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Atomistic simulations of diffusion mechanisms in off-stoichiometric Al-rich Ni₃Al

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Abstract

This paper presents dynamics simulation results of diffusion in off-stoichiometric Al-rich Ni₃Al (Ni₇₃Al₂₇) at temperature ranging from 1300 to 1550 K. The interatomic forces are described by the Finnis–Sinclair type N -body potentials. Particular attention is devoted to the effect of the extra 2% of Al atoms sitting on the Ni sublattice as antisite point defects (Al_{Ni}) on diffusion. Simulation results show that Ni atoms mainly diffuse through the Ni sublattice at the temperatures investigated. Al atoms diffuse via both the intrasublattice and antistructure bridge (ASB) mechanisms. The contribution to Al diffusion from the ASB mechanism decreases at the lower temperature ($T < 1400$ K). The presence of antisite point defects (Al_{Ni}) enhances both Al and Ni diffusion in Ni₇₃Al₂₇. The Ni–Al coupled diffusion effect is observed and understood at the atomic level for the first time.

1. Introduction

Although diffusion and defects in stoichiometric Ni₃Al have been extensively studied both experimentally [1–20] and theoretically [21–28], relatively little work has been done at off-stoichiometric composition [29–32].

The experimental results of the composition dependence of Ni diffusion in Ni₃Al by Hoshino *et al* [32] and Shi *et al* [31] show that the diffusion of Ni at high temperatures ($T > 1300$ K) is independent of the Ni concentration over the composition range of 73–77 at.% Ni; while a minimum is found at stoichiometry or close to stoichiometry at lower temperature ($T < 1300$ K) and becomes more pronounced as the temperature decreases.

Due to the rarity and expensiveness of the ²⁶Al isotope, direct measurement of the tracer diffusion of Al in Ni₃Al is difficult. Only experimental results by Larikov *et al* [4] are doubtful because the Ni diffusion data measured in the same experiment are higher than results estimated by other researchers. The research has been devoted to studying Al diffusion in Ni₃Al with

Al substitute elements [29]. The most recent intrinsic diffusion [31] and interdiffusion [32] and experiments show that Al diffusivity is lower than Ni by a factor of 0.2–0.3 and increases monotonically with the concentration of Al. Numakura *et al* [6] explain the monotonic trend observed for Al in Ni₃Al in the framework that Al atoms diffuse as impurity atoms in the Ni sublattice, and Al diffusivity is proportional to the concentration of the Ni vacancies and Ni antisites (Al_{Ni}).

Athènes *et al* modelled diffusion in the $L1_2$ ordered structure of wide composition range (A₇₃B₂₇–A₇₇B₂₃) using the Monte Carlo method [27]. The simulations show that vacancy–antisite interactions contribute to the diffusion of the minority species B; the antisite-assisted sequence also enhances the diffusion of the majority species A in the B-rich composition. Bilova *et al* found in Monte Carlo simulations that Ni and Al diffusion is coupled in the presence of antisite defects [28].

Despite this experimental and theoretical research already bringing good understanding of the diffusion behaviour in Ni₃Al, there is still a theoretical thrust to understand more. For example, the diffusion mechanisms of off-stoichiometric Ni₃Al are still not clear at atomic level.

With a desire to tackle the above problems, we perform molecular dynamics simulations of diffusion mechanisms in off-stoichiometric Al-rich Ni₃Al (Ni₇₃Al₂₇) at the temperature region (1300–1550 K) with constant concentration of point defects. The emphasis is put on the effect of the extra 2 at.% of Al atoms sitting on the Ni sublattice as antisite defects on the diffusion of both Ni and Al atoms in Ni₇₃Al₂₇. This paper is also the extension of the previous paper on dynamics simulations of diffusion in stoichiometric composition. The rest of the paper is organized as follows. The theory and methods are described in section 2. The results and discussion are presented in section 3. The conclusions are drawn in section 4.

