Theoretical Treatment of Nitriding and Nitrocarburizing of Iron

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Mathematical models are developed for both nitriding and nitrocarburizing of iron taking into account the diffusion of N or C and N through various phases and the thermodynamic properties of the ternary Fe-C-N system. Analytical solutions are obtained for the ε/γ' bilayer growth of the compound layer assuming constant diffusion coefficients, and the results are compared with those obtained from numerical simulations taking into account the concentration-dependent diffusivities. No significant difference was found between these two methods for nitriding of iron. For nitrocarburizing of iron, it was found that the off-diagonal diffusivities of the ε and γ' phases must be taken into account in the analytical solution in order to obtain reasonable results. In addition, it is shown that the phase constitution of the compound layer produced during nitrocarburizing of iron can be predicted by the numerical simulation.

I. INTRODUCTION

NITRIDING and nitrocarburizing are thermochemical surface treatments by which N or C and N are introduced into steel workpieces usually at 550 °C 580 °C. The case produced can be subdivided in a compound layer, consisting predominantly of ε and/or γ' (Fe$_4$N) phases, which is responsible for the good tribological and anticorrosion properties of the surface, and a diffusion zone, where N or C and N are dissolved interstitially in the ferritic matrix, leading to improved fatigue resistance.[1]

Although a large number of articles have been published on the characteristics of the compound layers formed during nitriding and nitrocarburizing,[2–8] a straightforward prediction of the growth rate and the constitution of the compound layer, especially for nitrocarburizing, is still lacking. As a first step toward a deeper understanding of the processes, the thermodynamic properties of the Fe-N and Fe-C-N systems were reassessed,[9] and the diffusion data of N in the ε and γ' phases were recently evaluated.[10] In the present work, we consider diffusion of N or C and N through the various phases during nitriding and nitrocarburizing of iron and develop mathematical models based on diffusion equations. Analytical solutions may be obtained if the diffusion coefficients can be approximated as constants and the boundary conditions are simple enough, but in the general case, numerical simulations must be used. In the present report, we shall use the DICTRA program[11] and try to predict the phase constitution of the compound layer under different boundary conditions.

II. THE MODEL

A. Flux Balance and Local Equilibrium

Consider a phase β growing in another phase α. If the two phases have different compositions, the phase trans-

formation must be accompanied by some diffusion in either one or both of the two phases. If we apply the volume fixed frame of reference for the diffusion and assume the case where the two phases contain the same substitutional elements, and further all the substitutional elements of a phase have the same partial molar volume, we will have $n - 1$ flux balance equations at the β/α interface in an n-component system[11]

$$\frac{v^{\beta/\alpha}}{V_s^\beta}(u_k^{\beta/\alpha} - u_k^{\alpha/\beta}) = J_k^\beta - J_k^\alpha \quad (k=1,2\ ...,\ n-1) \quad [1]$$

where $v^{\beta/\alpha}$ is the migration rate of the β/α phase interface measured in the β-phase frame of reference and V_s^β is the partial volume per mole of substitutional atom of β phase. $u_k^{\alpha/\beta}$ and $u_k^{\beta/\alpha}$ are the content of k on the α and the β side of the interface. The concentration variable u_k is related to the ordinary mole fraction by means of

$$u_k = \frac{x_k}{\sum x_j} \quad [2]$$

where x_k is the mole fraction of component k. The summation in the denominator is only performed over the substitutional components. J_k^α and J_k^β are the diffusion fluxes of k on the α and β side of the phase interface. The fluxes can be written as functions of the $n - 1$ independent concentration gradients in the phase under consideration as[12]

$$J_k = -\sum_{j=1}^{n-1} \frac{D_{kj}^n}{V_s} \text{grad } u_j \quad [3]$$

where D_{kj}^n is the diffusivity of component k when grad u_n is chosen as the dependent gradient and is the most convenient one for practical calculations.[12]

It is common to assume that thermodynamic equilibrium is established locally at the moving phase interface. In a binary system, $n = 2$ and there is only one flux balance equation. The contents $u_k^{\beta/\alpha}$ and $u_k^{\alpha/\beta}$ can be read directly from the phase diagram for a given temperature and pressure, and the growth rate can subsequently be calculated from Eq. [1]. In a system with $n > 2$, there is no unique tie-line but an infinite number of possible tie-lines. However, each possible tie-line is determined by $n - 2$ activities when pressure and temperature are fixed. These activities are unknown and the total number of unknowns then is 1

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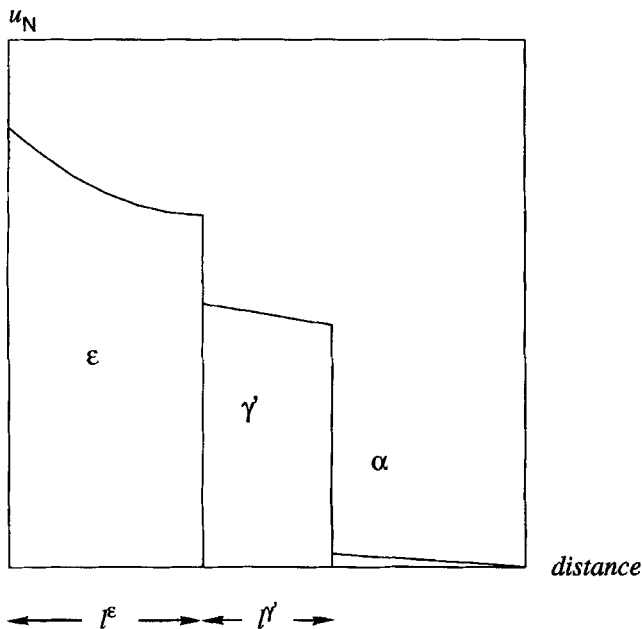Manuscript submitted December 13, 1994.

Fig. 1—Schematic N concentration profile for the ε/γ' bilayer growth into the α-iron matrix unsaturated with N during nitriding.

$+ n - 2 = n - 1$. Thus, we have the same number of unknowns as flux balance equations and there may thus be a unique solution to Eq. [1]. The proper tie-line is chosen in such a way that all the equations give the same growth rate. Rather than reading the compositions from a phase diagram, one should calculate them from the thermodynamic properties if these are known. It is then indeed possible to apply ordinary equilibrium calculation methods to obtain both the unknown tie-line and the growth rate that fulfills all the flux balance equations.

B. Analytical Solution vs Numerical Simulation

For the general case of concentration-dependent diffusivities, the nonlinear Eq. [1] must be solved by numerical methods. However, as pointed out by Kirkaldy and Young,[13] if the relative range of concentration differences is less than about 20 pct, the diffusion coefficients may be approximated by their average values, and one may apply analytical solutions to Eq. [1].

