Pt diffusion in B2-type ordered NiAl intermetallic compound and its diffusion mechanisms

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Received 30 November 2000; accepted 5 December 2000

Abstract

Diffusion of platinum element which increase protectivity of NiAl layer for hot corrosion and oxidation of Ni-base superalloys was investigated in NiAl compound with compositions of 43.7–51.9 at\% Al at 1373–1673 K by the diffusion couple method. The diffusion coefficients, \(D_{\text{Pt}}\), exhibit a large concentration dependence of valley type-shape; the \(D_{\text{Pt}}\) has the minimum value quite near the stoichiometric composition and it increases with deviation from the stoichiometry. On the other hand, the activation energy, \(Q\), shows the maximum value near the stoichiometry. \(Q\) slightly decreases with Ni composition in Ni-rich side, while it decrease dramatically with Al composition in Al-rich side. Diffusion of platinum element in NiAl occurs mainly by the Triple defect mechanism at stoichiometry, by the anti-site atom bridge mechanism in considerably off-stoichiometry in Ni-rich side and by the next nearest neighbor-jump mechanism with constitutional Ni vacancies in quite off-stoichiometry in Al-rich side. © 2001 Published by Elsevier Science Ltd.

Keywords: Intermetallic compound; NiAl; Platinum; Diffusion; Activation energy; Frequency factor; Ordering; Vacancies; Divacancy; Anti-site atoms; Triple defects; Nearest neighbor jumps; Next nearest neighbor jumps

1. Introduction

NiAl compound has the highest melting temperature of 1911 K among the compounds in Ni-Al system and retains the ordered structure of B2-type up to its melting point [1]. Aluminide coatings with the NiAl phase alloy are used to extend the life of Ni-base superalloys because it contains a light element of aluminum up to about half of composition, which forms good protective oxide films for the high- and low-temperature hot corrosion resistances. This intermetallic aluminide coating is formed by the AI-diffusion coating methods such as the chemical vapor deposition, slurry spraying and sintering, and especially pack-cementaion exposing the Ni-based superalloys surface to an aluminum-rich environment at elevated temperatures [2]. In addition, it has been reported that the addition of elements such as platinum to the diffusion aluminide coating layers increases the protectivity under hot corrosion and oxidation environments; a aluminum–platinum-type coating is made by first electrolytically depositing a platinum layer less than 10 μm thick, then pack aluminizing to substrate [3]. The microstructure of aluminum–platinum-type coating layers formed by diffusion reaction during aluminizing are as follows, although it depends on the factors of temperature, time, amount of Pt and Al; a continuous PtAl\(_2\) surface layer, two phase region of PtAl\(_2\) + NiAl(Pt in solution), single phase region of NiAl(Pt), typical inner interdiffusion region of substrate and Ni base superalloy. Furthermore, the degradation process for coatings is closely related to the diffusion phenomena of platinum and constituent atoms in the above region. Thus, the diffusion phenomena in the Ni base superalloys and the NiAl compound coating layers are one of the important factors for controlling the hot corrosion and high temperature oxidation resistances. However, the Pt diffusion in NiAl has not been reported yet, and the diffusion data are not enough in NiAl and Ni base superalloys. Therefore, we have reported the diffusion of Pt element in Ni matrix phase alloys (γ) and NiAl compound (γ') which are main and basic phases of Ni base superalloy, as well as the diffusion data of the other elements [4–12]. On the other hand, it is worthwhile to investigate the diffusion of platinum in NiAl compound, because the diffusion data have been limited to the elements of Ni, In and Co elements in NiAl [13–16].

In a perfect crystal of NiAl compound with the B2-type ordered structure at stoichiometry, the Ni atoms occupy the body-centered sites (referred so as α-sites) while the Al atoms occupy the corner sites (β-sites) of the unit cell as...
shown in Fig. 1. In this ordered structure, the jumps of Al or Ni atoms to vacancies at the nearest neighbor (nn) sites inevitably bring about a local disordering since different kinds of atoms on α- and β-sites surround each other. Therefore, some diffusion-complicated mechanisms such as 6 jumps vacancy cycle (6JVC) mechanism have been presented until now. For example, the 6JVC mechanism requires a single vacancy to make a sequence of six correlated nn jumps mutually between α- and β-sites in order to keep the local disordering as small as possible, and it produces a quite complicated defect cluster in the high configuration energy state due to the high ordering energy of NiAl during its diffusion process. It is very hard to consider the complicated diffusion mechanism such as the 6JVC one as the responsible mechanism for diffusion in NiAl.

Either two vacancies at α- and β-sites, \( V^{(\alpha)} \) and \( V^{(\beta)} \), must be formed (one on each site) to maintain the stoichiometry, that is a balanced number of sites on each sublattice at stoichiometry [17]. Such pair of vacancies in NiAl as well as ordered B2 intermetallics of group-VIII transition metals and group-IIIIB elements forms a triple defect (TD) structure which consists of two \( V^{(\alpha)} \)'s and an antisite Ni atom on the β-site, \( Ni^{(\beta)} \) [18]. Moreover, over wide ranges of homogeneity of NiAl as large as about 28 at%, the kinds and amount of defects change drastically with deviations from the stoichiometric composition [17]; mainly constitutional \( Ni^{(\beta)} \)'s in the Ni-rich side and constitutional \( V^{(\alpha)} \)'s in Al-rich side, although there exist various types of defects, \( V^{(\alpha)} \), \( V^{(\beta)} \), \( Ni^{(\beta)} \), Al antisite atoms, \( Al^{(\beta)} \) and some complicated defects. Since the diffusion behaviors depend not only on the kinds and amount of defects but also on their mobilities, the diffusion mechanisms should be considered especially from the point of view of the contributions of various kinds of defects on diffusion.

The purposes of this research are to measure the diffusion behavior of Pt as the important added element in NiAl compound over wide range of concentrations, and to throw light on the diffusion mechanisms in NiAl compound with B2 type ordered structures.

In this experiment, the diffusion coefficients of Pt in NiAl were obtained by the diffusion couples which consist of the NiAl compound and the NiAl one with very dilute concentration of Pt; (NiAl)/(NiAl–Pt) couples. When compared with the tracer method in which the diffuse element of Pt is deposited on the surface of NiAl and after annealing the diffusion profiles are measured near the surface of sample, the advantages of the diffusion couple method in which the dilute element of Pt dissolved in NiAl diffuse in to the NiAl compound and after annealing the diffusion profiles are measured in inner part of diffusion couples are as follows: (1) measurement of the diffusion profiles in inner part of diffusion couples avoids the effect of the evaporation of constituent elements of NiAl on diffusion; especially, in tracer method, Al composition near the surface of NiAl decreases by the evaporation, and this decrease is more serious in the Al-rich region, for example, the composition in inner part is Al-rich while that near the surface is stoichiometry; (2) to avoid reactions between the deposited Pt and NiAl; in the diffusion couple of (NiAl)/(NiAl–Pt) there is no formation of some compounds layer which constitute a barrier against diffusion fluxes, and no melt of Pt on the surface of NiAl which penetrates into NiAl matrix; (3) to avoid the trapping and diffusion barrier by the oxide layer on the surface of NiAl which are severe problems in the tracer method.