2. Theory and methods

2.1. Diffusion description

The simulation method applied in the simulations has been extensively discussed in the previous paper [43]. Here is the major point summarized. There are four types of point defects in Ni₃Al. They are Ni and Al vacancies, Ni_v and Al_v, in the Ni and Al sublattices, respectively; and Al atoms sitting on the Ni sublattice as the Ni antisite defects Ni_{Al} or vice versa. The simplest diffusion process via the vacancy mechanism occurs by a jump of an atom to one of its nearest vacant lattice sites. Such a jump is an elementary jump. There are six possible elementary jumps of Ni and Al in Ni₃Al, as illustrated in figure 1. The Ni vacancy can jump within the Ni sublattice (Ni + V_{Ni} → Ni + V_{Ni}); the Ni atom can also jump onto an Al vacancy site creating a Ni antisite (Ni + V_{Al} → V_{Ni} + Ni_{Al}), or a Ni antisite jumps back to a Ni vacancy via an ordering jump (V_{Ni} + Ni_{Al} → Ni + V_{Al}). Similarly, Al atoms have six Ni sublattice sites as the nearest neighbour sites. Thus, Al atoms can jump through the Ni sublattice via a Ni vacancy (V_{Ni} + Al_{Ni} → V_{Ni} + Al_{Ni}), or do a disordering jump (Al + V_{Ni} → V_{Al} + Al_{Ni}) or an ordering jump (Al_{Ni} + V_{Al} → Al + V_{Ni}). All possible diffusion mechanisms in Ni₃Al known thus far can be decomposed into the above six elementary jumps. In other words, diffusion mechanisms in Ni₃Al can be described by one or a combination of several elementary jumps. The molecular dynamics code is modified in such a way that the six possible jumps can be recorded in the dynamics simulations. However, the code is not limited to monitoring the nearest neighbouring jumps; other possible jumps such as Al atoms migrating through the Al sublattice (the next nearest neighbouring jump) can be snapshot as well. The diffusion mechanisms can be quantified by analysing the trajectories of the MD simulations. For

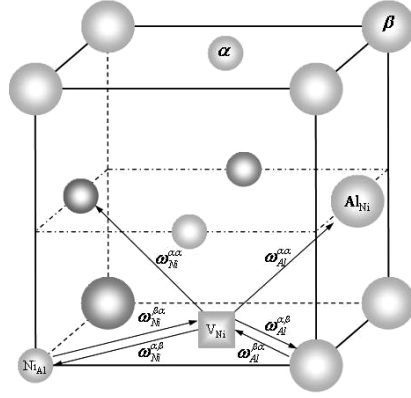


Figure 1. The unit cell of Ni_3Al . Ni atoms occupy Ni sublattices (denoted as α), Al atoms occupy Al sublattices (denoted as β). $\omega_{\text{Ni}}^{\alpha\alpha}$ is the jump of a Ni atom from one α sublattice site to another α sublattice site. $\omega_{\text{Ni}}^{\alpha\beta}$ is the jump of a Ni atom from an α sublattice site to a β sublattice site. $\omega_{\text{Ni}}^{\beta\alpha}$ is the jump of a Ni atom from a β sublattice site to an α sublattice site. The notes for Al atoms have analogous meanings.

example, the intrasublattice (Intra.) mechanism consists of a series of jumps of the same atom through the same lattice site. The antistructure bridge (ASB) mechanism happens via two successive intersublattice jumps. If the total number of a particular diffusion event i present is n_i in a molecular dynamics simulation trajectory having a total of N atomic jumps, then the probability of this diffusion event i is n_i/N .

Manning [33] defined the diffusion coefficient for each atomic species (D_i^*) in a multi-component system and the Einstein equation is applied to each of them directly without considering the specific diffusion mechanism,

$$D_i^* = \langle \vec{R}_i^2 \rangle / 6t, \quad (1)$$

where $\langle \vec{R}_i^2 \rangle$ is the mean square displacement for atomic species i and t is the diffusion time.

The simulated self-diffusion data for Ni and Al are fitted to the Arrhenius law

$$D_i^* = D_i^0 \exp(-E_m / \kappa_B T) = D_0^{\text{NiNi}} \exp(-E^{\text{NiNi}} / \kappa_B T) + D_0^{\text{NiAl}} \exp(-E^{\text{NiAl}} / \kappa_B T), \quad (2)$$

where D_i^* and E_m are the pre-exponential factors and the migration energies, respectively. E^{NiNi} and E^{NiAl} are the migration energies for the Intra. and Inter. sublattice jump, respectively. Thus, E_m is the average value including contributions from different jumps. κ_B is the Boltzmann constant and T is the absolute temperature.