C. Application of the Model to Nitriding and Nitrocarburizing of Iron—the Analytical Solution

Depending on the N activity imposed at the iron surface, the compound layer formed contains either γ' monolayer or ε/γ' bilayer during nitriding.[10] The situation is more complicated during nitrocarburizing of iron. The compound layer formed is quite inhomogeneous in microstructure, e.g., particles of cementite and/or γ' phases are present in the ε layer.[14] However, the ε/γ' bilayer structure could also be expected during nitrocarburizing if the applied C activity is relatively low and the N activity is relatively high.[5,8] In the present work, mathematical models are derived for the ε/γ' bilayer growth case during both nitriding and nitrocarburizing of iron. In addition, the following assumptions are applied for the sake of simplicity: (1) all interfaces are planar and parallel to the surface; (2) the α-Fe matrix is semi-infinite; (3) the iron surface is in equilibrium with the

nitriding or nitrocarburizing medium, which gives a constant N or C and N activity and surface contents during nitriding or nitricarburizing, and thus the growth of the layer obeys a parabolic law; and (4) the partial molar volume is the same for all the phases under consideration, i.e., $V_s^\varepsilon = V_s^{\gamma'} = V_s^\alpha = V_s$ (Appendix).

1. Nitriding of iron

A schematic concentration profile for the ε/γ' bilayer growth is shown in Figure 1. Applying Eq. [1] at both ε/γ' and γ'/α interfaces ($n = 2$, $k = $ N) yields

$$\varepsilon/\gamma': \frac{V^{\varepsilon/\gamma'}}{V_s} (u_N^{\varepsilon/\gamma'} - u_N^{\gamma'/\varepsilon}) = J_N^\varepsilon - J_N^{\gamma'} \quad [4]$$

$$\gamma'/\alpha: \frac{V^{\gamma'/\alpha}}{V_s} (u_N^{\gamma'/\alpha} - u_N^{\alpha/\gamma'}) = J_N^{\gamma'} - J_N^\alpha \quad [5]$$

where

$$J_N^\phi = -\frac{D_{NN}^{Fe(\phi)}}{V_s} \frac{\partial u_N}{\partial y} \quad (\phi = \varepsilon, \gamma', \text{ or } \alpha) \quad [6]$$

By assuming that $D_{NN}^{Fe(\phi)}$ is constant and that the boundary concentrations are constant, which is the case if local equilibrium prevails at all phase interfaces and between the nitriding medium and the iron surface under isothermal conditions, we can express the concentration profile in each phase by means of the error function

$$u_N^\phi = a_1^\phi + a_2^\phi \, \text{erf} \frac{y}{\sqrt{4D_{NN}^{Fe(\phi)}t}} \quad (\phi = \varepsilon, \gamma', \text{ or } \alpha) \quad [7]$$

where the coefficients a_1^ϕ and a_2^ϕ are determined from the following boundary conditions:

$$u_N^\varepsilon (y=0) = u_N^{\varepsilon 0}, \qquad u_N^\varepsilon (y=l^\varepsilon) = u_N^{\varepsilon/\gamma'}$$

$$u_N^{\gamma'} (y=l^\varepsilon) = u_N^{\gamma'/\varepsilon} \qquad u_N^{\gamma'} (y=l^\varepsilon+l^{\gamma'}) = u_N^{\gamma'/\alpha} \quad [8]$$

$$u_N^\alpha (y=l^\varepsilon+l^{\gamma'}) = u_N^{\alpha/\gamma'} \qquad u_N^\alpha (y=\infty) = u_N^{\alpha\infty}$$

where $u_N^{\varepsilon 0}$ and $u_N^{\alpha\infty}$ are the N content at the surface and the initial N content of iron specimen, respectively. Considering also the parabolic growth, we have

$$l^\varepsilon = k^\varepsilon\sqrt{t}, \qquad l^{\gamma'} = k^{\gamma'} \sqrt{t} \quad [9]$$

where k^ε and $k^{\gamma'}$ are the growth rate constants of ε and γ', respectively, and t is the time. The flux of N in each phase is expressed according to Eq. [6] as

$$J_N^\varepsilon (\varepsilon/\gamma') = -\frac{1}{V_s} \frac{\sqrt{D_{NN}^{Fe(\varepsilon)}}}{\sqrt{\pi t}} \frac{(u_N^{\varepsilon/\gamma'} - u_N^{\varepsilon 0}) \exp [-(k^\varepsilon)^2/4D_{NN}^{Fe(\varepsilon)}]}{\text{erf} (k^\varepsilon/\sqrt{4D_{NN}^{Fe(\varepsilon)}})} \quad [10]$$

$$J_N^{\gamma'} (\varepsilon/\gamma') =$$
$$-\frac{1}{V_s} \frac{\sqrt{D_{NN}^{Fe(\gamma')}}}{\sqrt{\pi t}} \frac{(u_N^{\gamma'/\alpha} - u_N^{\gamma'/\varepsilon}) \exp [-(k^\varepsilon)^2/4D_{NN}^{Fe(\gamma')}]}{\text{erf} [(k^\varepsilon+k^{\gamma'})/\sqrt{4D_{NN}^{Fe(\gamma')}}] - \text{erf} (k^\varepsilon/\sqrt{4D_{NN}^{Fe(\gamma')}})} \quad [11]$$

$$J_N^{\gamma'} (\gamma'/\alpha) =$$
$$-\frac{1}{V_s} \frac{\sqrt{D_{NN}^{Fe(\gamma')}}}{\sqrt{\pi t}} \frac{(u_N^{\gamma'/\alpha} - u_N^{\gamma'/\varepsilon}) \exp [-(k^\varepsilon+k^{\gamma'})^2/4D_{NN}^{Fe(\gamma')}]}{\text{erf} [(k^\varepsilon+k^{\gamma'})/\sqrt{4D_{NN}^{Fe(\gamma')}}] - \text{erf} (k^\varepsilon/\sqrt{4D_{NN}^{Fe(\gamma')}})} \quad [12]$$

$$J_N^\alpha (\gamma/\alpha) =$$

$$-\frac{1}{V_s} \frac{\sqrt{D_{NN}^{Fe(\alpha)}}}{\sqrt{\pi t}} \frac{(u_N^{\alpha\infty} - u_N^{\alpha/\gamma'}) \exp\left[- (k^\varepsilon + k^{\gamma'})^2/4D_{NN}^{Fe(\alpha)}\right]}{1 - erf\left[(k^\varepsilon + k^{\gamma'})/\sqrt{4D_{NN}^{Fe(\alpha)}}\right]}$$