2. Experiments

Six kinds of ingots of NiAl compound and other six kinds of ingots of NiAl–Pt compound containing about 1 at% Pt were made by melting high-purity metals of 99.97 mass% Ni, 99.993 mass% Al and 99.95 mass% Pt more than seven times with overturning the ingots in an argon arc furnace. For homogeneity, each ingot was crushed to fine pieces after the arc-melting, and then these fine pieces were remelted to the ingots by the repeated arc-melting more than seven times with overturning. The ingots were cut into alloy bars of about 10 × 10 × 50 mm³. The NiAl and NiAl–Pt bars were sealed into quartz capsules with argon gas about 20 kPa and then annealed at 1573 K for 108–151 ks for homogenization. After the homogenization, the capsules were cooled in air to prevent the possible breakage of the compounds by thermal shock. The homogeneity of ingots was verified by a metallurgical optical microscope and an electron probe microanalyzer (EPMA). The compositions of the compounds which were measured by the chemical analysis are listed in Table 1.

The blocks of 5 × 5 × 1.5 mm³ were cut from the compound bars, and their surface was polished metallographically with 0.3 μm alumina powder. Immediately, the diffusion couples were made from the compound blocks by using a diffusion bonding apparatus; each couple was heated to 1273 K at the rate of 2.8 K/s under the vacuum of 4 × 10⁻⁴ Torr and then pressed with the loading of about 10 kN for 330 ks. After the bonding, the couples were cooled to room temperature at the rate of 2.8 K/s. The combination of compounds in diffusion couples are listed in Table 1. The aluminum concentration of
each compound in the diffusion couples is similar to each other.

The diffusion couples were sealed into quartz capsules with Ar gas, whose pressure was 90 kPa at annealing temperatures, and then annealed at 1373–1673 K for 14.4–604.8 ks. After the diffusion annealing, the silica capsules were cooled in air for 0.36 ks, and subsequently broken in ice-water; this procedure prevented the possible breakage of the compounds by thermal shock. The annealed diffusion couples were mounted in quick-mount resin and sectioned parallel to the diffusion direction. The sections were polished with 0.3 μm alumina powder. The X-ray spectra of \( L_\alpha \), X-radiations of Pt and \( K_\alpha \) lines of Al were measured on the polished surface of diffusion couples parallel to the diffusion direction for concentration profiles by the EPMA. These X-ray intensities were converted to the concentrations by the ZAF method [19].

The interdiffusion in ternary Ni–Al–Pt alloys are defined by Fick’s first law as follows [20]:

\[
\begin{align*}
\dot{J}_\text{Pt} &= -D_{\text{PtPt}}^{\text{Ni}} \frac{\partial C_{\text{Pt}}}{\partial x} - D_{\text{PtAl}}^{\text{Ni}} \frac{\partial C_{\text{Al}}}{\partial x}, \\
\dot{J}_\text{Al} &= -D_{\text{AlPt}}^{\text{Ni}} \frac{\partial C_{\text{Pt}}}{\partial x} - D_{\text{AlAl}}^{\text{Ni}} \frac{\partial C_{\text{Al}}}{\partial x},
\end{align*}
\]

where \( \dot{J}_\text{Pt} \) and \( \dot{J}_\text{Al} \) are the interdiffusion fluxes of elements Pt and Al (Ni is the solvent); \( C_{\text{Pt}} \) and \( C_{\text{Al}} \), the concentrations of elements Pt and Al; \( D_{\text{PtPt}}^{\text{Ni}} \) and \( D_{\text{PtAl}}^{\text{Ni}} \), the direct coefficients; \( D_{\text{AlPt}}^{\text{Ni}} \) and \( D_{\text{AlAl}}^{\text{Ni}} \), the indirect coefficients; and \( x \), the distance from Matano interface. When the molar fraction of element Pt, \( N_{\text{Pt}} \), goes to zero, the following relations are given [10]:

\[
\begin{align*}
\lim_{N_{\text{Pt}} \to 0} D_{\text{PtPt}}^{\text{Ni}} &= D_{\text{PtPt}}^{\text{Ni}(\text{NiAl})}, \\
\lim_{N_{\text{Pt}} \to 0} D_{\text{PtAl}}^{\text{Ni}} &= 0.
\end{align*}
\]

According to Eqs. (3) and (4), the direct coefficient \( D_{\text{PtPt}}^{\text{Ni}} \) in the NiAl compound becomes equal to the tracer diffusion coefficient of element Pt in the NiAl compound, \( D_{\text{PtPt}}^{\text{Ni}(\text{NiAl})} \), and the indirect coefficient \( D_{\text{PtAl}}^{\text{Ni}} \) becomes zero for very dilute concentration of Pt. Furthermore, since the aluminum concentration of each compound in the diffusion couples are designed to be similar to each other as shown in Table 1, the concentration gradient of Al, \( \partial C_{\text{Al}}/\partial x \), in Eq. (1) is fairly small. Therefore, the interdiffusion flux of element Pt in Eq. (1) becomes simple for \( C_{\text{Pt}} \approx 0 \)

\[
\dot{J}_{\text{Pt}} = -D_{\text{PtPt}}^{\text{Ni}(\text{NiAl})} \frac{\partial C_{\text{Pt}}}{\partial x}.
\]

Since Eq. (5) has the same shape of diffusion equation for binary alloys, Hall’s method which evaluate the diffusion coefficient by analysis of the end of the diffusion profiles can be applied to the diffusion profiles in the dilute concentration range of element Pt in the ternary Ni–Al–Pt alloy [21].

