to [3] with respect to the interaction of interstitials (denominated there as impurities) with the lattice atoms in metals (Al and Mg) and [2] for carbon trapping by Cr atoms in an Fe lattice. As a relevant paper concerning the role of point defects, especially vacancies and vacancy clusters, the paper by Klaver et al [4] is referred to. This case is of specific interest, since a vacancy may trap not only one but several H atoms. Here, we refer to the extensive discussion by Kirchheim [5, 6] based on the Gibbs adsorption isotherm and by Tateyama and Ohno [7] based on density functional theory studies. They have come to the conclusion that the formation energy of vacancies itself decreases with the number of trapped H atoms. For an ‘excess’ of 5–7 H atoms, the formation energy of vacancies even becomes negative; see also the very recent paper by Gao et al [8]. Of high relevance, we also consider the recent DFT study by Hepburn et al [9], who show that a vacancy may trap up to two C or N atoms with a trapping energy $\Delta E_k = 40 \text{kJ mol}^{-1}$ or 60 kJ mol$^{-1}$, respectively. It is interesting to note that such a binding of interstitials to a vacancy does not result in trapping of the vacancy itself. Vacancy C and N complexes can diffuse at velocities comparable to those of single vacancies.

Foreign substitutional atoms have been considered in several studies, e.g. [1, 2], as possible traps, with the assumption in most of these studies that the foreign atoms are distributed in a sufficiently dilute way. This means their site fraction is rather low, and the interstitials may feel only one or no foreign atom. However, there is clear experimental evidence that, although the foreign atoms are rather dilute, more than one foreign atom can also be situated in the intermediate neighbourhood of an interstitial atom. We consider this, therefore, as motivation for the following.

- To determine the molar volume $V_{Tk}$ of each individual type of trap, represented by interstitial positions being surrounded by $k$ foreign atoms.
- To extract the trapping energy $\Delta E_k$ for each individual type of trap from existing thermodynamic databases. Here, we extend the concept developed very recently by the present authors, see [2], which allows us to find the trapping energy $\Delta E$ for one type of trap from the chemical potential of interstitial atoms available, e.g. from CALPHAD-type thermodynamic databases.
To evaluate the chemical-composition-dependent diffusion coefficient of the interstitial element.

This modelling concept accounts for interstitial–substitutional interactions and does not include interstitial–interstitial interactions, which may have some influence on the chemistry as well as on the diffusion kinetics. A review on this problem for C atoms has been published by Bhadeshia [10]. To keep the model as simple as possible, this interaction effect is not met in the current version of the model and is left to future work.

The model of diffusion [1, 2] assumes point traps and neglects the fact that an interstitial atom may jump out of the trap to another lattice position and then jump back into the trap. Moreover, the model neglects the possibility that an interstitial atom can diffuse along interconnected traps. The authors are aware of these facts. The paper is, however, concentrated only on the treatment of the primary trapping effect to keep the current version of the model as clear as possible.

### 2. Problem formulation

#### 2.1. Aspects of lattices

Let us consider body-centred- (bcc) and face-centred- (fcc) cubic lattices, where interstitials may occupy octahedral (O), tetrahedral (T) and crowdion (C) positions; see, e.g. [9]. We skip in our further elaboration the last one (C), since for ‘typical’ interstitials such as H, C, N or O atoms, either T or O positions are mostly observed.

The molar volume of the substitutional elements is denoted as $\Omega$. According to Krom and Bakker [11] and the open literature on crystallography, one can introduce the molar volume $V$, $[V] = m^3 \text{ mol}^{-1}$, of interstitial positions, which is given in table 1.

We concentrate now on the situation where a foreign atom (e.g. a Cr atom in an Fe lattice) converts some interstitial positions in its immediate neighbourhood into traps. The number $n$ of lattice positions, surrounding an O or T position, follows for both bcc and fcc as $n = 6$ for the O position and $n = 4$ for the T position. However, in the case of an O position in bcc, two lattice positions are at the distance of $a/2$ (with $a$ being the lattice parameter), being nearest neighbours, and four lattice positions are at the distance of $\sqrt{2}a/2$, being next-nearest neighbours. One can thus assume that in bcc the foreign atom converts $n = 2$ or $n = 6$ O positions into traps.

