Effect of Lanthanum on the Precipitation of NbC in Ferritic Steels

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The effect of lanthanum on the precipitation of NbC in ferritic steel has been studied within the experimental and theory methods. The diffusion coefficients of Niobium resulted from the diffusion couple experiment shows that Nb diffuses slightly faster in the presence of La than that in pure $\alpha$-Fe. Using the first-principles calculations based on the density functional theory, we studied the interactions between any two defects of La, Nb and vacancy, as well as the variation of diffusion activation energies caused by the presence of La. The interactions between La and Nb are calculated to be repulsive in both the first and the second nearest neighbor configurations, and the vacancy is expected to form in the La-Nb clustering area, which leads to the decrease of the diffusion activation energy of Nb. To elucidate the effect of La on the precipitation of NbC in ferritic steel, the above diffusion coefficients were substituted into the precipitation kinetics model. Agree with the experimental data, the simulated evolutions of the fractions and radius of NbC precipitate reveal that the addition of La leads to the faster precipitation kinetics of NbC in ferritic steels.

KEY WORDS: La; NbC; precipitation; ferritic steel.

1. Introduction

Ferritic stainless steels (FSS), as the most commonly used material in automotive exhaust systems, have relatively low strength at elevated temperature compared to austenitic steels. The improvements in mechanical properties can be achieved by the selection of steel composition in conjunction with the thermo-mechanical processing.1) Moderate or high interstitial levels of FSS usually require the addition of stabilizing elements such as Nb, Ti, V and Zr, acting as strong carbide and nitride formers, to prevent high temperature embrittlement or intergranular corrosion. Niobium containing FSS have been developed to satisfy these high temperature requirements by solid solution strengthening and precipitation hardening.2–4) The addition of Niobium may provide effective methods for further strengthening via the following microstructural mechanisms: retarding austenite recrystallisation, refining the final microstructure, and precipitation strengthening.5–7) Generally, solute Nb is readily precipitated out as carbonitride when the steel used at high temperature for a long time, the high temperature strength can be affected due to the Nb(C,N) precipitation in Nb containing ferritic stainless steel.8)

As strong forming elements of carbide and nitride, the precipitation evolution of Nb and V depends on various factors, such as liquid/solid condition, solid solubility, and interaction of other elements.9) The previous study show that the introduction of small amounts of rare earth (RE) elements, such as yttrium, cerium, lanthanum, is beneficial to improve the mechanical properties, the high-temperature oxidation resistance and the corrosion resistance in niobium containing steels,10,11) these effects has been proved to be induced by RE and reactive element effect.

Although there are studies reported about the various effects of RE on the properties of Nb–V stabilized ferritic stainless steel, the further systematical investigation of effect mechanism of RE on the precipitation of NbC in ferrite matrix has not been conducted. Several explanations have been given for the RE effect, but no clear conclusions have been drawn.

The aim of the present paper was to provide a better understanding of the effects of La addition on the NbC precipitation in FSS. The diffusion coefficients of Nb in $\alpha$-Fe matrix, in the case of with and without the presence of La, were investigated by the means of diffusion bonding experiment, which followed by the first-principles calculations to clarify the fundamental effect mechanism of La on the Nb diffusion coefficients. Then, the precipitation kinetics was simulated by substituting the diffusion coefficients into a precipitation model, and the results were compared with the experimental data.

2. Experimental and Computational Approach

2.1. Diffusion Bonding Experiment

The materials used in the presence diffusion research consisted of four Fe based alloys, and the chemical compositions are shown in Table 1. The diffusion welding was applied to the NbFe-Fe bonding and NbFeLa-FeLa...
2.2. First Principles Methodology

The first-principles calculations based on the density functional theory is an appropriate method to investigate the interactions and diffusivity of solute atoms and consequently to understand the atomic mechanism involved. Here, to investigate the effect of La on the diffusion trends of Nb, the interactions of La with Nb in α-Fe were calculated, then the vacancy formation energies of Nb were studied by computing the vacancy formation energies and migration energies under the conditions that with and without La presence in the matrix.