To have a detailed insight into the particular diffusion mechanism, the pre-exponential frequency factor γ_{mech}^0 and the migration energy E_{mech} are obtained by fitting the jump frequency data to the Arrhenius law,

$$\Gamma_{\text{mech}} = \gamma_{\text{mech}}^0 \exp(-E_{\text{mech}} / \kappa_B T). \quad (3)$$

2.2. Simulation procedure

A simulation block is cubic in shape and has $10 \times 10 \times 10$ unit cells, that is 4000 atoms. According to the thermodynamics calculation [43], the thermal equilibrium concentration of Ni and Al vacancies in $\text{Ni}_{73}\text{Al}_{27}$ is of the order of 10^{-4} and 10^{-6} in the temperature range of 1400–1550 K, respectively. The extra 2% Ni antisites (Al_{Ni}) have been introduced, which is equal to 80 Al atoms. They are separated as far as possible through the Ni sublattice. One

Table 1. The Arrhenius parameters for diffusion of Ni in Ni₃Al.

| Self-diffusion coefficient | | Intra. mechanism | | ASB mechanism | |
|--|---------------|---|---------------|---|---------------|
| $D_0 \times 10^6$ (m ² s ⁻¹) | E_m (eV) | $\Gamma_0 \times 10^{14}$ (s ⁻¹) | E_m (eV) | $\Gamma_0 \times 10^{16}$ (s ⁻¹) | E_m (eV) |
| 5.83 ± 2.02 | 1.12 ± 0.05 | 3.05 ± 0.67 | 1.27 ± 0.03 | — | 1.52 ± 0.46 |

Ni vacancy is also introduced, which is the same as the thermal equilibrium concentration of 10^{-4} Ni vacancies at the temperature range of 1400–1550 K. No Al vacancy is introduced in the first place, since its thermal equilibrium concentration is very low for the simulation box. In MD simulation, the simulation block with one Ni vacancy and antisite defects is adjusted to its thermal equilibrium volume (i.e., the lattice parameter is increased from 3.567 Å at 0 K to 3.687 Å at 1550 K), corresponding to simulation temperatures in the range of 1400–1550 K with intervals of 50 K and an additional one at 1300 K and relaxed. It should be noted that the initial defect structure in Ni₇₃Al₂₇ is designed to be the same for all temperatures simulated. This is still a good approximation for such a simulation block. The periodic boundary condition is employed. The MD simulations are carried out by heating the system from 0 K to the desired temperature and equilibrating at this temperature until the number of antisite defects reaches a dynamic equilibrium. Production dynamics simulations were then performed for a reasonably long trajectory, from which averages are computed. The simulation time depends on the simulation temperature and jump frequencies of defects, but usually takes more than 30 ns with the timestep of 0.8 fs to simulate 3000 vacancy jumps at 1400 K, for example. The trajectories are integrated with the predictor–corrector algorithm. There are two main classes of n -body central potentials based on either the ‘embedded-atom method’ (EAM) of Daw and Baskes [34] or the method of Finnis and Sinclair (FS) [35]. Foiles *et al* [36] and Vitek *et al* [37] parameterized the Ni–Al system using the EAM and the FS model, respectively. Gao and Bacon [38, 39] modified Vitek’s interatomic potential [37]. The results were compared with those obtained by Caro *et al* [40] using the EAM interatomic potential. These modified FS type interatomic potentials are also used in other research [41–43]. In the previous simulations [44], the energy barriers for the elementary jumps and the diffusion mechanisms in Ni₃Al are calculated; the results obtained using two types of interatomic potentials, namely, the EMA and the modified FS model, agree qualitatively. In the present simulations, the modified interatomic potential [38, 39] is applied.