Since each surrounding lattice position of an interstitial position can be occupied by a foreign atom, the number of possible types of trap amounts to $n$. The probability that a lattice position is occupied by a foreign element is given by its site fraction $y_F$, and the probability that a lattice position is occupied by a lattice-forming element is given by its site fraction $1 - y_F$. The probability that all $n$ lattice positions are occupied by a lattice-forming element is $p_0 = (1 - y_F)^n$, and the probability that all $n$ lattice positions are occupied by a foreign element is $p_n = y_F^n$. Generally, the probability $p_k$ that an interstitial position is surrounded by

<table>
<thead>
<tr>
<th>Trap position/lattice</th>
<th>$V$ for bcc</th>
<th>$V$ for fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$ for O</td>
<td>$\Omega/3$</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$V$ for T</td>
<td>$\Omega/6$</td>
<td>$\Omega/2$</td>
</tr>
</tbody>
</table>
$k$ foreign atoms and $(n - k)$ lattice-forming atoms is given by

$$p_k = (1 - y_F)^{(n-k)} \cdot y_F^k \cdot \frac{n!}{k!(n-k)!}, \quad k = 0, \ldots, n. \quad (1)$$

Note that $\sum_{k=0}^{n} p_k = 1$ by using the binomial development of $((1 - y_F) + y_F)^n$.

Let us now denote the volume corresponding to 1 mol of interstitial lattice positions as $V_L$, $[V_L] = \text{m}^3 \text{ mol}^{-1}$. Then, the volume $V$, see table 1, corresponding to 1 mol of interstitial positions follows as

$$\frac{1}{V} = \frac{1}{V_L} + \sum_{k=1}^{n} \frac{1}{V_{Tk}}. \quad (2)$$

We can now express $V_L$ and $V_{Tk}$ by the probabilities defined above. The molar volume $V_L$ of the interstitial lattice atoms, diffusing freely in the lattice, is given by

$$V_L = \frac{V}{p_0}. \quad (3)$$

The molar volume $V_{Tk}$, corresponding to just $k$ foreign atoms surrounding an interstitial position (we ignore the individual arrangement of the foreign atoms), follows as

$$V_{Tk} = \frac{V}{p_k}, \quad k = 1, \ldots, n. \quad (4)$$

### 2.2. Site fractions, molar fractions and molar concentrations

The molar concentration of the interstitial atoms being trapped in a trap of sort $k$ is denoted as $c_{Tk} = y_{Tk}/V_{Tk}$ and that of the freely diffusion interstitial atoms as $c_L = y_L/V_L$. The total molar concentration $c$ follows as

$$c = c_L + \sum_{k=1}^{n} c_{Tk}, \quad (5)$$

which can be related to the mean site fraction $y$ of the interstitial atoms as

$$y = cV, \quad (6)$$

with $V$ from table 1.

Since very often molar fractions instead of site fractions are used, we repeat now a statement from [2] relating the site fractions and the molar fractions as follows.

- We denote the molar fractions (fractions related to 1 mol of atoms) as $X_I$, $X_F$, $X_M$ with $X_I$ being the molar fraction of the interstitial atoms, $X_F$ that of the foreign atoms and $X_M$ that of the lattice-forming elements. The sum of the molar fractions yields...
\[ X_I + X_F + X_M = 1. \]  

- As site fractions (fractions related to 1 mol of substitutional lattice positions) we introduce the quantities \( y_I, y_F \) and \( y_M \) with the same notation (subscripts) as for the molar fractions. The site fractions are constrained as

\[ y_F + y_M = 1. \]

- Consequently, the site fractions and the molar fractions are related as

\[
\begin{align*}
    y_I &= \frac{X_I}{1 - X_I}, \quad y_F = \frac{X_F}{1 - X_I}, \quad y_M = \frac{X_M}{1 - X_I}.
\end{align*}
\]

- The site fraction \( y_I \) of the interstitial atoms is related to their mean site fraction \( y \) by

\[
\begin{align*}
    c &= \frac{y}{V} \text{ or } c = \frac{y_I}{\Omega_1} \text{ and, thus,}
    y_I &= \frac{y}{\Omega_1} / V;
\end{align*}
\]

see equation (6) and table 1.

2.3. Energetics of trapping

Thermodynamic equilibrium of the freely diffusing and trapped interstitial atoms leads to an equilibrium relation between \( y_{Tk} \) and \( y_L \) as

\[ y_{Tk} = \frac{y_L}{K_k + y_L (1 - K_k)}, \quad k = 1, \ldots, n. \]

Let us repeat here \( K_k \) as \( \exp\left(\frac{-\Delta E_k / R_g T}{\Delta E_k / R_g T}\right) \) with \( \Delta E_k \) the trapping energy of the type \( k \) of trap. A detailed derivation of equation (11) can be found in [1]. It should be mentioned that equation (11) can be denominated as a generalized Oriani equation, since Oriani was the first to report such a type of relation for one type of trap in 1970 [11].