$$[13]$$

By inserting Eqs. [10] through [13] into Eqs. [4] and [5] and taking into account that

$$v^{\varepsilon/\gamma'} = \frac{dl^\varepsilon}{dt} = \frac{k^\varepsilon}{2} \frac{1}{\sqrt{t}} \quad v^{\gamma'/\alpha} = \frac{d(l^\varepsilon + l^{\gamma'})}{dt} = \frac{(k^\varepsilon + k^{\gamma'})}{2} \frac{1}{\sqrt{t}} \quad [14]$$

we obtain the following flux balance equations at the interfaces:

$$\varepsilon/\gamma': \frac{k^\varepsilon}{2} (u_N^{\varepsilon/\gamma'} - u_N^{\gamma'/\varepsilon}) =$$

$$-\frac{\sqrt{D_{NN}^{Fe(\varepsilon)}}}{\sqrt{\pi}} \frac{(u_N^{\varepsilon/\gamma'} - u_N^{\varepsilon 0}) \exp\left[- (k^\varepsilon)^2/4D_{NN}^{Fe(\varepsilon)}\right]}{erf\left(k^\varepsilon/\sqrt{4D_{NN}^{Fe(\varepsilon)}}\right)}$$

$$+\frac{\sqrt{D_{NN}^{Fe(\gamma')}}}{\sqrt{\pi}} \frac{(u_N^{\gamma'/\alpha} - u_N^{\gamma'/\varepsilon}) \exp\left[- (k^\varepsilon)^2/4D_{NN}^{Fe(\gamma')}\right]}{erf\left[(k^\varepsilon + k^{\gamma'})/\sqrt{4D_{NN}^{Fe(\gamma')}}\right] - erf\left(k^\varepsilon/\sqrt{4D_{NN}^{Fe(\gamma')}}\right)}$$

$$[15]$$

$$\gamma'/\alpha: \frac{k^\varepsilon + k^{\gamma'}}{2} (u_N^{\gamma'/\alpha} - u_N^{\alpha/\gamma'}) =$$

$$-\frac{\sqrt{D_{NN}^{Fe(\gamma')}}}{\sqrt{\pi}} \frac{(u_N^{\gamma'/\alpha} - u_N^{\gamma'/\varepsilon}) \exp\left[- (k^\varepsilon + k^{\gamma'})^2/4D_{NN}^{Fe(\gamma')}\right]}{erf\left[(k^\varepsilon + k^{\gamma'})/\sqrt{4D_{NN}^{Fe(\gamma')}}\right] - erf\left(k^\varepsilon/\sqrt{4D_{NN}^{Fe(\gamma')}}\right)}$$

$$+\frac{\sqrt{D_{NN}^{Fe(\alpha)}}}{\sqrt{\pi}} \frac{(u_N^{\alpha\infty} - u_N^{\alpha/\gamma'}) \exp\left[- (k^\varepsilon + k^{\gamma'})^2/4D_{NN}^{Fe(\alpha)}\right]}{1 - erf\left[(k^\varepsilon + k^{\gamma'})/\sqrt{4D_{NN}^{Fe(\alpha)}}\right]}$$

$$[16]$$

For a given N activity at the iron surface, $u_N^{\varepsilon 0}$ can be calculated from the thermodynamics of the ε phase of the Fe-N system. The two unknowns, k^ε and $k^{\gamma'}$, can thus be determined from the solution of the preceding two equations. The equations are nonlinear and must be solved numerically.

2. Nitrocarburizing of iron

Similar to the procedure in Section 1, we now apply Eq. [1] to the nitrocarburizing case by taking $n = 3$ and $k = 1$ or 2 (note: "1" denotes C and "2" denotes N):

$$\varepsilon/\gamma': \frac{v^{\varepsilon/\gamma'}}{V_s} (u_k^{\varepsilon/\gamma'} - u_k^{\gamma'/\varepsilon}) = J_k^\varepsilon - J_k^{\gamma'} \quad [17]$$

$$\gamma'/\alpha: \frac{v^{\gamma'/\alpha}}{V_s} (u_k^{\gamma'/\alpha} - u_k^{\alpha/\gamma'}) = J_k^{\gamma'} - J_k^\alpha \quad [18]$$

where

$$J_k^\phi = - \sum_{j=1}^{2} \frac{D_{kj}^{Fe(\phi)}}{V_s} \frac{\partial u_j}{\partial y} \quad (\phi = \varepsilon, \gamma', \text{ or } \alpha) \quad [19]$$

Assuming constant diffusion coefficients, Kirkaldy[15] presented solutions of the diffusion equation applicable to the planar growth of grain boundary nucleated ferrite and carbide in supersaturated ternary austenite. We now apply his method to the bilayer growth of ε and γ' during nitrocarburizing of iron.

Let us first consider the diffusion of C and N in the ε

phase and derive an expression for the flux $J_k^\varepsilon (\varepsilon/\gamma')$. According to Kirkaldy,[15] the concentration profile of C or N in the ε phase can be written as

$$u_k^\varepsilon = a_{k0} + \sum_{j=1}^{2} a_{kj} \, erf\left(\frac{y}{\sqrt{4w_j t}}\right) \quad [20]$$

where

$$w_j = \sum_{i=1}^{2} D_{ki}^{Fe(\varepsilon)} a_{ij}/a_{kj} \quad [21]$$

The coefficients a_{k0}, a_{kj}, and w_j are determined in terms of the diffusion coefficients and the boundary conditions

$$u_k^\varepsilon (y=0) = u_k^{\varepsilon 0}, \quad u_k^\varepsilon (y=l^\varepsilon) = u_k^{\varepsilon/\gamma'} \quad [22]$$