3. Results and discussion

3.1. Temperature dependence of Ni and Al diffusion in Ni₇₃Al₂₇

The Ni and Al self-diffusion coefficients are calculated with equation (2) at each simulation temperature when the system reaches the thermal equilibrium. The temperature dependences of the Ni and Al self-diffusion coefficients, D_{Ni}^* and D_{Al}^* , are plotted over the temperatures simulated, as shown in figure 2. The jump frequencies for each particular diffusion mechanism are calculated. These diffuse data are fitted into the Arrhenius law. The estimated pre-exponential factors and migration energies are presented in table 1. The Ni diffusion data including self-diffusion coefficient and the intrasublattice jump frequency can be fitted into the Arrhenius law with good accuracy. The antistructure bridge jump frequency, however, cannot be fitted with good accuracy. It can be seen from table 1 that the migration energy for Ni self-diffusion in Ni₇₃Al₂₇ (1.12 ± 0.05 eV) is very close to that for the intrasublattice jump

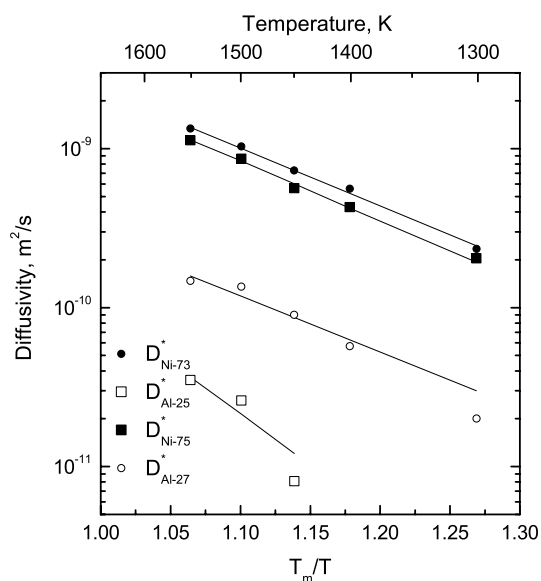


Figure 2. The molecular dynamics simulated temperature dependence of the Ni and Al diffusion coefficient per unit vacancy in $\text{Ni}_{73}\text{Al}_{27}$. The simulation results for $\text{Ni}_{75}\text{Al}_{25}$ are also presented for comparison.

(1.27 ± 0.03 eV). The fact suggests that Ni atoms in $\text{Ni}_{73}\text{Al}_{27}$ mainly diffuse via the Intra. mechanism. As stated in section 3.2, diffusion of Ni in $\text{Ni}_{73}\text{Al}_{27}$ occurs mainly through the Ni sublattice, which forms a penetrating structure. Therefore, the correlation factor for Ni diffusion, f_v , can be estimated with caution using $f_v = D^*/D_v$, which is initially defined for the random alloys, where D_v is the self-diffusion coefficient for the vacancy. The correlation factor for Ni diffusion in $\text{Ni}_{73}\text{Al}_{27}$ is estimated to be 0.72 ± 0.05 . This value is close to 0.688 in $\text{Ni}_{75}\text{Al}_{25}$, indicating that Ni diffusion in these two compositions follows a similar mechanism—the Intra. mechanism.

Due to lack of statistics, it is hard to fit Al self-diffusion data into the Arrhenius law with a good accuracy. However, they are also presented in figure 2 for information. But the Al self-diffusion coefficient is lower than the Ni self-diffusion coefficient by an order of magnitude. The migration energy for Al in both $\text{Ni}_{73}\text{Al}_{27}$ and $\text{Ni}_{75}\text{Al}_{25}$ is 1.06 ± 0.262 eV and 2.14 ± 0.97 eV, respectively. These values are estimated roughly due to the limited statistics but could be used as an informative reference. Compared with that of Ni diffusion, it seems a big difference for Al diffusion in both cases. As defined in equation (2), the migration energies for Al estimated in the dynamics simulations are the average values including the contributions from various diffusion mechanisms such as the Intra. and ASB mechanisms. The contribution to diffusion from Al diffusion accounts for up to 25%, of which 61% is the Intra. jumps, in $\text{Ni}_{73}\text{Al}_{27}$, compared with 6%, of which 10% is the Intra. jumps, in $\text{Ni}_{75}\text{Al}_{25}$ at the temperature of 1300 K. Moreover, it is difficult to observe Al diffusion when the temperature is below 1400 K in $\text{Ni}_{75}\text{Al}_{25}$. Thus, the migration energy for Al in both cases is significantly different. While the Ni diffusion is predominated with the Intra. mechanism in both cases, the migration energy for Ni diffusion in both cases is very close.