The first-principles calculations presented here were performed with DFT as implemented in Vienna Ab Initio Simulation Package (VASP) with the projector augmented wave (PAW) method and the generalized gradient approximation of Perdew-Burke-Ernzerhof functional (GGA-PBE). All calculations were performed in spin polarized. The computations performed within a 4×4×4 supercell including 128 atoms. The binding, vacancy formation and migration energies were calculated with 350 eV plane-wave cutoff and 10×10×10 k-point meshes. The residual atomic forces in the relaxed configurations were lower than 0.01 eV/Å. The migration energies of Nb atom in α-Fe and the possible minimum energy paths (MEPs) are determined using nudged elastic band (NEB) method as implemented in VASP.

The interaction of two defects (solute or vacancy) is captured by the binding energy, which can be calculated by the following equation:

\[ E_{b}^{X-Y} = E(\text{Fe}_{N-1}, X) + E(\text{Fe}_{N-1}, Y) - E(\text{Fe}_{N-2}, X, Y) - E(\text{Fe}_{N}) \]  

where \( E(\text{Fe}_{N-1}, X) \) and \( E(\text{Fe}_{N-1}, Y) \) are the total energies of the supercell with the single defect of \( X \) and \( Y \), respectively, \( E(\text{Fe}_{N-1}, X, Y) \) is the total energy of the supercell containing both \( X \) and \( Y \), \( E(\text{Fe}_{N}) \) is the total energy of the pure α-Fe supercell, \( N \) is the number of the lattice sites. The sign convention whereby positive value of \( E_{b}^{X-Y} \) correspond to the favorable binding between the two defects.

In the present work, we study the diffusion process based on the assumption that the Nb diffusion is mediated by a vacancy mechanism. The activation energy of Nb diffusion in α-Fe involves the vacancy formation and migration energies, and can be obtained by:

\[ Q = E_{f}^{V} + E_{m}^{Nb} \]  

where \( E_{f}^{V} \) is the vacancy formation energy and \( E_{m}^{Nb} \) is the migration energy of Nb jumping to a first nearest neighbor (1nn) vacancy. The vacancy formation energy in the presence of a Nb atom is expressed by the following:

\[ E_{f}^{V} = E(\text{Fe}_{N-2}, \text{Nb}, V) - E(\text{Fe}_{N-1}, \text{Nb}) + \frac{1}{N} E(\text{Fe}_{N}) \]  

The vacancy formation energy of α-Fe supercell containing both Nb and La solute atoms can be obtained using the similar procedure:

\[ E_{f}^{V} = E(\text{Fe}_{N-3}, \text{Nb}, \text{La}, V) - E(\text{Fe}_{N-2}, \text{Nb}, \text{La}) + \frac{1}{N} E(\text{Fe}_{N}) \]  

2.3. Modeling of Precipitation Kinetics

The previous studies suggest that the heterogeneous nucleation plays a prominent role in carbide particles precipitation kinetics in the ferrite matrix, and the precipitation tends to occur on dislocations instead of in a homogeneous manner. The present precipitation model is based on the model by F. Perrard et al. The following assumptions are in this model: i) the precipitation is purely diffusion controlled, ii) precipitate particles are stoichiometric and spherical. The precipitation of NbC involves nucleation, growth and coarsening, we consider this precipitation process as two stages: i) the simultaneous nucleation and growth, ii) the simultaneous growth and coarsening.