The results are listed here:

$$w_1 = (D_{11}^{Fe(\varepsilon)} + D_{22}^{Fe(\varepsilon)} + D)/2 \quad [23]$$

$$w_2 = (D_{11}^{Fe(\varepsilon)} + D_{22}^{Fe(\varepsilon)} - D)/2 \quad [24]$$

$$D = \sqrt{(D_{11}^{Fe(\varepsilon)} - D_{22}^{Fe(\varepsilon)})^2 + 4D_{12}^{Fe(\varepsilon)} D_{21}^{Fe(\varepsilon)}} \quad [25]$$

$$a_{11} =$$

$$-\frac{(w_1 - D_{22}^{Fe(\varepsilon)})[(w_2 - D_{22}^{Fe(\varepsilon)})(u_2^{\varepsilon/\gamma'} - u_2^{\varepsilon 0}) - D_{21}^{Fe(\varepsilon)}(u_1^{\varepsilon/\gamma'} - u_1^{\varepsilon 0})]}{D_{21}^{Fe(\varepsilon)} (w_1 - w_2) \, erf\left(k^\varepsilon/\sqrt{4w_1}\right)}$$

$$[26]$$

$$a_{12} = \frac{(w_2 - D_{22}^{Fe(\varepsilon)})[(w_1 - D_{22}^{Fe(\varepsilon)})(u_2^{\varepsilon/\gamma'} - u_2^{\varepsilon 0}) - D_{21}^{Fe(\varepsilon)}(u_1^{\varepsilon/\gamma'} - u_1^{\varepsilon 0})]}{D_{21}^{Fe(\varepsilon)} (w_1 - w_2) \, erf\left(k^\varepsilon/\sqrt{4w_2}\right)}$$

$$[27]$$

$$a_{21} = \frac{(w_2 - D_{22}^{Fe(\varepsilon)})(u_2^{\varepsilon/\gamma'} - u_2^{\varepsilon 0}) - D_{21}^{Fe(\varepsilon)}(u_1^{\varepsilon/\gamma'} - u_1^{\varepsilon 0})}{(w_1 - w_2) \, erf\left(k^\varepsilon/\sqrt{4w_1}\right)} \quad [28]$$

$$a_{22} = \frac{(w_1 - D_{22}^{Fe(\varepsilon)})(u_2^{\varepsilon/\gamma'} - u_2^{\varepsilon 0}) - D_{21}^{Fe(\varepsilon)}(u_1^{\varepsilon/\gamma'} - u_1^{\varepsilon 0})}{(w_1 - w_2) \, erf\left(k^\varepsilon/\sqrt{4w_1}\right)} \quad [29]$$

According to Eq. [19] and taking into account Eq. [20], the flux of C or N in the ε phase at the ε/γ' interface is expressed as

$$J_k^\varepsilon (\varepsilon/\gamma') = - \frac{1}{V_s} \sum_{j=1}^{2} D_{kj}^{Fe(\varepsilon)} \sum_{i=1}^{2} \frac{a_{ji}}{\sqrt{\pi w_i t}} \exp\left(\frac{-(k^\varepsilon)^2}{4w_i}\right) \quad [30]$$

In principle, the flux of C or N in the γ' phase can also be obtained in the same way by using the error function expression for the concentration distribution in the γ' phase, as was done for the nitriding case (Section 1). However, the expression of the flux will be considerably simplified if we assume stationary diffusion, which is expected to be a good approximation for the γ' phase due to the narrow composition range in the phase.[10] The fluxes of C or N in the γ' phase at the ε/γ' and γ'/α interfaces can thus be written as

$$J_k^{\gamma'} (\varepsilon/\gamma') = J_k^{\gamma'} (\gamma'/\alpha) = - \frac{1}{V_s} \sum_{j=1}^{2} D_{kj}^{Fe(\gamma')} \frac{(u_j^{\gamma'/\alpha} - u_j^{\gamma'/\varepsilon})}{k^{\gamma'}\sqrt{t}} \quad [31]$$

Since the solubilities of C and N in the α phase are very low, the off-diagonal diffusion coefficients are much smaller than the diagonal ones and may be neglected. This

will also simplify the expression for the flux of C or N in the α phase from Eq. [19] to the same expression as the nitriding case by substituting N with k in Eq. [13]:

$$J_k^\alpha (\gamma'/\alpha) =$$

$$- \frac{1}{V_s} \frac{\sqrt{D_{kk}^{Fe(\alpha)}}}{\sqrt{\pi t}} \frac{(u_k^{\alpha\infty} - u_k^{\alpha/\gamma'}) \exp [- (k^\varepsilon + k^{\gamma'})^2 / 4D_{kk}^{Fe(\alpha)}]}{1 - erf [(k^\varepsilon + k^{\gamma'})/\sqrt{4D_{kk}^{Fe(\alpha)}}]}$$

[32]

Inserting Eqs. [14] and [30] through [32] into Eqs. [17] and [18], the flux balance equations at each interface for nitrocarburizing of iron are now expressed as

$$\varepsilon/\gamma': \frac{k^\varepsilon}{2} (u_k^{\varepsilon/\gamma'} - u_k^{\gamma'/\varepsilon})$$

$$=$$

[33]

$$- \sum_{j=1}^2 D_{kj}^{Fe(\varepsilon)} \sum_{i=1}^2 \frac{a_{ji}}{\sqrt{\pi w_i}} \exp \left(\frac{-(k^\varepsilon)^2}{4w_i}\right)$$

$$+ \sum_{j=1}^2 D_{kj}^{Fe(\gamma')} \frac{(u_j^{\gamma'/\alpha} - u_j^{\gamma'/\varepsilon})}{k^{\gamma'}}$$

$$\gamma'/\alpha: \frac{k^\varepsilon + k^{\gamma'}}{2} (u_k^{\gamma'/\alpha} - u_k^{\alpha/\gamma'}) = - \sum_{j=1}^2 D_{kj}^{Fe(\gamma')} \frac{(u_j^{\gamma'/\alpha} - u_j^{\gamma'/\varepsilon})}{k^{\gamma'}}$$

$$+ \frac{\sqrt{D_{kk}^{Fe(\alpha)}}}{\sqrt{\pi}} \frac{(u_k^{\alpha\infty} - u_k^{\alpha/\gamma'}) \exp [- (k^\varepsilon + k^{\gamma'})^2 / 4D_{kk}^{Fe(\alpha)}]}{1 - erf [(k^\varepsilon + k^{\gamma'})/\sqrt{4D_{kk}^{Fe(\alpha)}}]}$$

[34]

where the coefficients a_{ji} and w_i are given by Eqs. [23] through [29].

Thus, we have four equations. If the activities of C and N at the iron surface are known, we can calculate $u_k^{\varepsilon 0}$ from the thermodynamic properties of the ε phase. Consequently, we have only four unknowns, namely, k^ε, $k^{\gamma'}$, the tie-line at the ε/γ' interface defined by its C or N activity, and the tie-line at the α/γ' interface defined by its C or N activity. The unknown quantities may thus be uniquely determined by Eqs. [33] and [34].

III. RESULTS AND DISCUSSIONS

Analytical solutions to Eqs. [15] and [16] and Eqs. [33] and [34] under certain boundary conditions were found by applying the PARROT program developed by Jansson.[16] The program performs equilibrium calculations and allows the user to add extra conditions in a rather flexible way. The thermodynamic descriptions of the Fe-N and Fe-C-N systems were taken from Reference 9. Numerical simulations of nitriding and nitrocarburizing of iron were also performed using the DICTRA program.[11] The program is interfaced with Thermo-Calc,[17] which handles all thermodynamic calculations needed.