In Hall’s method, the diffusion profiles are presented in terms of a relative concentration variable, \( C_{\text{Pt}}', \) defined by

\[
C_{\text{Pt}}' = \frac{C_{\text{Pt}} - C_{\text{Pt}}^{-\infty}}{C_{\text{Pt}}^\infty - C_{\text{Pt}}^{-\infty}}
\]

\[
C_{\text{Pt}}' = \frac{1}{2} \left[ 1 + \text{erf}(kh^{1/2} + k) \right],
\]

where \( C_{\text{Pt}}^{-\infty} \) and \( C_{\text{Pt}}^\infty \) are the terminal concentrations of element Pt in the diffusion couples (in this research, they are 0 at% Pt and about 1 at% Pt), \( t \) is the diffusion time, \( h \) and \( k \) are the slope and intercept of the straight line on the probability paper respectively when \( C_{\text{Pt}}' \) of diffusion profiles are plotted against \( x/t^{1/2} \) on the probability paper. The diffusion coefficient is given by

\[
D_{\text{Pt}}(C_{\text{Pt}}')_{(\text{NiAl})} = \frac{1}{4h^2} + \frac{k\sqrt{\pi}}{2h^2} \exp(u^2)(1 + \text{erf}(u)).
\]

Eq. (7) can be applied only to the linear end portions of lines near the terminal concentrations, and it becomes simple when \( x \) goes to \( \pm \infty \) at the end of diffusion profiles as follows [22]:

\[
D_{\text{Pt}}(C_{\text{Pt}}')_{(\text{NiAl})} = \frac{1}{(2h^*^*)^2}
\]

\[
D_{\text{Pt}}(C_{\text{Pt}}')_{(\text{NiAl})} = \frac{1}{(2h^*)^2},
\]

where \( h^* \) and \( h^* \) are the slopes of two straight lines. In this study, the application of Eq. (8) to the end of diffusion profiles in the very dilute region of element Pt [near 0 at% Pt] yields realistic estimates of the \( D_{\text{Pt}}(C_{\text{Pt}}')_{(\text{NiAl})} \) as indicated by Eq. (3).

3. Results

Fig. 2 shows, by way of example, the diffusion profiles of Pt and Al elements in the NA47 couple annealed at 1523 K for 86.4 ks and the NA50 couple at 1523 K for 259.2 ks. The diffusion profiles are plotted as a function of \( x/t^{1/2} \) to compare the diffusion profiles of the different diffusion times. The Al concentrations in both couples are almost constant, while the Pt concentrations exhibit the typical S-curves, in which the Pt element diffuses from the ternary NiAl–Pt compound into the binary NiAl one. The diffusion
distance of Pt element in the NA47 couple is longer than that in the NA50 couple. This indicates that the Pt element diffuses faster in NA47 couple than in NA50 one, that is, the diffusion rates largely depend on the Al concentration. Fig. 3 shows the probability plot of $C_{\text{Pt}}^{t}$ in the NA47 couple annealed at 1448 K for 259.6 ks as an example of analysis by Hall’s method. The plots have a small curvature near $C_{\text{Pt}}^{t} = 0.5$, but they exhibit two straight lines through each set of points near the terminal compositions of 0 and about 1 at% Pt. From the slope of the straight line near 0 at% Pt, the $D_{\text{Pt}}(0)_{\text{(NiAl)}}$ at $C_{\text{Pt}} = 0$ in NiAl compounds were determined by Eq. (8). As mentioned above, these $D_{\text{Pt}}(0)_{\text{(NiAl)}}$ are equivalent to the $D_{\text{Pt}}^{*}_{\text{(NiAl)}}$ according to Eq. (3), and so they are hereafter denoted as $D_{\text{Pt}}$ for simplicity.

Fig. 4 shows the concentration dependence of $D_{\text{Pt}}$ of this study. The $D_{\text{Pt}}$ exhibit the concentration dependence of valley-type shape; the $D_{\text{Pt}}$ at 49.7 at% Al have the smallest values at various temperature, and the $D_{\text{Pt}}$ increase with the deviation from the chemically stoichiometric composition. The valleys of $D_{\text{Pt}}$ near the stoichiometric composition are not deep, and they become shallower with increasing diffusion temperatures. This suggests that the diffusion mechanisms at stoichiometry would have somewhat simple diffusion processes and their activation energies would not be far from that expected from random diffusion. Fig. 5 shows the comparison of diffusion coefficients of $D_{\text{Pt}}$ at 1523 K with the diffusion coefficients of Ni, Co and In elements evaluated from the previous data [13–16]. Their variations are similar to each other. However, the concentrations exhibiting minimum diffusion coefficients, $C_{\text{min}}$, for Pt diffusion and In diffusion by Minamino et al. are quite near the stoichiometric composition, while the $C_{\text{min}}$ of In, Co and Ni locate in the Al-rich region. This inconsistency is due to the evaluation of the composition of the sample. The compositions of samples for Pt and In diffusion by Minamino et al. were measured by the chemical analysis, while the evaluation method for the sample compositions was not written in the paper of In diffusion by Lutze-Birk and Jacobi [14] and the sample compositions of the researches on Ni diffusion by Hancock and Macdonnell [13] and Co diffusion by Berkowitz et al. [15] were estimated by the comparison between the specimen’s density or X-ray lattice spacing measurements of the diffusion samples and the density- or lattice parameter-composition curves given by Bradley and Taylor (in 1939) [23] which exhibited the maximum lattice parameter at about 50.5 at% Al. Recently, Chang and Neuman [24] reviewed the experimental data on lattice parameters and showed the lattice parameter has the maximum value at the stoichiometric composition. In addition, Miracle [17] also observed the physical properties of NiAl, and he pointed out that surface oxidation and subsequent Al depletion of annealed NiAl powders has been.
proposed to account for a peak in the lattice constant away from stoichiometry, and it has been noted that longer annealing times at higher temperatures were typically used in X-ray studies which report a maximum in the lattice constant displaced from stoichiometry. Taylor and Doyle (in 1972) reinvestigated the lattice parameters and obtained new results which have the maximum at 50.05 at% Al which is quite near the stoichiometric composition [25]. We revalued the $C_{\text{min}}$ of In, Co and Ni diffusion by the other researchers by using the data renewed by Taylor and Doyle, and found that the $C_{\text{min}}$ of In [14], Co [15] and Ni [13] diffusion shifts to the stoichiometric composition. Therefore, it is concluded that the minimum in the diffusion coefficients at each temperatures locates quite near or at the stoichiometric composition.

Fig. 6(a) and (b) show the temperature dependences of the $D_{\text{Pt}}$. The $D_{\text{Pt}}$ of this study satisfy the following Eq. (9) and fall on straight lines:

$$D_i = D_0 \exp \left( \frac{-Q}{RT} \right).$$

where $Q$ is the activation energy of diffusion of element $i$ in NiAl; $D_0$ the frequency factor, $T$ the absolute temperature and $R$ is the gas constant. The gradients of the straight lines become gentler with the deviation from the stoichiometric compositions. The $Q$s and $D_0$s evaluated from the temperature dependence of the $D_{\text{Pt}}$s are listed in Table 2, and they are drawn in Fig. 7(a) and (b), together with the previous data of $Q$s and $D_0$s of Ni, In and Co in NiAl [13–16]. The $Q$s have the maximum values of 299 kJ/mol at 49.7 at% Al for Pt diffusion, 307 kJ/mol at 50 at% Al for Ni, 337 kJ/mol at 49.3 at% Al for Co and 243 kJ/mol at 50 at% Al for In. In the Ni-rich region, the $Q$s gently decrease to 230 kJ/mol with the deviation from the stoichiometric composition to 43 at% Al, while in the Al-rich region they rapidly decrease to 250 kJ/mol at 52 at% Al.