2.3.1. Nucleation and Growth

Considering the probability that a solute atom diffuses to nucleate a precipitate or to join an existing precipitate, the nucleation rate can be expressed as:

\[ J_{n} = J_{c} \left[ 1 - \exp \left( -\frac{\Delta T}{\Delta t_{2}} \right) \right] \]  

where \( J_{n} \) and \( J_{c} \) are the time for a solute atom to form a nucleus and to feed an existing precipitate, respectively, and can be obtained by \( \Delta t_{2} = \rho \Delta t \) and \( \Delta t_{2} = d^{2} / 2D_{\text{Nb}}^{\text{dis}} \) in which \( \rho \) is the density of dislocations, \( d \) is the average distance between two precipitates and \( D_{\text{Nb}}^{\text{dis}} \) is the pipe diffusion coefficient of Nb along dislocations. \( J_{c} \) represents the steady nucleation rate of precipitate on dislocations, in which \( N_{0} \) is the number of nucleation sites, \( \Delta G^{\ast} \) is the activation energy of nucleation, \( k_{B} \) is the Boltzmann constant, and \( T \) is the
temperature. Z and $b'$ are the Zeldovich factor and condensation rate, respectively, and the expressions are

$$Z = \frac{V_{\text{NbC}}}{2\pi R^2} \sqrt{\frac{\gamma}{k_B T}} \quad \text{and} \quad b' = \frac{4\pi R^2 D_{\text{Nb}} X_{\text{Nb}}^c}{a^4}$$  \hspace{1cm} (6)

where $V_{\text{NbC}}$ and $\gamma$ denote the molecular volume of NbC and the interfacial energy of precipitate particles, respectively, $R$ is the critical radius of nucleation. $D_{\text{Nb}}$ is the diffusion coefficient of Nb in $\alpha$-Fe, $X_{\text{Nb}}^c$ is the concentration of Nb in the matrix, $a$ represents the lattice parameter of $\alpha$-Fe. The activation energy of nucleation, $\Delta G'$, can be obtained by:

$$\Delta G' = -\frac{16\pi \rho^3}{3\Delta g^3} \quad \text{and} \quad \Delta g = -\frac{k_B T}{V_{\text{NbC}}} \ln \left( \frac{X_{\text{Nb}}^c}{X_{\text{Nb}}^c} \right)$$  \hspace{1cm} (7)

where $\Delta g$ denotes the driving force for precipitation, $K^c$ denotes the solubility product of NbC in the matrix.

The precipitate radius evolution involves the growth rate of the existing NbC precipitates and the arrival of new nuclei at nucleation radius:

$$\frac{dR}{dt}_{\text{nb}} = \frac{dR}{dt}_{\text{b}} + \frac{1}{N} J_a (R^* - R)$$  \hspace{1cm} (8)

where the first term represents the real growth rate of NbC particles, and can be obtained by:

$$\frac{dR}{dt}_{\text{b}} = \frac{2}{3} \left( \frac{3}{8\sqrt{4R'}} \right)^{1/3}$$  \hspace{1cm} (9)

where $R'$ denotes the solubility product of NbC in the matrix.

2.3.2. Growth and Coarsening

In the regime of growth and coarsening, the nucleation rate decreases continuously with the decreasing of solute super saturation, and the coarsening fraction $f_{\text{coars}}$ is introduced to weight the evolutions of radius and density:

$$\frac{dN}{dt} = \left( 1 - f_{\text{coars}} \right) \frac{dN}{dt}_{\text{in}} + f_{\text{coars}} \frac{dN}{dt}_{\text{coars}}$$  \hspace{1cm} (10)

The coarsening fraction is expressed as

$$f_{\text{coars}} = \sup \left[ 1 - 100 \left( \frac{f_v}{f_{\text{eqGR}}} - 1 \right)^2 , 0 \right]$$  \hspace{1cm} (11)

where $f_{\text{eqGR}}$ is the equilibrium volume fraction. The growth rate for coarsening is

$$\frac{dR}{dt}_{\text{coars}} = \frac{4}{27} \frac{X_{\text{Nb}}^c R_{\text{Nb}} D_{\text{Nb}}}{V_{\text{NbC}} / X_{\text{Nb}}^c - X_{\text{Nb}}^c} \left( \frac{1}{R^2} \right) + 8\times 10^{-2} X_{\text{Nb}}^c R_{\text{Nb}} D_{\text{Nb}} b \left( \frac{1}{R^2} \right)$$  \hspace{1cm} (12)

2.3.3. Transition Criterion

To judge the transition from nucleation-growth stage to growth-coarsening stage, one can consider the criterion that the decrease of precipitate density caused by coarsening is larger than the nucleation rate:

$$\frac{dN}{dt} \bigg|_{\text{coars}} > J_a$$  \hspace{1cm} (13)

The detailed calculation procedures could be found in Ref. 21.