The diffusion data of N in the ε and γ' phases were recently assessed by Du and Ågren,[10] and the diffusion data of C and N in the α phase were evaluated by Jönsson.[18] Due to the lack of experimental information, the intrinsic diffusivity of C in the ε or γ' phase is assumed as

$$D_C^{*(\phi)} = D_N^{*(\phi)} \frac{D_C^{*(\gamma)}}{D_N^{*(\gamma)}} \quad (\phi = \varepsilon \text{ or } \gamma') \quad [35]$$

where $D_N^{*(\phi)}$ is the intrinsic diffusivity of N in the ϕ phase[10] and $D_C^{*(\gamma)}$ and $D_N^{*(\gamma)}$ are the intrinsic diffusivities of C and N in the γ phase, respectively. $D_C^{*(\gamma)}$ was evaluated by Ågren:[19] as

$$D_C^{*(\gamma)} = 4.53 \cdot 10^{-7} [1 + y_C(1 - y_C) \frac{8339.9}{T}] \exp$$

$$[-(\frac{1}{T} - 2.221 \cdot 10^{-4})(17,767 - y_C \, 26,436)] \; (m^2 \; s^{-1}) \quad [36]$$

where y_C is the site fraction of C in γ. However, $D_C^{*(\phi)}$ was calculated by neglecting the composition dependence of $D_C^{*(\gamma)}$, i.e., y_C was put as zero when Eq. [36] was inserted into Eq. [35]. $D_N^{*(\gamma)}$ was taken from Reference 20.

A. Nitriding of Iron

Since the α phase is a dilute solution of N, $D_{NN}^{Fe(\alpha)}$ is almost constant and is calculated to be $9.68 \cdot 10^{-12}$ m^2 s^{-1} at 848 K.[18] The variation of $D_{NN}^{Fe(\varepsilon)}$ and $D_{NN}^{Fe(\gamma')}$ with the concentration of N is illustrated in Figures 2(a) and (b), respectively.[10] Note that $D_{NN}^{Fe(\gamma')}$ approaches infinity as $u_N^{\gamma'}$ approaches the stoichiometric composition 0.25. This is due to the fact that the γ' phase was modeled as Fe$_4$(N,Va) thermodynamically,[9] which shows that the calculated thermodynamic factor approaches infinity as y_{Va} approaches zero.[10] However, as indicated in Reference 9, the N concentration in the γ' phase is always below the stoichiometric composition.

Recently, Du et al.[21] conducted some nitriding experiments at 575 °C and found that a homogeneous ε/γ' bilayer could form on an iron surface shortly after nitriding if the samples were preheated in air at 300 °C for 1 hour (the NI1 series). The N contents determined by X-ray diffraction analysis on the surfaces of the samples nitrided for 20 and 120 minutes are very close, and therefore, one may assume that a constant N content (N activity) was maintained at the iron surface during the experiment. The calculated k^ε and $k^{\gamma'}$ corresponding to such a surface content, 8.00 wt pct N ($u_N^{\varepsilon 0} = 0.3466$), according to Eqs. [15] and [16] are compared with the result obtained from a numerical simulation by DICTRA taking into account the concentration-dependent diffusivities and the experimental data in Figure 3. The initial N content in the Fe material is 0.002 wt pct N ($u_N^{\alpha\infty} = 8.0 \cdot 10^{-5}$). The constant diffusivities of N in the ε and γ' phases were chosen to be the ones corresponding to an average composition in each phase in the analytical solution as (Figures 2(a) and (b))

$$u_N^\varepsilon = 0.3368, \qquad D_{NN}^{Fe(\varepsilon)} = 7.11 \cdot 10^{-14} \; m^2 \; s^{-1}$$

$$u_N^{\gamma'} = 0.2445, \qquad D_{NN}^{Fe(\gamma')} = 5.48 \cdot 10^{-14} \; m^2 \; s^{-1}$$

It is interesting to see that the analytical solution (dashed lines) agrees, within the experimental scatter, with the experimental results and the results from the numerical simulation, which actually give a slightly higher growth rate of the γ' layer than observed experimentally.