Combining equations (5), (6) and (11) yields

\[ c = c_L + \sum_{k=1}^{n} \frac{V_L}{V_{Tk}} K_k + V_L (1 - K_k) c_L. \]

2.4. Thermodynamics and diffusion equation

Since the thermodynamics and the diffusion equation for an interstitial element, also subjected to trapping, has been treated in detail in previous papers, see, e.g. [12] and later [1, 2], we report only the leading equations with assumptions and definitions as below.

2.4.1. Chemical potentials. We consider the existence of a non-dilute distribution for a foreign atom, forming a rather dense distribution of traps, but a rather dilute distribution of interstitial atoms, allowing the assumption of their ideal solution. The minimization of the total Gibbs energy of the system, as a necessary condition for the thermodynamic equilibrium, yields, for an ideal solution of the interstitial element the chemical potentials \( \mu_L, \mu_{Tk}, [\mu_L, \mu_{Tk}] = J \text{ mol}^{-1} \) (see also [2] and [13]),

\[
\begin{align*}
    \mu_L &= \mu_0 + R_g T \ln \frac{y_L}{1 - y_L}, \quad (13) \\
    \mu_{Tk} &= \mu_0 + R_g T \ln \frac{y_{Tk}}{1 - y_{Tk}} - \Delta E_k. \quad (14)
\end{align*}
\]

The quantity \( \mu_0 \) represents the contribution to the chemical potential independent of \( y_L \) and \( y_{Tk} \) and may significantly vary for different metals. The values of chemical potentials given by equations (13) and (14) are identical in thermodynamic equilibrium, and the Oriani equation, equation (11), is a direct consequence of this identity.
2.4.2. Diffusive fluxes. First of all, it should be mentioned that we do not assume any remarkable flux in the traps, e.g. the quasi-rotational motion of an interstitial atom through the traps surrounding a foreign atom. Then, the diffusive flux $j$ of the interstitial component in a system with traps is given by a modified Fick first law as

$$j = -D_L (c_L) \cdot \text{grad} (c_L). \quad (15)$$

The quantity $D_L$ is the diffusion coefficient of the interstitial component moving freely along the interstitial trap-free lattice positions. The diffusion coefficient $D_L$ can be dependent on $c_L$ (see e.g. Ågren [14] for austenite), for two reasons: (i) the chemistry providing a thermodynamic factor different from unity and (ii) the increasing concentration of interstitial atoms causing expansion of the lattice, which leads to a decreasing barrier for diffusion (decrease of activation energy). We follow the so-called ‘Kirchheim c-concept’ (see [15] and the corresponding relations in [12]), which is given by

$$j = -D_L (c_L) \cdot \frac{dc_L}{dc} \cdot \text{grad}(c) = -\tilde{D} \text{grad}(c), \quad (16)$$

with $\tilde{D} (c_L) = D_L (c_L) \cdot \frac{dc_L}{dc}$ for fixed space coordinates $x$ and time $t$. The quantity $\tilde{D}$ is denoted as the (generalized) chemical diffusion coefficient; see also [15]. The derivative $\frac{dc_L}{dc}$ can be found by differentiation of equation (12) with respect to $c_L$ as

$$\frac{dc_L}{dc} = \left[1 + \sum_{k=1}^{n} \frac{V_L}{V_{Tk}} \left[\frac{K_k}{K_k + V_L (1 - K_k) c_L} \right]^2 \right]^{-1}. \quad (17)$$

Using equation (17) one obtains a dependence of $\tilde{D}$ on $c_L$; however, $\tilde{D}$ as function of $c$ is needed. The functional relation between $c$ and $c_L$ (see equation (12)) can be inverted and applied to the relation $\tilde{D} (c_L)$ below equation (16). As already outlined in section 3.3 of [1], this inversion can easily be done by a numerical solution technique within a pre-processing procedure. Thus, one can expect in the next step that the dependence $\tilde{D} (c)$ is known.