2.4. Precipitation Experiment

The materials used in the present work consist of two high-Nb steels, as listed in Table 2, the chemical compositions of these two steels are almost comparable except for the La content. The experimental steels were prepared by vacuum induction melting and cast into ingots. The ingots were homogenized at 1573 K for 2 h, and then hot rolled from 28 mm to 12 mm thickness. To assure Nb to be dissolved, the rolled materials were reheated to 1573 K for 45 min, and water quenched. To study the precipitation kinetics of NbC in $\alpha$-Fe, the samples were heat treated at 973 K for various times. The microstructure was characterized by the field emission scanning electron microscope (FESEM, ZEISS Supra 55) equipped with a nanometer probe energy dispersive spectrometer (EDS). The amount of Nb precipitated was measured by the inductively coupled plasma optical emission spectrometry (ICP-OES).

3. Result and Discussion

The concentrations of Nb atom in Fe (FeLa) sides of the diffusion bonds are listed in Table 3. The diffusion of Nb atom in Fe (FeLa) is equal to the diffusion in the semi-infinite rod and the concentration of Nb at the distance $x$ at a certain time $t$ can be obtained by the following equation:

$$C(x, t) = \frac{C_0}{2} \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right]$$  \hspace{1cm} (14)

where $C_0$ is the initial concentration of Nb in Nb contained

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Nb</th>
<th>P</th>
<th>S</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.043</td>
<td>0.086</td>
<td>0.007</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.042</td>
<td>0.087</td>
<td>0.007</td>
<td>0.005</td>
<td>0.0048</td>
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<table>
<thead>
<tr>
<th>Diffusion distance (µm)</th>
<th>Bond side</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1113 1128 1143 1158</td>
</tr>
<tr>
<td>3</td>
<td>Fe</td>
<td>FeLa</td>
</tr>
<tr>
<td></td>
<td>0.112</td>
<td>0.122 0.129 0.139</td>
</tr>
<tr>
<td></td>
<td>FeLa</td>
<td>0.126 0.131 0.124 0.135</td>
</tr>
<tr>
<td>6</td>
<td>Fe</td>
<td>FeLa</td>
</tr>
<tr>
<td></td>
<td>0.066</td>
<td>0.065 0.083 0.189</td>
</tr>
<tr>
<td></td>
<td>FeLa</td>
<td>0.059 0.083 0.095 0.110</td>
</tr>
<tr>
<td>9</td>
<td>Fe</td>
<td>FeLa</td>
</tr>
<tr>
<td></td>
<td>0.029</td>
<td>0.033 0.046 0.066</td>
</tr>
<tr>
<td></td>
<td>FeLa</td>
<td>0.032 0.049 0.063 0.068</td>
</tr>
<tr>
<td>12</td>
<td>Fe</td>
<td>FeLa</td>
</tr>
<tr>
<td></td>
<td>0.008</td>
<td>0.019 0.022 0.035</td>
</tr>
<tr>
<td></td>
<td>FeLa</td>
<td>0.015 0.024 0.041 0.051</td>
</tr>
</tbody>
</table>
sides of the diffusion bonds, $D$ is the diffusion coefficient of Nb. Equation (14) can be transformed to:

$$erf\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - \frac{2 C(x, t)}{C_0} \quad \text{............... (15)}$$

By supposing $\beta = \frac{x^2}{4D' t}$, and given $C(x, t)$, $C_0$, $x$ and $t$, the error function on the left side of Eq. (15) can be computed, then we determine the value of $\beta$ according to the error function table. The diffusion coefficient $D$ can be calculated consequently by:

$$D = \frac{x^2}{4\beta^2 t} \quad \text{............... (16)}$$

For the case of diffusion at a certain temperature, based on the data listed in Table 3, the diffusion coefficient can be obtained by taking the average of the calculated values of the different diffusion distances according to Eqs. (15) and (16).