Table 2: Activation energies and pre-exponential factors of diffusion in NiAl

| at% Al | $Q$ (kJ/mol) | $D_0$ ($\mathrm{m^2/s}$) | $T$ (K) |
|-------|--------------|--------------------------|--------|
| 40.6  | 290          | $5.2 \times 10^{-4}$     | 1423–1623 |
| 44.7  | 311          | $1.1 \times 10^{-3}$     | 1423–1623 |
| 48.0  | 322          | $9.8 \times 10^{-4}$     | 1423–1623 |
| 49.4  | 336          | $2.0 \times 10^{-3}$     | 1423–1623 |
| 50.5  | 311          | $4.6 \times 10^{-4}$     | 1523–1623 |
| 51.4  | 274          | $4.4 \times 10^{-5}$     | 1523–1623 |
| 52.3  | 271          | $1.6 \times 10^{-4}$     | 1523–1623 |

4. Discussion

The Pt and Co atoms preferentially occupy the Ni sites, while In atoms preferentially substitute Al atoms in NiAl [26,27]. In order to comprehend the diffusion behavior of Pt element in NiAl, it is requisite and useful to discuss the diffusion mechanisms of Ni and Al elements because it can be expected that the diffusion of Pt and Co atoms is similar to that of Ni atoms, and diffusion of In is about equivalent to that of Al atoms.

4.1. Diffusion jumps in NiAl at the stoichiometric composition

In the stoichiometric NiAl with B2-type ordered structure, the random jumps of constituent atoms to nn sites inevitably bring about the local disordering because the different kinds of atoms on α- and β-sites surround each other. If a lot of such jumps would occur in the stoichiometric NiAl, the NiAl should become a random alloy. But, the NiAl retains the ordered structure even up to its melting point in fact, although the diffusion jumps are fairly active at
such high temperatures. Therefore, special diffusion processes should be operative to maintain the ordered structure even up to high temperatures.

In the stoichiometric NiAl, thermal \( V^{(a)} \) and \( V^{(b)} \) must be generated in pairs to conserve stoichiometry. The formation energies, \( H_f \), for \( V^{(a)} \) and \( V^{(b)} \) were respectively obtained to be 71 and 190 kJ/mol with a combination of statical mechanics and with ab initio electron theory by Mishin and Farkas [28]. Some of vacancies exist as the isolated vacancies, and others form divacancies whose \( H_f \) is 255 kJ/mol because of small binding energy of 6 kJ/mol [28]. The isolated \( V^{(a)} \) and \( V^{(b)} \) in divacancy are metastable due to their higher \( H_f \) of 190 kJ/mol. The \( H_f \) for an \( Ni^{(b)} \) was also calculated to be 71 kJ/mol [28], and therefore the \( H_f \) of the \( V^{(a)} \) paired with nn-\( Ni^{(b)} \) (referred to as \( V^{(a)}(Ni^{(b)}) \)) is about 143 kJ/mol because the binding energy between \( V^{(a)} \) and \( Ni^{(b)} \) is \(-1 \) kJ/mol. This \( H_f \) of \( V^{(a)}(Ni^{(b)}) \) is lower than 190 kJ/mol of \( V^{(b)} \). So, most of the \( V^{(b)} \)s are transformed to a \( V^{(a)} \) paired with a nn \( Ni^{(b)} \) by exchange between the \( V^{(b)} \) and a Ni atom at its nn \( \alpha \)-site [28,29], and most of divacancies are also transformed to TD, consisting of \( Ni^{(b)} \) and two \( V^{(a)} \)s [24,30,31]. The Al\( ^{(a)} \)s also exist at the stoichiometry according to Kim et al. [32]. The \( H_f \) for Al\( ^{(a)} \) was evaluated to be 228 kJ/mol [28]. However, the number of Al\( ^{(a)} \) is quite small because the \( H_f \) of Al\( ^{(a)} \) is quite high [18,28]. Thus, there exist the thermal isolated \( V^{(a)} \)s, \( V^{(b)} \)s, \( Ni^{(b)} \)s, Al\( ^{(a)} \)s and the specific kinds of defect complexes such as \( V^{(a)}(Ni^{(b)}) \)s, divacancies and the TD in the stoichiometric NiAl.

The \( Q \) of diffusion at stoichiometric composition is the difference in the energies of a perfect NiAl crystal and a NiAl crystal with an atomic configuration in the activated state of diffusion. The \( Q \) is the sum of the formation energy of defects, \( H_f^{\text{defect}} \), and migration energy of defects, \( H_m^{\text{defect}} \), as follows:

\[
Q = H_f^{\text{defect}} + H_m^{\text{defect}}. \tag{10}
\]

The \( Q \)s for diffusion by the jumps due to various defects are evaluated by Eq. (10), and they are listed in Table 3. For example, in the case where a \( V^{(b)} \) and Al\( ^{(a)} \) at the next nearest neighbor (nnn) \( \beta \)-site exchange to each other in the stoichiometric NiAl (referred to as nnn \( V^{(b)} \)-jump), the \( H_f^{\text{defect}} \) must be the sum of \( H_f \)s for thermal \( V^{(a)} \) and \( V^{(b)} \) because the \( V^{(a)} \) and \( V^{(b)} \) must be generated in pairs to conceive stoichiometry. On the other hand, the \( H_m^{\text{defect}} \) is the migration energy for the nnn \( V^{(b)} \)-jump. As mentioned later, this \( Q \) is 425 kJ/mol (JP-7 in stoichiometric NiAl in Table 3).

The isolated \( V^{(a)} \)s have four possible diffusion jump processes as shown in Fig. 8; the 6JVC mechanism (referred to as JP-1), nnn jump (JP-2) [33–35], nn jumps (JP-3) and the exchange between the \( V^{(a)} \) and Al\( ^{(a)} \)(JP-4).