2.4.3. Mass balance and diffusion equation. The mass balance for an interstitial component follows with equations (5) and (16) as

$$\frac{dc}{dt} = -\text{div} (j) = \text{div} \left( \tilde{D}(c) \text{grad}(c) \right). \quad (18)$$

3. Evaluation of the trap parameters

3.1. Theoretical concept

Let the system be described by $y_L$ and $y_F$, as well as by the values of $\Delta E_k$, $k = 1, \ldots, n$. Moreover, we assume the following simple relation for $\Delta E_k$:

$$\Delta E_k = \Delta E_1 k^\alpha. \quad (19)$$

The task is now to find, by fitting, the two parameters, $\Delta E_1 > 0$ and $\alpha$. Note that the sign of $\alpha$ allows for increasing or decreasing depths of traps with increasing $k$.

We can now calculate the mean site fraction $y$ by using equations (1)–(6) and by defining the equilibrium constant $K_0 = 1$ as

$$y = cV = \left(\sum_{k=0}^{n} \frac{p_k}{K_k + y_L (1 - K_k)} \right) y_L. \quad (20)$$
Figure 1. Sum of squares for different values of $\alpha$ (a), $\Delta E_1$ (b) and $\mu_0$ (c) for ferrite at 500° C and $n = 2$; the minimum is marked with a black circle.

Note that $p_k$ is a non-linear function in $y_F$, see equation (1), so $y$ is a non-linear function of $y_L$ and $y_F$. Using equations (8) and (9) allows expression of the molar fractions $X_I$ and $X_F$ by $y$ and $y_F$ as

$$X_I = \frac{y\Omega/V}{1 + y\Omega/V}, \quad X_F = \frac{y_F}{1 + y\Omega/V}. \quad (21)$$

Inserting equation (20) in equation (21) allows the expression of $X_I$ and $X_F$ by $y_L$ and $y_F$.

We intend now to extract the values $\Delta E_1$, $\alpha$ (see equation (19)), as well as $\mu_0$ (see equation (13)), from the chemical potential $\mu_I(T, X_I, X_F)$ of the interstitial component provided by a thermodynamic database. For selected data pairs $X_{I,j}, X_{F,j}$ (the actual number of the pair
Table 2. Fitted values of $\Delta E_1$, $\alpha$ and $\mu_0$ for different conditions.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$\Delta E_1$ (kJ mol$^{-1}$)</th>
<th>$\alpha$</th>
<th>$\mu_0$ (kJ mol$^{-1}$)</th>
<th>Least sum of squares (kJ mol$^{-1}$)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite, 500°C, $n = 2$</td>
<td>24.6</td>
<td>1.22</td>
<td>72.1</td>
<td>4700</td>
</tr>
<tr>
<td>Ferrite, 600°C, $n = 2$</td>
<td>24.2</td>
<td>1.24</td>
<td>66.0</td>
<td>2340</td>
</tr>
<tr>
<td>Ferrite, 700°C, $n = 2$</td>
<td>24.2</td>
<td>1.23</td>
<td>60.0</td>
<td>980</td>
</tr>
<tr>
<td>Ferrite, 800°C, $n = 2$</td>
<td>23.1</td>
<td>1.27</td>
<td>53.3</td>
<td>308</td>
</tr>
<tr>
<td>Ferrite, 500°C, $n = 6$</td>
<td>15.1</td>
<td>1.01</td>
<td>72.1</td>
<td>914</td>
</tr>
<tr>
<td>Ferrite, 600°C, $n = 6$</td>
<td>14.4</td>
<td>1.03</td>
<td>65.9</td>
<td>266</td>
</tr>
<tr>
<td>Ferrite, 700°C, $n = 6$</td>
<td>14.1</td>
<td>1.02</td>
<td>59.6</td>
<td>102</td>
</tr>
<tr>
<td>Ferrite, 800°C, $n = 6$</td>
<td>13.8</td>
<td>1.00</td>
<td>53.3</td>
<td>172</td>
</tr>
<tr>
<td>Austenite, 900°C, $n = 6$</td>
<td>10.1</td>
<td>1.07</td>
<td>8.3</td>
<td>520</td>
</tr>
<tr>
<td>Austenite, 1000°C, $n = 6$</td>
<td>10.1</td>
<td>1.07</td>
<td>3.8</td>
<td>580</td>
</tr>
<tr>
<td>Austenite, 1100°C, $n = 6$</td>
<td>10.5</td>
<td>1.03</td>
<td>−0.7</td>
<td>632</td>
</tr>
</tbody>
</table>

is $j$, we can calculate the pairs $y_{L,j}, y_{F,j}$ by a procedure outlined in the next section. The chemical potential $\mu_{L,j}$ can then be calculated from equation (13). The quantities $\Delta E_1$, $\alpha$ and $\mu_0$ can be obtained by fitting, i.e. from the requirement of the minimum of the sum of squares of differences between $\mu_{L,j}$ and $\mu_{I,j}$, later denoted as ‘least sum of squares’, expressed as

$$\min \left( \sum_{j=1}^{J} \left( \mu_{L,j} - \mu_{I,j} \right)^2 \right), \tag{22}$$

where $\mu_{I,j}$ is the value of $\mu_I$ for the pair $X_{I,j}, X_{F,j}$.