Of course, the DICTRA program can also perform simulations using constant diffusivities, yielding the same results as the analytical solution, and allows a convenient direct comparison of extra information, such as concentration profiles, diffusion paths, etc., with the simulations using concentration-dependent diffusivities. Such a simulation
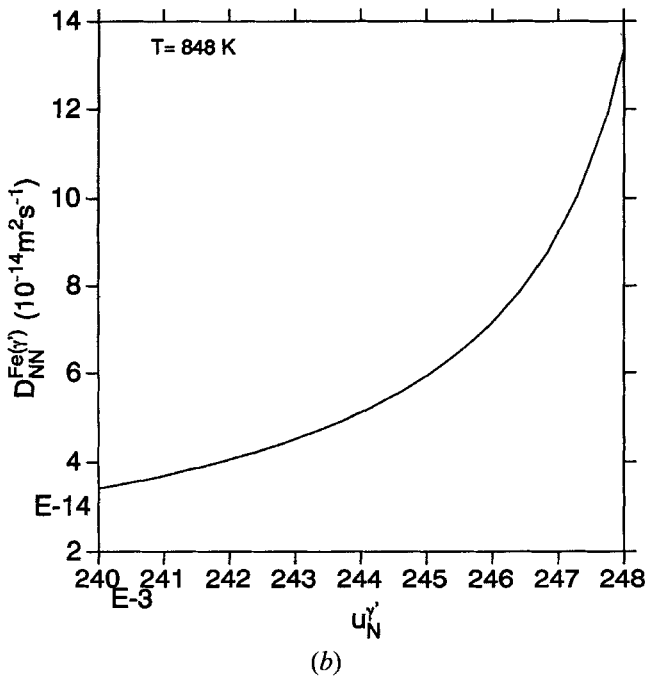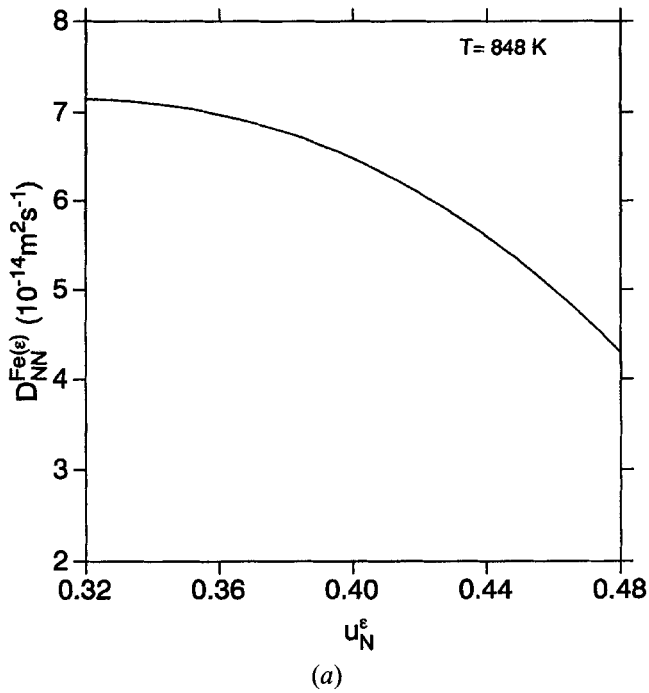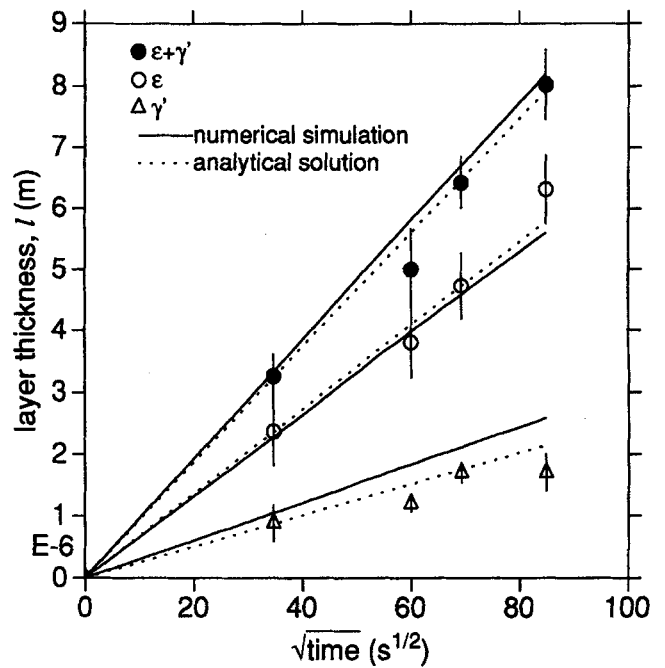
Fig. 3—The calculated layer thickness of $\varepsilon + \gamma'$, ε, and γ' vs the square root of nitriding time at 575 °C according to the analytical solution (the dashed lines) and the numerical simulation with concentration-dependent diffusivities (the solid lines), together with the experimental measurements[21] ($u_N^{\varepsilon 0} = 0.3466$).

Fig. 2—The variation of the diffusivity (a) $D_{NN}^{Fe(\varepsilon)}$ and (b) $D_{NN}^{Fe(\gamma')}$ with the concentration of N.[10]

was made corresponding to the preceding analytical solution for the experiment by Du et al.,[21] and the calculated N concentration profiles at 1 and 2 hours are plotted together with those obtained by the fully numerical simulation in Figure 4. Again, there are no large discrepancies between the analytical and numerical results.

B. Nitrocarburizing of Iron

A series of calculations may be performed for different combinations of C and N activities at the surface of iron, i.e., different $u_C^{\varepsilon 0}$ and $u_N^{\varepsilon 0}$ values, at certain nitrocarburizing temperatures according to Eqs. [33] and [34]. However, it
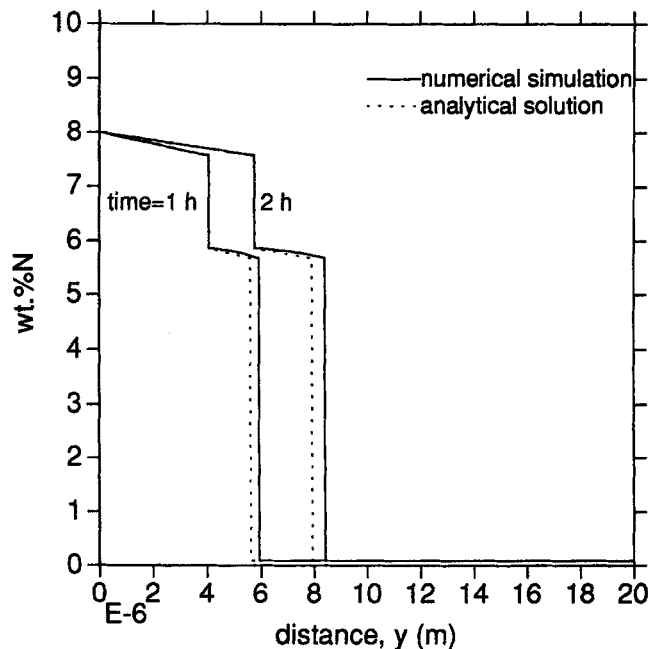

Fig. 4—The calculated N concentration profiles at 1 and 2 h according to the analytical solution (the dashed lines) and the results obtained from the numerical simulation with concentration-dependent diffusivities (the solid lines) during nitriding of iron ($T = 575$ °C, $u_N^{\varepsilon 0} = 0.3466$).

is difficult to find any experimental data to compare such calculations with, since most of the nitrocarburizing experiments were performed on steels rather than on iron. Furthermore, when experiments on nitrocarburizing iron were investigated previously,[5,8] activities at the specimen surface were not well determined or the growth rate of the layer was not explicitly given. Therefore, here, we only

Table I. Calculated Diffusivities, $D_{kj}^{Fe(\phi)}$, Corresponding to an Average Composition in the ε, γ', and α Phases, Respectively, by DICTRA for the Analytical Solution of Nitrocarburizing Iron ($T = 575$ °C)