In the case of JP-1 as shown in Fig. 8(a), a single vacancy is required to make a sequence of six correlated mutual nn jumps between \( \alpha \)- and \( \beta \)-sites in order to keep the local disordering as small as possible. The first half of the sequent six vacancy jumps brings about a complicated defect cluster consisting of one \( Ni^{(b)} \), two Al\( ^{(a)} \)s and one \( V^{(b)} \). However this complicated defect cluster is in the high configuration energy state, because the ordering energy of the NiAl is quite high. After the later half of jumps, the number of defects and the ordering is returned to the original state, but the Ni atom exchanges the site with the nnn \( V^{(a)} \), and two Al atoms replace the site each other. When the JP-1 operates in stoichiometric NiAl, the Al and Ni diffusion are closely correlated to each other. As shown in Fig. 8(a), the defects concerned are a \( V^{(a)} \) which contributes the 6JVC and a \( V^{(a)}(Ni^{(b)}) \) which is necessary from the conservation for stoichiometry. Therefore, the \( H_f^{\text{defect}} \) is the sum of the 71 kJ/mol for \( V^{(a)} \) and 143 kJ/mol for \( V^{(a)}(Ni^{(b)}) \) [28], and the \( H_m^{\text{defect}} \) for \( V^{(a)} \) during the 6JVC process was calculated to be
|        | $H_i$ (kJ/mol) | $H_m$ (kJ/mol) | $Q$ (kJ/mol) |
|--------|----------------|----------------|---------------|
| NiAl   |                |                |               |
| JP-1   | $2 \times 71$  | $71$           | $1$           |
| JP-2   | $2 \times 71$  | $71$           | $1$           |
| JP-3   | $71$           | $71$           | $1$           |
| JP-4   | $2 \times 71$  | $71$           | $1$           |
| JP-5   | $2 \times 71$  | $71$           | $1$           |
| JP-6   | $71$           | $71$           | $1$           |
| JP-7   | $71$           | $71$           | $1$           |
| JP-8   | $71$           | $71$           | $1$           |
| JP-9a  | $71$           | $71$           | $1$           |
| JP-9b  | $71$           | $71$           | $1$           |
| JP-10a | $71$           | $71$           | $1$           |
| JP-10b | $71$           | $71$           | $1$           |
| Ni-rich|                |                |               |
| JP-1   | $107$          | $107$          | $107$         |
| JP-2   | $107$          | $107$          | $107$         |
| JP-3   | $107$          | $107$          | $107$         |
| JP-4   | $107$          | $107$          | $107$         |
| JP-5   | $107$          | $107$          | $107$         |
| JP-6   | $107$          | $107$          | $107$         |
| JP-7   | $107$          | $107$          | $107$         |
| JP-8   | $107$          | $107$          | $107$         |
| JP-9a  | $107$          | $107$          | $107$         |
| JP-9b  | $107$          | $107$          | $107$         |
| JP-10a | $107$          | $107$          | $107$         |
| JP-10b | $107$          | $107$          | $107$         |
| Al-rich|                |                |               |
| JP-1   | $0$            | $261$          | $85$          |
| JP-2   | $0$            | $261$          | $85$          |
| JP-3   | $0$            | $261$          | $85$          |
| JP-4   | $0$            | $261$          | $85$          |
| JP-5   | $0$            | $261$          | $85$          |
| JP-6   | $0$            | $261$          | $85$          |
| JP-7   | $0$            | $261$          | $85$          |
| JP-8   | $0$            | $261$          | $85$          |
| JP-9a  | $0$            | $261$          | $85$          |
| JP-9b  | $0$            | $261$          | $85$          |
| JP-10a | $0$            | $261$          | $85$          |
| JP-10b | $0$            | $261$          | $85$          |

236 kJ/mol [29]. From these values, the $Q$ for JP-1 is evaluated to be 450 kJ/mol as listed in Table 3. The JP-2 is the exchange between a $V^{(a)}$ and one of six Ni atoms at nn sites (nn $V^{(a)}$-jump) as shown in Fig. 8(b). This direct exchange by the nn jump can occur without the disordering. When the JP-2 operates, the Ni atom diffuse independently of Al diffusion. In this jump process, the $V^{(a)}$ has to pass through the saddle point consisting of four Al atoms with the large radius. Its $H_f^{\text{defect}}$ was also calculated to be 200 kJ/mol [29]. The $Q$ of diffusion by the JP-2 is evaluated to be 414 kJ/mol, because the $H_f^{\text{defect}}$ is also the sum of 71 kJ/mol for $V^{(a)}$ and 143 kJ/mol for $V^{(a)} (Ni^{(b)})$. The JP-3 is the nn exchange between a $V^{(a)}$ with low $H_f$ and one of Al atoms at nn sites as shown in Fig. 8(c). This exchange forms a $V^{(b)}$ and Al($^{(a)}$, $H_f^S$ is higher than those of $V^{(a)}$. Therefore, the sum of 190 kJ/mol for $V^{(b)}$, 228 kJ/mol for Al($^{(a)}$, and 143 kJ/mol for $V^{(a)} (Ni^{(b)})$ should be considered as the $H_f^{\text{defect}}$ for this exchange. The value of $H_f^{\text{defect}}$ of JP-3, unfortunately, has not been reported yet. However, it could be roughly estimated as follows. In the limited space surrounded with 26 Ni atoms like a cage, one vacancy and eight Al atoms form the body centered cubic (bcc) crystal of Al. The jump of vacancy by JP-3 in such limited space can be considered to be almost equivalent to the jumps of vacancy in the bcc Al. According to Gorecki [36], the ratio of $Q_s$ for random diffusion in bcc and fcc structure metals is 3/4,

$$Q_{bcc}/Q_{fcc} = 3/4.$$  

(11)

By using this relation, the $H_f^{\text{defect}}$ of nn jump in bcc Al can be estimated to be 45 kJ/mol from the experimental value of 60 kJ/mol for nn-jump in the face centered cubic (fcc) Al [37]. From this value, the $Q$ is obtained to be 606 kJ/mol. The Al diffusion by JP-3 is quite difficult due to the high $Q$. The JP-4 is the nn exchange of $V^{(a)}$ and Al($^{(a)}$, as shown in Fig. 8(d). When the JP-4 operates, the Al atoms diffuse
independently of Ni diffusion. The \( Q \) for diffusion by JP-4 is more than 441 kJ/mol because the \( H_m^{\text{defect}} \) is 441 kJ/mol as the sum of 228 kJ/mol for \( V^{(\alpha)} \) and \( V^{(\beta)} \) (Ni\(^{\beta}\)) and 71 kJ/mol for \( V^{(\alpha)} \). The \( H_m^{\text{defect}} \) for nnn jump of Al atom through saddle point formed by four Al atoms is similar to 200 kJ/mol by JP-2 (nnn jump of Ni atom through the saddle point formed by four Al atoms) and 164 kJ/mol by JP-7 (nnn jump of Al atom through the saddle point formed by four Ni atoms as mentioned later). Therefore, the \( Q \) of JP-4 is estimated to be about 605–641 kJ/mol. These evaluated values are too high when compared with the experimental \( Q \)s of about 300 kJ/mol.