3.2. Numerical evaluation

The chemical potential of carbon, $\mu_C = \mu_I$, in an Fe–Cr–C system was taken for various chemical compositions, $X_C = X_I$ from $10^{-4}$ to $5 \times 10^{-2}$ and $X_{Cr} = X_F$ from $10^{-4}$ to $2 \times 10^{-1}$, at 31 × 31 data points, providing $J = 961$ data pairs, from a thermodynamic database for Fe-based alloys available in the thermo-kinetic software MatCalc [16]. For a selected data pair and assuming testing values for $\Delta E_1$, $\alpha$, $\mu_0$, one can calculate $y_F$ from equation (9) and $y_L$ by the following procedure:

- $K_k$ follows from $K_k = \exp \left( -\Delta E_k / R T \right)$ with equation (19),
- $p_k$ follows from equation (1),
- $V_L$ and $V_{Tk}$ can be calculated with table 1 and equations (3) and (4),
- to obtain $y$, one must analytically invert equation (21)$_1$,
- to eventually obtain $y_L$, one must numerically invert equation (20).

Then $y_L$ makes it possible to calculate the chemical potential $\mu_L$ according to equation (13).

A sufficiently dense three-dimensional matrix of the testing values of $\Delta E_1$, $\alpha$, $\mu_0$ is chosen. The corresponding values of $\sum_{j=1}^{J} \left( \mu_{L,j} - \mu_{I,j} \right)^2$ are calculated, and its minimum value, together with fitted values of $\Delta E_1$, $\alpha$, $\mu_0$ is determined. The results of calculation of the sum of squares for ferrite (bcc) at 500°C and $n = 2$ are presented in figure 1.
Figure 2. Comparison of chemical potential $\mu_I$ of carbon from CALPHAD database (solid line) and fitted chemical potential $\mu_L$ of carbon (dashed line) for different values of $X_C$ ($10^{-4}, 0.04, 0.08, 0.12, 0.16$ and $0.2$) (a) and $X_C$ ($10^{-4}, 0.01, 0.02, 0.03, 0.04$ and $0.05$) (b), for ferrite at 500 °C and $n = 2$.

4. Results of simulations and their discussion

The results of fitting, with the values of parameters $\Delta E_1$, $\alpha$, $\mu_0$ provided, are summarized for different conditions in table 2, where the quality of the fit can also be estimated from the minimum value of the sum of squares (least sum of squares), given by equation (22) and presented in the last column in table 2. From the values of the least sum of squares (the higher the value the worse the agreement), it is evident that for ferrite the present model is more realistic with $n = 6$ than with $n = 2$. Moreover, one can see that the values of $\Delta E_1$ and $\alpha$ are practically temperature independent and $\mu_0$ varies linearly with the temperature, which supports the assumptions of the model.
The quality of the fitting can also be judged from figures 2–5. The comparison of figures 2 and 3 shows a much better agreement by selecting \( n = 6 \) compared to \( n = 2 \) for ferrite at 500 °C. However, for ferrite at 800 °C the agreement also becomes very good for \( n = 2 \) (see figure 4). For austenite, there is no possibility to select different values of \( n \), and a very good agreement is also obtained in this case for 900 °C; see figure 5.