In order to understand the effect of an extra 2% of Ni antisite defects on Ni and Al diffusion in $\text{Ni}_{73}\text{Al}_{27}$, the Ni and Al self-diffusion data obtained from the simulations of diffusion in $\text{Ni}_{75}\text{Al}_{25}$ [43] are also presented in figure 2 for comparison. It can be seen in figure 2 that the

Table 2. Statistical results of Ni and Al diffusion in $\text{Ni}_{73}\text{Al}_{27}$.

| Temp. (K) | Ni | | | Al | |
|--------------|----------------|---------------|------------|---------------|------------|
| | Tot. Ni (%) | Intra. (%) | ASB (%) | Intra. (%) | ASB (%) |
| 1550 | 74.00 | 92.00 | 1.08 | 39.00 | 21.40 |
| 1500 | 75.00 | 92.00 | 1.44 | 43.00 | 14.30 |
| 1450 | 78.00 | 91.00 | 0.95 | 36.00 | 21.10 |
| 1400 | 74.00 | 87.00 | 0.65 | 48.00 | 17.20 |
| 1300 | 74.00 | 89.00 | 0.33 | 61.00 | 3.50 |

Ni self-diffusion coefficient in $\text{Ni}_{73}\text{Al}_{27}$ is 15–20% higher than that in $\text{Ni}_{75}\text{Al}_{25}$ depending on the temperature. In contrast, the Al self-diffusion coefficient in $\text{Ni}_{73}\text{Al}_{27}$ is at least four times as high as that in $\text{Ni}_{75}\text{Al}_{25}$. These results indicate that Ni and Al self-diffusion in $\text{Ni}_{73}\text{Al}_{27}$ must be enhanced somehow. To get a deeper insight into this phenomenon, Ni and Al diffusion mechanisms in $\text{Ni}_{73}\text{Al}_{27}$ are analysed in detail in section 3.2.3.

3.2. Diffusion mechanisms in $\text{Ni}_{73}\text{Al}_{27}$

3.2.1. Ni diffusion mechanisms in $\text{Ni}_{73}\text{Al}_{27}$. I try to identify these jumps which contribute to diffusion in $\text{Ni}_{73}\text{Al}_{27}$. The molecular dynamics simulation trajectories consisting of a series of elementary jumps are analysed using a code developed to exhaustively track and sort information pertaining to all possible mechanisms occurring during the dynamics simulations. An elementary jump can be categorized into either the intrasublattice jumps or the intersublattice jumps. Given that the information regarding the intrasublattice is known, the information about intersublattice jumps is also available. The intrasublattice jumps for Ni atoms, for example, are Ni atoms migrating through the Ni sublattice. The ASB mechanism for Ni atoms consists of two intersublattice jumps happening successively. As a result, the proportions of different types of jumps, such as the Intra. and ASB jump of both Ni and Al atoms at different temperatures, are listed in table 2. The data are calculated as follows. The second column is the Ni atom jumps as a percentage of the total atomic jumps. The third and fourth columns are the Intra. jumps and ASB jumps as percentages of the number of total Ni atom jumps, respectively. Since the summation of the number of Ni atom and Al atom jumps is the total number of atomic jumps, the information about Al atom jumps is not listed for brevity. The data for Al atoms (listed in table 2) have analogous meaning.

As shown in table 2, Ni atom diffusion accounts for around 75% of the total number of atomic jumps in $\text{Ni}_{73}\text{Al}_{27}$ depending on the temperatures simulated. Around 90% of the total number of Ni atom jumps are the intrasublattice jumps in which Ni atoms diffuse through the Ni sublattice, which is a three-dimensional penetrating sublattice as shown in figure 1. Fewer than 1% of the total number of Ni atom jumps are the ASB jump of two successive Ni atom jumps starting with an ordering jump ($\text{Ni}_{\text{Al}} + \text{V}_{\text{Ni}} \rightarrow \text{V}_{\text{Al}} + \text{Ni}$) followed by a disordering jump ($\text{Ni} + \text{V}_{\text{Al}} \rightarrow \text{Ni}_{\text{Al}} + \text{V}_{\text{Ni}}$) as illustrated in figure 3. The other jumps are the order and disordering jumps.