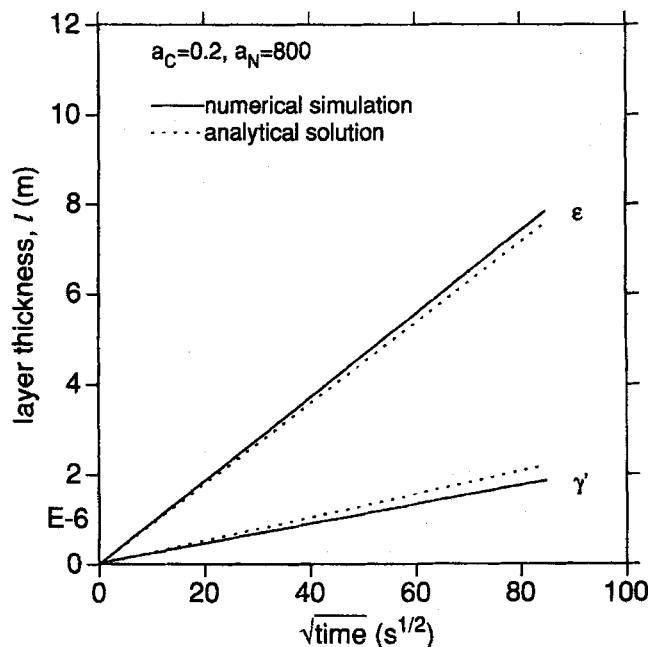| Phase	Average Composition		Diffusivities (10^{-14} m^2 s^{-1})			
	u_1	u_2	D_{11}^{Fe}	D_{12}^{Fe}	D_{21}^{Fe}	D_{22}^{Fe}
ε	0.030	0.33	9.41	-1.45	-3.28	6.37
γ'	0.002	0.244	0.732	0.272	6.83	7.08
α	$8\cdot10^{-5}$	$3.5\cdot10^{-3}$	780	—	—	968

Fig. 5—The calculated layer thickness of ε and γ' vs the square root of nitrocarburizing time at 575 °C according to the analytical solution (the dashed lines) and the numerical simulation with concentration-dependent diffusivities (the solid lines).
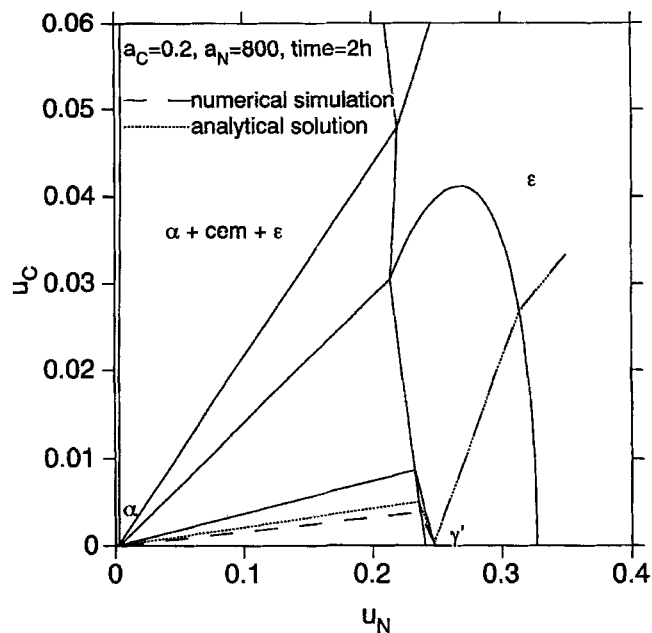

Fig. 6—The calculated diffusion path of C and N at 2 h according to the analytical solution (the dotted lines) and the numerical simulation with concentration-dependent diffusivities (the dashed lines) ($T = 575$ °C).

present one of the calculations at 575 °C to demonstrate the difference between the analytical solution and numerical simulation.

The C and N activities were chosen as $a_C = 0.2$ and $a_N = 800$ (reference state: C—graphite, N—1 atm N$_2$ gas), which correspond to $u_C^0 = 0.033$ and $u_N^0 = 0.35$, respectively. The diffusivities, $D_{kj}^{Fe(\phi)}$, were again calculated as an average of composition in ε, γ', and α, respectively, applying the DICTRA program (Table I). The initial N and C contents in the Fe material were chosen as 0.002 wt pct N ($u_N^\infty = 8.0 \cdot 10^{-5}$) and 0.006 wt pct C ($u_C^\infty = 2.79 \cdot 10^{-4}$). The α-Fe was assumed to be slightly saturated with C, since no absolutely "pure" iron exists in reality.

The calculated k^ε and $k^{\gamma'}$ from Eqs. [33] and [34], corresponding to such a boundary condition, are compared with the result obtained from a fully numerical simulation considering concentration-dependent diffusivities by DICTRA in a layer thickness vs square root of time plot in Figure 5. The calculated diffusion path at 2 hours by DICTRA using the same constant diffusivities (Table I) is also compared with the one from the fully numerical simulation in Figure 6. No significant differences were found between the analytical and numerical methods.

As can be seen from Table I, the off-diagonal diffusivi-

ties in both ε and γ' phases have the same order of magnitude as the diagonal diffusivities, indicating strong thermodynamic interactions between C and N in these two phases. It would be interesting to examine the effect of the off-diagonal diffusivities on the analytical solution by neglecting all the off-diagonal diffusivities in both ε and γ' phases. The resulted flux balance equations would look exactly the same as those obtained for nitriding iron except that N should be substituted by k ($k = $ C or N) in Eqs. [15] and [16]. The calculated growth rates k^ε and $k^{\gamma'}$ do not differ very much compared with the ones obtained from Eqs. [33] and [34] or the numerical simulation. However, the resulting diffusion path (time = 2 hours) in the potential phase diagram, i.e., a_N vs a_C, shows a significant difference compared with those obtained by taking the off-diagonal diffusivities (analytical and numerical) into account (Figure 7). The C activity gradients across the ε and γ' sublayers have the opposite direction to those calculated considering the off-diagonal diffusivities, yielding a lower C activity at the surface than at the ε/γ' interface. This is not reasonable during nitrocarburizing. It is thus demonstrated that it is important to consider the off-diagonal diffusivities in phases that have strong ternary interactions between different elements when ternary diffusion problems are solved analytically.