The \( V^{(\alpha)} \) (Ni\(^{\beta}\)) makes two types of exchanges (JP-5 and JP-6) as shown in Fig. 9(a) and (b). The JP-5 is the nnn exchange between the \( V^{(\alpha)} \) and one of the Ni atoms at nnn-sites, while the JP-6 is the nnn exchange between the \( V^{(\alpha)} \) and adjacent Ni\(^{\beta}\). When the JP-5 or JP-6 operates, the Ni atoms diffuse independently of Al diffusion. The \( H_m \) of the JP-5 may be about equal to or somewhat lower than 200 kJ/mol of JP-2, because the saddle point through which the \( V^{(\alpha)} \) jumps to one of nnn sites in the Ni cage consists of one Ni atom with small radius and three Al atoms with large radius instead of four Al atoms. The \( Q \) for diffusion by JP-5 is estimated to be slightly less than 414 kJ/mol by JP-2. In the JP-6, the \( V^{(\alpha)} \) (Ni\(^{\beta}\)) exchanges with the adjacent Ni\(^{\beta}\), and it transforms to the \( V^{(\beta)} \) which is metastable due to its higher \( H_b \). The value of \( H_m^{\text{defect}} \) of JP-6 can be also estimated by Eq. (11). The nnn jump of vacancy by JP-6 is considered to be similar to a jump in a bcc Ni, also because the eight Ni atoms and one vacancy form the bcc structure in the limited space surrounded with twenty six Al atoms with large atomic radius. The \( H_m^{\text{defect}} \) of nnn jump in bcc Ni can be estimated to be 100 kJ/mol from the experimental 133 kJ/mol for nnn jump in the fcc Ni [37]. Therefore, the \( Q \) for diffusion by JP-6 is 361 kJ/mol as the sum of the 71 kJ/mol for \( V^{(\alpha)} \), 190 kJ/mol for \( V^{(\beta)} \) and 100 kJ/mol for \( H_m^{\text{defect}} \) of nnn-jump.

By the way, the \( V^{(\alpha)} \) in the Al cage have possibilities to jump out of the Al cage by JP-2, while the \( V^{(\beta)} \) in the Al cage transfers to the next Al cage by nnn-exchange (JP-7) with one of six Al atoms at the nnn-\( \beta \)-sites as shown in Fig. 9(c). The \( Q \) of JP-2 is 414 kJ/mol as mentioned above, and the \( Q \) of JP-7 is 425 kJ/mol as the sum of the \( H_m^{\text{defect}} \) for nnn jump (164 kJ/mol [29]) and the \( H_f^{\text{defect}} \) (71 kJ/mol for \( V^{(\alpha)} \) and 190 kJ/mol for \( V^{(\beta)} \)). The JP-7 for Al diffusion is quite less possible because of its high \( Q \) as well as the JP-2. Therefore, the vacancy in the Al cage is almost unable to escape from the Al cage, that is, it continues to make sequent exchange of JP-6 in the limited space surrounded with twenty six Al atoms with large atomic radius, and there is no effective diffusion by the JP-6.

As shown in Fig. 10(a), one of nnn jumps (JP-8) by each of two \( V^{(\alpha)} \)s in a TD produce a divacancy consisting of \( V^{(\alpha)} \) and \( V^{(\beta)} \) in the Al cage The next exchange by JP-8 in the Al cage reforms one of various TD’s including the original TD. Thus, the two vacancies repeat to jump to one of sites in the Al cage, in similar ways to the JP-6. However, the \( H_m^{\text{defect}} \) related to divacancy is lower than that of single vacancy, and it can be also evaluated to be 59 from 79 kJ/mol of divacancy migration in fcc Ni by Eq. (11). Therefore, the \( Q \) for diffusion by JP-8 is 314 kJ/mol which is slightly less than the 361 kJ/mol of JP-6. The \( V^{(\beta)} \) of divacancy makes
other exchanges (JP-9a and 9b) as shown in Fig. 10(b) and (c). The $V^{(b)}$ exchanges one of six Al atoms at nnn $\beta$-sites: the jump to one of three $\beta$-sites (JP-9a) or three $\beta$-sites adjacent to the $V^{(a)}$ of the divacancy (JP-9b). By the JP-9a the TD dissolves into an isolated $V^{(a)}$ and an isolated $V^{(b)}$. The JP-9a is quite similar to the JP-7, and its $Q$ by JP-9a is about equal to the high value of 425 kJ/mol of JP-7. On the other hand, the JP-9b is the exchange between the $V^{(b)}$ and Al atoms adjacent to the $V^{(a)}$. The $E_{m}^{defect}$ of JP-9b is quite lower than that of the JP-7 because one of the four atoms in

![Diagram](image-url)
the configuration at saddle point is missing. The $H_{\text{m}}^{\text{defect}}$ for JP-9b can be also estimated by Eq. (11). The $H_{\text{m}}^{\text{defect}}$ for divacancy in fcc Al were reported to be 40 kJ/mol [37]. From this value, the $H_{\text{m}}^{\text{defect}}$ for bcc Al are estimated to be 30 kJ/mol. Therefore, the $Q$ of JP-9b is 285 kJ/mol as the sum of 71 kJ/mol for $V^{(a)}$, 190 kJ/mol for $V^{(b)}$, the binding energy of 6 and 30 kJ/mol of $H_{\text{m}}^{\text{defect}}$, and it is fairly lower than 425 kJ/mol of JP-7 and JP-9a. Because of this low $Q$, the $V^{(b)}$ continues to jump around the $V^{(a)}$. However, the combination of JP-8 and JP-9b allows the TD to migrate freely. This exchange process is the TD mechanism presented by Stolwijk et al. [38]. The $Q$ of diffusion by TD with mutual JP-8 (314 kJ/mol) and JP-9b (285 kJ/mol) is about 314 kJ/mol because the jump process with the high $Q$ is the rate-controlling one.

In addition to above jumps, the anti-structure bridge (ASB) mechanism was given by Kao and Chang [39] as shown in Fig. 10(d) and (e). In the ASB mechanism, two nn jumps of vacancy construct the nn jump, n4 jump, or n6 jump in the unit cells with the bridges formed by structural $N_{\text{ASB}}$ through which the vacancies can migrate. Hereafter, the ASB mechanism with $N_{\text{ASB}}$ is referred to as Ni-ASB or Al-ASB respectively. The $Q$s of diffusion by the ASB mechanism with $n \times Al^{(a)}$ (JP-10a, Al-ASB) or $n \times Ni^{(a)}$ (JP-10b, Ni-ASB) are, respectively, the sum of $H_{\text{m}}^{\text{defect}}$, $n \times H$ for $n \times Al^{(a)}$, $H_{f}$ for $V^{(b)}$ and $H_{i}$ for $V^{(a)}$, or the sum of $H_{\text{m}}^{\text{defect}}$, $(n+1) \times H_{f}$ for $(n+1) \times N_{\text{ASB}}$ and $2 \times H_{f}$ for $2 \times V^{(a)}$, where $n$ is the number of antisite atom ($n \geq 1$). In the case of $n = 1$, the $Q$s are 534 kJ/mol for Al-ASB and 361 kJ/mol for Ni-ASB. The JP-6 type jump is one of the jumps in the ASB mechanism ($n = 1$).