It can be concluded that the intrasublattice and antistructure bridge jump promote Ni atom diffusion in $\text{Ni}_{73}\text{Al}_{27}$ and do not change the order of the crystal.

3.2.2. Al diffusion mechanisms in $\text{Ni}_{73}\text{Al}_{27}$. The statistics of different types of Al atom jumps are presented in table 2. The number of Al atom jumps accounts for approximately

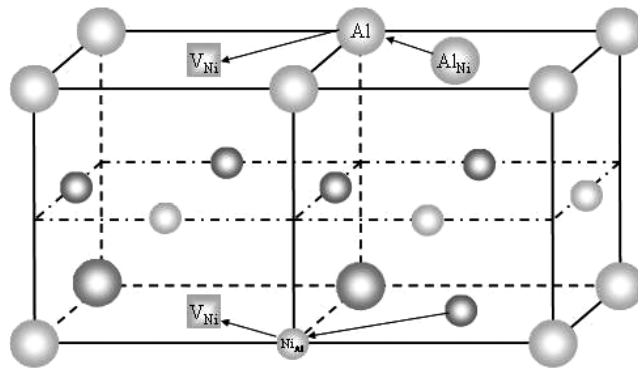


Figure 3. A scheme of the atomic arrangements according to the antistructure bridge mechanism in Ni_3Al . The above is the ASB jump for Al atoms. The vacancy first exchanges with a regular atom on the Al sublattice and then with an antisite as follows: $V_{\text{Ni}} + \text{Al} \rightarrow \text{Al}_{\text{Ni}} + V_{\text{Al}}$, $V_{\text{Al}} + \text{Al}_{\text{Ni}} \rightarrow V_{\text{Ni}} + \text{Al}$; these exchanges include displacements of two Al atoms. The extra antisite Al_{Ni} created by the first jump is eliminated by the second jump, so that the initial order is restored. The bottom is the ASB jump for Ni atoms, having analogous meanings.

25% of atomic jumps in the simulated temperatures in $\text{Ni}_{73}\text{Al}_{27}$ in comparison with 10% in $\text{Ni}_{75}\text{Al}_{25}$ [44]. Al atoms diffuse by both the Intra.mechanism and ASB mechanism, accounting for 40–60% and 15–20% of total atomic jumps, respectively. The summation of the intrasublattice and ASB jumps accounts for around 60% of the total Al atomic jumps in the temperature and composition investigated; however, the Intra.mechanism becomes significantly predominant at lower temperature ($T < 1400$ K), as shown in table 2. As mentioned before, both the ASB and Intra.diffusion mechanisms of Al diffusion are proportional to the concentration of the Ni antisite defects and the Ni vacancy. Therefore, it is reasonable to conclude that diffusion of Al atoms is enhanced by the presence of 2 at.% Ni antisite defects given that the concentration of the Ni vacancy is fixed in present simulations.