As was mentioned, the ε/γ' bilayer structure can only be obtained when the C activity at the iron surface is not too high during a nitrocarburizing experiment. Actually, the phase constitution of the compound layer under given N and C activities at the surface during nitrocarburizing of iron can be predicted by performing fully numerical simulations using DICTRA. One may assume that the compound layer contains only ε monolayer when making such a simulation and examine the corresponding diffusion path at some moment. Three simulations were performed for $a_N = 800$: $a_C = 0.2$, 1.5, and 4.0, respectively. The calculated diffusion path at 2 hours was plotted in Figure 8 for each
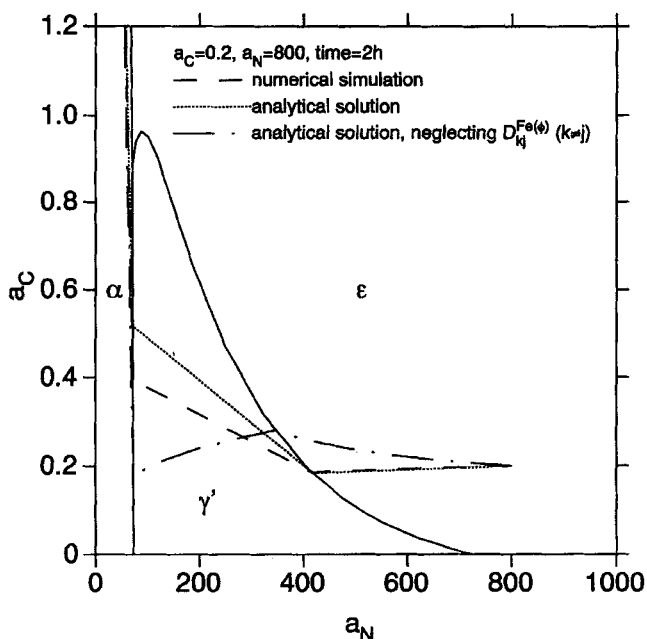
Fig. 7—The calculated diffusion path of C and N at 2 h shown in a potential phase diagram according to the analytical solution with the off-diagonal (the dotted lines) and neglecting the off-diagonal diffusivities (the dash-dotted lines), as well as the numerical simulation with concentration-dependent diffusivities (the dashed lines) $(T = 575\ °C)$.
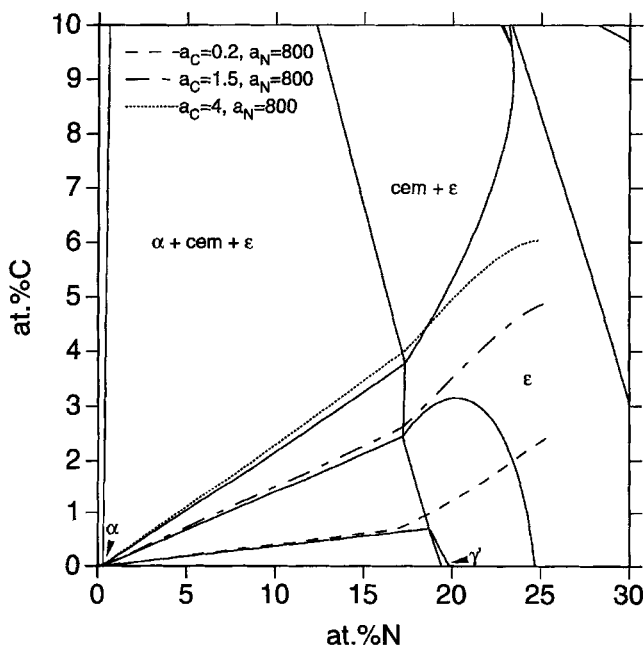

Fig. 8—The calculated diffusion path at 2 h under a fixed N activity but different C activities at the iron surface according to the numerical simulations with concentration-dependent diffusivities $(T = 575\ °C)$.

surface condition. The one with $a_C = 0.2$ (the dashed line) cuts through the $\varepsilon + \gamma'$ two-phase region, which means that the γ' phase should actually be stable between the ε and α phases. The one with $a_C = 1.5$ (the dash-dotted line) only passes through the $\alpha + \varepsilon$ phase region, indicating that there is no solution to the flux balance equations assuming ε/γ' bilayer growth. The one with $a_C = 4.0$ (the dotted line) even cuts through the cem + ε and α + cem + ε regions, and therefore, the compound layer is expected to contain the cementite phase.

IV. SUMMARY

The bilayer growth of ε/γ' during nitriding and nitrocarburizing of iron has been analyzed theoretically. Results from the analytical solutions of the diffusion equations as well as the numerical simulations were presented and compared with each other. No significant difference was found between these two methods for nitriding of iron. For nitrocarburizing of iron, it was found that the off-diagonal diffusivities of the ε and γ' phases must be taken into account in the analytical solution in order to obtain reasonable results. It was also demonstrated through the numerical simulations that the γ' phase in the compound layer during nitrocarburizing of iron would become unstable as the C activity at the surface increased to a certain level. Further increase of the C activity would yield the formation of the cementite phase in the compound layer.

APPENDIX
Comparison of the partial molar volume of the ε, γ', and α phases

The partial molar volume of iron atom of the ϕ phase ($\phi = \varepsilon$, γ', or α) can be calculated as

$$V_s^\phi = N_{Av}\, V_\phi \qquad [A1]$$

where N_{Av} and V_ϕ are the Avogadro number and the volume of the unit cell per iron atom of the ϕ phase, respectively. Considering the structure of each phase, V_ϕ depends on the lattice parameter(s) of the ε (hcp), γ' (fcc), and α (bcc) phases as

$$V_\varepsilon = \frac{1}{4}\, a_\varepsilon^2\, c_\varepsilon\, \sqrt{3} \qquad [A2]$$

$$V_{\gamma'} = \frac{1}{4}\, a_{\gamma'}^3, \qquad [A3]$$

$$V_\alpha = \frac{1}{2}\, a_\alpha^3 \qquad [A4]$$

where

$$a_\varepsilon = \frac{1}{\sqrt{3}}\,(0.43535 + 0.1337\,\frac{u_k^\varepsilon}{1+u_k^\varepsilon})\quad (nm)\quad (Ref.\ 22)[A5]$$

$$c_\varepsilon = 0.423321 + 0.0578\,\frac{u_k^\varepsilon}{1+u_k^\varepsilon}\quad (nm)\quad (Ref.\ 22)\quad [A6]$$

$$a_{\gamma'} = 0.37988 + 0.095315 \\ (u_k^{\gamma'} - 0.25)\quad (nm)\quad (Ref.\ 23)\quad [A7]$$

$$a_\alpha = 0.28663 + 0.20505\, u_k^\alpha\quad (nm)\quad (Ref.\ 24)\quad [A8]$$

where $k = $ N or C + N. Considering the nitriding of iron

case (Section III–A) and taking the average value of u_N in each phase, one is able to calculate the corresponding V_s^ϕ at $T = 848$ K:

$$u_N^\varepsilon = 0.3368, \qquad V_s^\varepsilon = 8.37 \cdot 10^{-6} \text{ (m}^3\text{/mol)}$$

$$u_N^{\gamma'} = 0.2445, \qquad V_s^{\gamma'} = 8.22 \cdot 10^{-6} \text{ (m}^3\text{/mol)}$$

$$u_N^\alpha = 3.5 \cdot 10^{-3}, \qquad V_s^\alpha = 7.14 \cdot 10^{-6} \text{ (m}^3\text{/mol)}$$

Therefore, the partial molar volume of different phases can be approximated as the same, $i.e.$, $V_s^\varepsilon = V_s^{\gamma'} = V_s^\alpha = V_s$.

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