4.2. Diffusion jumps in NiAl with off-stoichiometric compositions

In the off-stoichiometric compositions, a lot of constitutional defects are formed in addition to the thermal defects. In the Ni-rich region extra Ni atoms go to the Al-sites, whereas in the Al-rich region the excess of Al atoms are balanced by additional vacancies created on the α-site. The number of these constitutional $V^{(a)}$'s and $N_{\text{ASB}}$ increase with the deviation from the stoichiometry [24]. The $H_{f}^{\text{defect}}$'s in the off-stoichiometric NiAl compound were also calculated; in the Ni-rich region 107 kJ/mol for $V^{(a)}$, 154 kJ/mol for $V^{(b)}$, 0 kJ/mol for $N_{\text{ASB}}$ and 299 kJ/mol for Al$^{(a)}$, and in the Al-rich region 0 kJ/mol for $V^{(a)}$, 261 kJ/mol for $V^{(b)}$, 214 kJ/mol for $N_{\text{ASB}}$ and 85 kJ/mol for Al$^{(a)}$ [28]. Since these $H_{f}^{\text{defect}}$'s are considerably different from those at the stoichiometry, some other diffusion jumps and mechanisms should be expected to operate in the off-stoichiometry. Furthermore, the constraint on the formation of vacancies for conservation stoichiometry in the stoichiometric NiAl is not required especially in the quite off-stoichiometric compositions, because the degree of ordering becomes considerably low. Therefore, the $Q$s in quite off-stoichiometry should be evaluated without consideration of such constraint.

4.2.1. Diffusion jumps in NiAl with Ni-rich compositions

In the Ni-rich region, the $Q$s of various types of jumps are evaluated by the manners mentioned above, as listed in Table 3; 307 kJ/mol for JP-2, 498 kJ/mol for JP-3, 570–606 kJ/mol for JP-4, slightly less than 307 kJ/mol for JP-5, 254 kJ/mol for JP-6, 318 kJ/mol for JP-7, 314 kJ/mol for JP-8, 425 kJ/mol for JP-9a, 285 kJ/mol for JP-9b, $(n \times 299 + 199)$ kJ/mol for JP-10a and 254 kJ/mol for JP-10b. Among them, the 254 kJ/mol by JP-6 and JP-10b is lowest for Ni diffusion in the Ni-rich region, while the 285 kJ/mol by JP-9b is lowest for Al diffusion.

The JP-6 and JP-10b by the Ni-ASB mechanism [39] play an more important role for Ni diffusion and become more operative with the deviation from the stoichiometric composition. The $Q$ by JP-10b in Ni-rich region is constant of 254 kJ/mol because the $H_{i}$ of Ni$^{(a)}$ is zero, although the $Q$ depends on the number of $n$ in stoichiometry and Al-rich region. The single vacancies can jump freely without changing the degree of ordering by the help of Ni$^{(a)}$'s with the Ni-ASB mechanism if unit cells with two anti-structure atoms on the border of a unit cell (one for entrance and one for exit) are adjacent each other, that is, the composition is less than 37.5 at% Al. In such off-stoichiometric compositions, quite a lot of Ni$^{(b)}$ can allow Ni atoms or vacancies to jump more randomly like in a disordered bcc Ni. Therefore, the $Q$ for diffusion by the ASB mechanism can be also evaluated by the other approach. By using the relation (11), the $Q$s for Ni, Pt, Co and In diffusion in bcc Ni are evaluated to be 209, 210, 212 and 191 kJ/mol from those in fcc Ni (279 kJ/mol for Ni [40], 280 kJ/mol for Pt [4], 282 kJ/mol for Co [11] and 255 kJ/mol for In [12]) respectively. Thus, the $Q$ by the ASB is about 254 or 191–212 kJ/mol. On the other hand, the $Q$ for diffusion of the Al and In atoms which substitute for Al atoms in NiAl by the Al-ASB mechanism becomes quite high because the $Q$ is $(n \times 299 + 199) kJ/mol$, that is, there are quite small number of Al$^{(a)}$ in Ni-rich region which form the bridges.

4.2.2. Diffusion jumps in NiAl with Al-rich composition

In the Al-rich region, the $Q$s of various types of jumps are also evaluated; 200 kJ/mol for JP-2, 391 kJ/mol for JP-3, 249–285 kJ/mol for JP-4, slightly less than 414 kJ/mol for JP-5, 361 kJ/mol for JP-6 type, 425 kJ/mol for JP-7 type, 314 kJ/mol for JP-8, 461 kJ/mol for JP-9a, 291 kJ/mol for JP-9b, $(n \times 85 + 306)$ kJ/mol for JP-10a (Al-ASB) and $(n \times 214 + 361)$ kJ/mol for JP-10b (Ni-ASB). Among them, the 200 kJ/mol by JP-2 is lowest for Ni diffusion with contribution of the $V^{(a)}$ with 0 kJ/mol. On the other hand, the JP-4 and JP-8 for Al diffusion have the low $Q$s of 249–285 and 285 kJ/mol, respectively. By the JP-4 the Al$^{(a)}$ with 85 kJ/mol and the Al$^{(a)}$ with 0 kJ/mol exchange each other, and by the JP-9b the divacancies contribute the diffusion. The Al and In atoms can migrate by the JP-4 of nnv-exchange independently of the Ni diffusion, and they are also partially independent of the Ni diffusion. The $Q$s for $V^{(a)}$ is somewhat lower than those for $V^{(b)}$. 

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4.3. Diffusion mechanisms in NiAl

At the stoichiometry, the experimental $Q_s$ of Ni, Co, Pt and In diffusion are about equal to each other; $Q_s$ of Ni diffusion (307 kJ/mol at 50 at% Al), Pt diffusion (299 kJ/mol at 49.7 at% Al), Co diffusion (337 kJ/mol at 49.3 at% Al) and In diffusion (336 kJ/mol at 49.4 at% Al). The $Q_s$ for diffusion of Ni, Co and Pt elements are about equal to each other, and the $Q_s$ for In diffusion is also similar to those of Ni, Co and Pt elements although the Pt and Co atoms preferentially occupy the Ni sites, while In atoms preferentially substitute Al atoms in NiAl [26,27]. As for the evaluated $Q_s$, the $Q_s$ by JP-6 (nn exchange in the cage) and by JP-8 and JP-9b (TD mechanism [38]) are lower as listed in Table 3. The exchange by JP-6 brings about no effective diffusion of the constituent atoms because a vacancy only continues to jump in the small limited space surrounded with 26 Al atoms. On the other hand, the exchanges by the mutual JP-8 and JP-9b produce the actual migration of the TD’s, which bring about the effective diffusion of Ni and Al atoms in the stoichiometric NiAl. As mentioned above, the $Q_s$ by the TD mechanism is evaluated to be about 314 kJ/mol. This $Q_s$ is in good agreement with the experimental values of 299–337 kJ/mol. It means that at stoichiometry the TD mechanism is dominant for Ni, Co, Pt and In diffusion when compared with the other mechanisms such as 6JVC, nnn-jump one and so on. The TD mechanism makes the Ni and Al atoms have the similar values of the $Q_s$ and diffusion coefficients for Ni and Al atoms because of the mutual jumps of Ni and Al atoms. In fact, the $Q_s$ of various elements are between 299 and 337 kJ/mol near the stoichiometric composition. Furthermore, the minimum diffusion coefficients of various elements near the stoichiometric composition at 1523 K are between about $3 \times 10^{-15}$ and $2 \times 10^{-14}$ m$^2$/s as shown in Fig. 5, in other words; the ratios of $D_{Ni}/D_{Al}$, $D_{Pt}/D_{Al}$ and $D_{Co}/D_{Al}$ respectively, about between 2 and 3, between 0.5 and 0.7, and between 2 and 3. These ratios are in the $13.3 > D_{Ni}/D_{Al} > 1/13.3$ which is derived from the mutual jumps of Ni and Al atom in the TD mechanism as pointed out by Stolwijk et al. [37].