The present model allows, for a given temperature \( T \), calculation of the dependence of the chemical diffusion coefficient \( \tilde{D} \) on the chemical composition, given by \( X_I = X_C \) and \( y_F = y_{Cr} \), using equations (16) and (17). If one assumes that the value of \( D_L \) is independent of the chemical composition, the dependences of \( D/D_L \) on \( X_C \) for selected values of \( y_{Cr} = 0.01, 0.05, 0.2 \) and for different conditions (temperatures and phases) are presented in figures 6–9. The dependences of \( D/D_L \) on \( y_{Cr} \) for \( X_C = 0.001 \) and different conditions are presented in figure 10. At a temperature of 500 °C, trapping reduces the diffusion coefficient
Figure 4. Comparison of chemical potential $\mu_I$ of carbon from CALPHAD database (solid line) and fitted chemical potential $\mu_L$ of carbon (dashed line) for different values of $X_{Cr}$ (10$^{-4}$, 0.04, 0.08, 0.12, 0.16 and 0.2) (a) and $X_C$ (10$^{-4}$, 0.01, 0.02, 0.03, 0.04 and 0.05) (b), for ferrite at 800 °C and $n = 2$.

by up to a factor of 1000 if small values of $X_C$ and large values of $y_{Cr}$ are selected (see figures 9 and 10).

Let us finally compare the current concept with the former concept for dilute systems published in [2]. In the former concept, we assumed that one foreign atom converts six neighbouring O positions into traps. In the current concept, we assume that each O position may convert to a trap and its depth depends on the number $k$ of neighbouring foreign atoms. For dilute ferritic systems it makes sense to work only with $k = 1$. If one has $N - 1$ ($N$ is a large number) matrix-forming atoms and one foreign atom in the system corresponding to the site fraction $y_F = 1/N$, then there are $3N$ O positions in the system, since their molar volume is one-third of that of the interstitial positions; see table 1. The probability that an O position is converted to a trap is $p_1 \approx n/N$; see equation (1) for $k = 1$, $1 - y_F \approx 1$. Thus, one
Figure 5. Comparison of chemical potential $\mu_I$ of carbon from CALPHAD database (solid line) and fitted chemical potential $\mu_L$ of carbon (dashed line) for different values of $X_{Cr}$ (10$^{-4}$, 0.04, 0.08, 0.12, 0.16 and 0.2) (a) and $X_{C}$ (10$^{-4}$, 0.01, 0.02, 0.03, 0.04 and 0.05) (b), for austenite at 900 °C and $n = 6$.

5. Summary

A recently developed trapping theory for dilute systems [2] is generalized to non-dilute systems in the frame of a random alloy approach. The present model assumes that each interstitial lattice position can be surrounded by up to $n$ foreign atoms, the number of which determines the depth of the trap. Moreover, the volume corresponding to 1 mol of lattice positions, along which the interstitial atoms can freely diffuse, and the volumes corresponding to 1 mol of trap positions

foreign atom converts $3Np_1 = 3n$ O positions into traps for ferrite, yielding with $6 = 3n$ directly $n = 2$. In the current concept, however, we check both $n = 2$ and 6 for ferrite. In an analogous way, one can show that the former concept is also consistent with the current concept for austenite with $n = 6$. 
Figure 6. The ratio $\tilde{D}/D_L$ as a function of $X_C$ for $y_{Cr} = 0.01$; the corresponding values of $\Delta E_1$ and $\alpha$ are taken from table 2.

Figure 7. The ratio $\tilde{D}/D_L$ as function of $X_C$ for $y_{Cr} = 0.05$; the corresponding values of $\Delta E_1$ and $\alpha$ are taken from table 2.

with a given number of surrounding foreign atoms, are calculated in dependence on chemical composition. If the depths of traps are known, the model also allows calculation of the chemical potential of the interstitial elements in dependence on chemical composition within the frame of an ideal solution concept neglecting the interstitial–interstitial interactions.

The model is applied to a non-dilute Fe–Cr–C system. Fitting of the chemical potential of C to that given by a thermodynamic database allows us to obtain the depths of traps for C. This procedure provides a very good agreement of the model data and the experimental data from the database. The evaluated depths of individual types of trap are nearly temperature independent, which indicates that the model is physically sound.
The chemical diffusion coefficient is calculated based on the model [1] for different chemical compositions. It is demonstrated that at medium temperatures, trapping can reduce the diffusion coefficient by several orders of magnitude for systems that are dilute with respect to the interstitial component and non-dilute with respect to foreign atoms, i.e. for conditions at which the assumptions of the model are justified.

It is quite realistic to expect that the present model can be combined with other models for calculating the chemistry of the alloys with interstitial components. Furthermore, the model is open to be applied to systems with other kinds of trap, such as defects produced by irradiation or mechanical alloying.
Figure 10. The ratio $\tilde{D}/D_i$ as a function of $y_{Cr}$ for $X_C = 0.001$; the corresponding values of $\Delta E_1$ and $\alpha$ are taken from table 2.

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