The diffusion equation can be expressed in an Arrhenius form as:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad \text{............... (17)}$$

where $D_0$ and $Q$ are the pre-factor and activation energy, respectively, $R$ is the universal gas constant, $T$ is the absolute temperature. Taking the double logarithm of Eq. (17), we can deduce the following expression:

$$\ln D = \ln D_0 - \frac{Q}{RT} \quad \text{............... (18)}$$

Equation (17) shows a linear relationship between $\ln D$ and $1/T$, the slope and intercept of the linear plot give the values of activation energy $Q$ and pre-factor $D_0$.

In accordance with Eqs. (15) to (18), from the values of $D$ obtained at each temperature, $\ln D$ is plotted versus $1/T$ in Fig. 1. The straight lines in Fig. 1 are the linear fittings according to Eq. (18), along with the published experimental values of Nb diffusion coefficient in $\alpha$-Fe. For Nb diffusion in $\alpha$-Fe, the experimental values are slightly higher than those due to Oono et al.\textsuperscript{25} but in the comparable order of magnitude. In the case of the presence of La, the solute Nb diffuses somewhat faster than that in pure $\alpha$-Fe matrix. According to the fitting lines of these two sets of experimental data, the diffusion equations for Nb diffusion in pure $\alpha$-Fe and with the presence of La, respectively, can be obtained:

$$D = 7.1 \times 10^{-4} \exp\left(-\frac{243 143}{RT}\right) \quad \text{............... (19)}$$

$$D = 1.6 \times 10^{-4} \exp\left(-\frac{226 740}{RT}\right) \quad \text{............... (20)}$$

In order to better understand the effect mechanism of La on the diffusion behavior in $\alpha$-Fe, by using the first principles method, the interaction of La and Nb in bcc Fe matrix was calculated, as well as the activation energies of Nb diffusion with and without La presence.

The binding energies of Nb-vacancy, La-vacancy and La-Nb pairs were evaluated for the pairs in their 1nn and 2nn coordinate shells, and the results are listed in Table 4. The interaction of Nb-vacancy is attractive (0.23 eV) in 1nn configuration, but exhibits a small repulsion ($-0.09$ eV) in 2nn configuration, which is in good agreement with results due to Olsson and Gorbatov\textsuperscript{26,27} For the case of La-Nb pair, the calculations indicate that repulsive interactions exist in both 1nn and 2nn shells. Similar results have been reported by You et al.\textsuperscript{28} From Table 4 it can be seen that referring to the 1nn and 2nn configurations of La-vacancy pairs, the binding energies are all positive, which implies that attraction between La and vacancy in the both nearest neighbor shells. This behavior is related to the strain relief effect,\textsuperscript{29,30} i.e. placing an oversized solute atom in bcc Fe matrix induces a significant strain in the local area and a vacancy next to this solute helps to relieve the strain. Furthermore, the 1nn and 2nn distances are very close in the body-centered cubic lattice, which explains the relatively strong interaction of La-vacancy in 2nn configuration.