3.2.3. Al–Ni coupled effect in diffusion in $\text{Ni}_{73}\text{Al}_{27}$. The primary interest of this paper is focused on the role of the extra 2% of antisite point defects in diffusion in $\text{Ni}_{73}\text{Al}_{27}$. As mentioned in section 3.1, diffusion of Ni atoms in $\text{Ni}_{73}\text{Al}_{27}$ is faster by about 15%–20% than that of Ni in $\text{Ni}_{75}\text{Al}_{25}$, indicating that transport of the Ni vacancy must be enhanced in some way. Meanwhile, it is interesting to note that the percentage of Al diffusion increases up to about 25% of the total atomic jumps in $\text{Ni}_{73}\text{Al}_{27}$, in comparison with 10% in $\text{Ni}_{75}\text{Al}_{25}$. The probability of the Intra.and ASB mechanism for Al diffusion is proportional to the concentrations of the Ni vacancy and the Ni antisite defect. Given that the concentration of the Ni vacancy is constant in the present simulations, it is clear that the presence of the extra 2 at.% of Al atoms on the Ni sublattice as the anti-site defects contributes to the enhancement of the Al diffusion via both the ASB mechanisms and the Intra.mechanism. As illustrated in figure 3, when the ASB jump of Al atoms finishes, a Ni vacancy is transported by one lattice parameter. Similarly, the Ni vacancy can also be transported by $\sqrt{2}/2$ lattice parameters via the Intra.mechanism, where Al atoms diffuse on the Ni sublattice. The link between Ni and Al diffusion can be made through the Ni vacancy, which is shared by diffusion of both Ni and Al. Consequently, the diffusion of Ni atoms in $\text{Ni}_{73}\text{Al}_{27}$ is enhanced via the fast transportation of Ni vacancies as a result of the enhanced ASB and Intra.jumps of Al atoms. Belova *et al* [28] reported a similar result obtained from Monte Carlo simulation, that the diffusion of both components in the ordered compounds of $L1_2$ structure is closely coupled

in the presence of certain amount of antisite defects. Athènes *et al* found in Monte Carlo simulations of diffusion in A_3B binary alloys having $L1_2$ order structure that A diffusion can be enhanced by the presence of A_β antisites [27]. As for the B-rich side, this allows the impurity mechanism to operate and results in enhancement of both A and B diffusion. The molecular dynamics simulation results presented here agree with those of Athènes [27] and Belova *et al* [28] quantitatively. But here is provided for the first time a clear picture of the Al–Ni coupled effect in diffusion in off-stoichiometric composition at the atomic level. It should be noted that the effect of the thermal equilibrium concentration of the Ni vacancy on diffusion in $Ni_{73}Al_{27}$ has not been involved in the present simulations. This allows me to focus on the effect of the extra 2 at.% of Al atoms on Ni and Al diffusion in $Ni_{73}Al_{27}$. The Al–Ni coupled effect might shed new light on understanding of the composition dependence of Ni diffusion in γ' -phase Ni_3Al . As a natural extension of the current study, diffusion in Ni-rich Ni_3Al will be discussed in the subsequent paper.

4. Conclusions

Diffusion in ordered alloy $Ni_{73}Al_{27}$ at elevated temperatures (1300–1550 K) is simulated with molecular dynamics using the Finnis–Sinclair interatomic potential. An innovative methodology is developed to study diffusion mechanisms in ordered binary alloy with deviation from stoichiometric composition. The results are very informative and instructive since the experimental investigations are really limited especially in the off-stoichiometric composition. The following are the major conclusions drawn from this work.

- (1) The migration energies for the Ni self-diffusion and individual diffusion mechanisms are estimated by fitting the diffusion data to the Arrhenius law. Due to limited statistic results in Al diffusion, the simulated diffusion data cannot be fitted with good accuracy. However, they still serve as a useful reference when the Al experimental data are unavailable.
- (2) Ni atoms mainly diffuse by the Intra. mechanism in $Ni_{73}Al_{27}$. Ni atom diffusion in $Ni_{73}Al_{27}$ is enhanced with the fast *diffusion* of Ni vacancies as a result of the Intra. and ASB jumps of Al atoms. Al atoms diffuse by both the Intra. mechanism and ASB mechanism in off-stoichiometric $Ni_{73}Al_{27}$. The presence of the extra 2 at.% of Ni antisite defects plays an important role in accelerating Al diffusion. This is the first time that the Al–Ni coupled diffusion effect has been explained at atomic level in off-stoichiometric Al-rich Ni_3Al .
- (3) The results from the current research are helpful to understand the composition dependence of Ni and Al diffusion in off-stoichiometric Ni_3Al , and motivate further study.

The controversial results of Shi *et al* [30] and Hoshino *et al* [31], where the Ni minimum diffusivity was found at 76% and 75% respectively when temperature was below 1000 K, are still a mystery. The continuous effort in simulations of diffusion in Ni_3Al at low temperature, say $T < 1000$ K, will eventually reveal the mechanisms for diffusion of Ni and Al, which will be useful for our understanding of the temperature and composition dependence of diffusion in Ni_3Al .

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