Based on the consideration of the equivalent positions of the nearest neighbor sites of a lattice site in the bcc structure, i.e. there are 8 1nn sites and 6 2nn sites around a lattice site, we investigated the effects of La on the Nb diffusion in the following situations: i) Nb atom is located at 1nn site of La atom, as shown on the left side of Fig. 2, we consider two different jumps of Nb atom to its adjacent vacancy, i.e. Nb atom jumps to the 2nn vacant site of La atom ($w_{1A}$) which is the nearest site among

<table>
<thead>
<tr>
<th>X-Y</th>
<th>$E_D^{2nn}$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>1nn</td>
<td>2nn</td>
</tr>
<tr>
<td>Nb-vac</td>
<td>0.23, 0.32\textsuperscript{20} 0.20\textsuperscript{27}</td>
</tr>
<tr>
<td>La-vac</td>
<td>0.66</td>
</tr>
<tr>
<td>La-Nb</td>
<td>-0.48, -0.54\textsuperscript{20}</td>
</tr>
</tbody>
</table>

\[\text{Table 4. Binding energies of solute-vacancy and solute-solute pairs in } \alpha\text{-Fe.}\]

Fig. 1. Plots of $\ln D$ vs. $1/T$ of Nb diffusion in $\alpha$-Fe and La containing $\alpha$-Fe, the symbols of square and triangle denote the experimental data, the solid and dashed lines are the corresponding fitting lines, and the dashed dot line is the published experimental data for Nb diffusion coefficient in $\alpha$-Fe.
the available target sites that Nb can diffuse to, and to the adjacent vacancy which is slightly farther away from La atom ($w_{1B}$), respectively; ii) Nb atom is located at 2nn site of La atom, as illustrated on the right side of Fig. 2, and two similar jumps ($w_{2A}$ and $w_{2B}$) are investigated.

The calculated vacancy formation, migration and diffusion activation energies are given in Table 5. In the case of La atom induced next to Nb atom in bcc Fe, the vacancy formation energy decrease from 2.28 eV to negative values (-0.10–0.18 eV). This suggests that the formation of vacancy is spontaneous in the local enrichment area of La and Nb which result from the non-equilibrium cooling process in α-Fe. For the migration energies, the values are predicted to increase in varying degrees compare with the Nb diffusion in pure α-Fe, i.e. from 0.16 eV to the range of 0.21–1.79 eV. For the four diffusion situations illustrated in Fig. 2, the binding energies of defect pairs should be taken into account. For the case of Nb-La in 1nn configuration, $w_{1A}$ represents the jump of Nb atom from 1nn site of La atom to 2nn of that, this process involves destroying the existing attractive interaction of 2nn La-vacancy (0.21 eV), and overcoming the repulsion of 2nn La-Nb (−0.29 eV), the sum of these two energies is bigger than the binding energy of 1nn Nb-vacancy. These lead to the higher migration energy of $w_{1A}$ (0.81 eV). For the case of $w_{1B}$, the trapping effect of La atom on the vacancy which is 3nn next to La atom, is relatively weak, as well as the interaction with Nb, which results in a smaller migration energy (0.44 eV) but still bigger than that in pure α-Fe. Based on the calculations of vacancy formation and migration energies, the activation energies of Nb in the presence of La show higher values, in the range of 0.11–1.64 eV, than that in pure α-Fe matrix, thanks to the negative vacancy formation energies.

In combination with the Nb diffusion coefficients obtained from the diffusion couple experiment, the precipitation model was applied to the two Nb containing steels presented in Table 2. For the diffusion coefficients of Nb in dislocation, we assume that the ratio of $D_{Nb \text{dis}}/D_{Nb}$ is 10². Table 6 presents a summary of the parameters used in this model.

Figure 3 shows the evolutions of the precipitate volume fraction and radius of NbC at 973 K calculated by the model, along with the experimental results. For the both steels, the model results are in good agreement with the experimental

### Table 5. Vacancy formation, migration and diffusion activation energies for Nb atom diffusion in α-Fe without and with the presence of La atom.

<table>
<thead>
<tr>
<th></th>
<th>$E_f^{Nb}$ (eV)</th>
<th>$E_m^{Nb}$ (eV)</th>
<th>$Q$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>2.28</td>
<td>0.16</td>
<td>2.47</td>
</tr>
<tr>
<td>Nb-La(1nn)-$w_{1A}$</td>
<td>−0.18</td>
<td>0.81</td>
<td>0.63</td>
</tr>
<tr>
<td>Nb-La(1nn)-$w_{1B}$</td>
<td>−0.13</td>
<td>0.44</td>
<td>0.31</td>
</tr>
<tr>
<td>Nb-La(2nn)-$w_{2A}$</td>
<td>−0.15</td>
<td>1.79</td>
<td>1.64</td>
</tr>
<tr>
<td>Nb-La(2nn)-$w_{2B}$</td>
<td>−0.10</td>
<td>0.21</td>
<td>0.11</td>
</tr>
</tbody>
</table>

### Table 6. The parameters used in the calculations of NbC precipitation kinetics.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>$a$</td>
<td>$2.86 \times 10^{-10} m$</td>
<td>31</td>
</tr>
<tr>
<td>$b$</td>
<td>$2.48 \times 10^{-10} m$</td>
<td></td>
</tr>
<tr>
<td>$K_{SNC} (wt%)$</td>
<td>4.33–9 830/T</td>
<td>32</td>
</tr>
<tr>
<td>$D_{Nb} (m^2/s)$</td>
<td>$7.1 \times 10^{-2} \exp (-243.143/RT)$</td>
<td>Present work</td>
</tr>
<tr>
<td>$D_{Nb \text{dis}} (m^2/s)$</td>
<td>$7.1 \times 10^{-2} \exp (-243.143/RT)$</td>
<td>Present work</td>
</tr>
<tr>
<td>$D_{Nb \text{doped}} (m^2/s)$</td>
<td>$1.6 \times 10^{-2} \exp (-226.740/RT)$</td>
<td>Present work</td>
</tr>
<tr>
<td>$D_{Nb \text{doped}} \text{disp} (m^2/s)$</td>
<td>$1.6 \times 10^{-2} \exp (-226.740/RT)$</td>
<td>Present work</td>
</tr>
<tr>
<td>$\gamma (J/m^2)$</td>
<td>0.5</td>
<td>33</td>
</tr>
<tr>
<td>$\rho (m^{-2})$</td>
<td>$2 \times 10^{14}$</td>
<td>17</td>
</tr>
<tr>
<td>$V_{SNC} (m^3/mol)$</td>
<td>$1.28 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$V_{f} (m^3/mol)$</td>
<td>$7.09 \times 10^{-6}$</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Schematic illustration of distinct jumps of Nb atom to the adjacent vacancies in the presence of La atom in α-Fe.

Fig. 3. Evolutions of the precipitate volume fraction (a) and radius (b) at 973 K calculated by the model, along with the experimental data, the solid and dashed lines are resulted from the model.
data. Due to the fact that the diffusion coefficient of niobium is very small than that of carbon, the former factor plays a major role in NbC precipitation process. According to the results of the above diffusion investigation, the diffusion activation energy of Nb is found to be decreased in the presence of La in α-Fe. This leads to the faster diffusivity of Nb, and consequently relatively fast precipitation rate of NbC in La containing steel.

4. Conclusions

In present study, the diffusion coefficients of Nb in α-Fe have been determined by the diffusion couple technique. It is found that Nb diffuses slightly faster in the presence of La than it in pure α-Fe. The atomic effect of La on the diffusivity of Nb was investigated by using the first-principles calculations based on the vacancy-mediated diffusion mechanism. There are repulsive interactions exist between La and Nb in both 1nn and 2nn configurations, and it could be expected that the formation of vacancy is spontaneous in the La-Nb clustering area since the negative vacancy formation energies in the presence of La. Theses result in the decrease of activation energy of Nb in La microalloyed ferritic steel. Finally, the precipitation of NbC was described by using the model of precipitation kinetics, which takes into account the diffusion coefficients of Nb in the situation of with and without La presence. The model simulation results reveal that the addition of La leads to faster precipitation kinetics of NbC in ferritic steel. The microstructure evolution of the model is in good agreement with the experimental data.

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