In the Ni-rich side, the experimental $Q_s$ of Ni and Pt decrease from 307 to 299 kJ/mol at the stoichiometry to about 240 kJ/mol at 43 at% Al. The extrapolated values of experimental $Q$ of Ni and Pt diffusion to 37.5 at% Al is 210–220 kJ/mol as shown in Fig. 7(a). The experimental decrease between the $Q_s$ at stoichiometry and the 37.5 at% Al is about 100 kJ/mol. As listed in Table 3, the evaluated $Q_s$ by the Ni-ASB mechanism is about 207–254 kJ/mol and lowest for Ni diffusion in the Ni-rich region. This $Q_s$ is by 59–123 kJ/mol lower than the $Q_s$ (314 kJ/mol by the TD mechanism) at stoichiometry. In fact, the evaluated value of $Q_s$ is close to the experimental $Q_s$ extrapolated to the 37.5 at% Al, and the decrease in the $Q_s$s from the stoichiometry to Ni-rich region is in good agreement with experimental one as schematically shown in Fig. 11. This supports that the nearly random diffusion occurs at the off-stoichiometric composition less than 37.5 at% Al, and the diffusion mechanism gradually transfer from the TD mechanism at stoichiometry to the ASB mechanism in the quite off-stoichiometric composition.
On the other hand, the diffusion of Al and In diffusion is not generated by the Ni-ASB and Al-ASB mechanisms, because the Al and In atoms cannot diffuse by utilizing the Ni$^{(b)}$s and the $H_t$ of Al$^{(a)}$ is quite high to contribute to diffusion. The TD is also more stable than the vacancy in Ni-rich region as well as in stoichiometry because the $H_t$ for TD is about 214 kJ/mol and that for vacancy is 255 kJ/mol. If this stable TD’s would mainly contribute to the diffusion of Al and In atoms in the Ni-rich region, the $Q$ should be constant in the Ni-rich region because the $Q$ of diffusion by TD mechanism consisting of JP-8 and JP-9b is 314 kJ/mol in the Ni-rich region as well as 314 kJ/mol at stoichiometry. However the experimental $Q$ of In diffusion shows the slight decrease with deviation from the stoichiometry. At the stoichiometry, the V$^{(a)}$s and V$^{(b)}$s only migrate mutually along with the migration of TD, that is, the V$^{(b)}$s in the vacancy continues to jump around the V$^{(a)}$ of this low $Q$ as shown in Fig. 9(b), and then the V$^{(a)}$s migrate by the JP-8. The TD migration is rate-controlled by the JP-8. On the other hand, the V$^{(a)}$s or Ni atoms can migrate freely by the Ni-ASB mechanism in the Ni-rich region less than 37.5 at% Al. This random diffusion of V$^{(a)}$ with JP-10b 191–254 kJ/mol in the Ni-rich region can contribute to the migration of V$^{(b)}$ or Al atoms (JP-9b) in steady of the JP-8 (314 kJ/mol). This means that the Al atoms can diffuse by the combination of JP-9b (nnn-Al jump with vacancy) with 285 kJ/mol and JP-10b (Ni-ASB) for V$^{(a)}$ with 254 kJ/mol as shown in Fig. 11. Therefore, the $Q$ for Al diffusion is 285 kJ/mol because the rate-controlling process is JP-9b. The evaluated $Q$ (285 kJ/mol) in the Ni-rich side is lower than the $Q$ (314 kJ/mol) by the TD at the stoichiometry, and the difference is about 30 kJ/mol. The experimental $Q$s of diffusion of In atoms which substitute for Al atoms decrease from 336 kJ/mol at the stoichiometry to about 290 kJ/mol at 40.6 at% In (the extrapolated value to 37.5 at% Al is about 280 kJ/mol). The experimental decrease in $Q$s for In diffusion from stoichiometry to quite off-stoichiometry is 56 kJ/mol, while the evaluated difference is 29 kJ/mol. They are in good agreement with each other. Thus, the $Q$ of In slightly decrease in the Ni-rich side in contrast to the $Q$ of Ni, Pt, and Co diffusion.

In the Al-rich region, the 200 kJ/mol by JP-2 is lowest for Ni diffusion, and the JP-4 and JP-9b for Al diffusion have the low $Q$s of 249–285 and 285 kJ/mol, respectively, as listed in Table 3. The $Q$s for diffusion of Ni and Al atoms are lowered by the constitutional V$^{(a)}$s without the formation energy, whose concentration increases with the deviation from the stoichiometry, that is, it is high of about 4% at 52 at% Al. The $Q$ is only the migration energy of Ni, Co and Pt atoms, that is, by JP-2 with 200 kJ/mol of $H_m$ (the nnn-jump mechanism). In fact, the experimental $Q$s of Ni, Co and Pt diffusion are about 200 kJ/mol. As for the Al diffusion, the $Q$'s of JP-4 and JP-9 are lowered by the contribution of the Al$^{(a)}$ with 85 kJ/mol as well as the V$^{(a)}$ with 0 kJ/mol. In the JP-4, the antisite atoms of Al or In diffuse by the nnn jumps to constitutional V$^{(a)}$s, and in the JP-9b the Al and In atoms make the nnn jump with help of divacancies. In fact, the experimental $Q$ (271 kJ/mol at 52.3 at% Al) for diffusion of In atom which substitutes for Al atoms is in good agreement with the evaluated $Q$ of 249–285 kJ/mol. This suggests that In anti-site atom, In$^{(a)}$, has the $H_t$ similar to that of Al$^{(a)}$. In addition, the $Q$ for In diffusion is higher than that for Ni, Co and Pt diffusion. The decrease in $Q$s for Ni, Co and Pt diffusion is from 355 kJ/mol at stoichiometry to 200 kJ/mol, while that for In diffusion is from 355 to 249–285 kJ/mol. The experimental difference between In diffusion and diffusion such as Ni is about 70 kJ/mol. This difference is in good agreement with the 85 kJ/mol for Al$^{(a)}$ formation.

Thus, the stable defects contribute diffusion in NiAl; the TD in the stoichiometric NiAl, Ni$^{(b)}$ in Ni-rich side, and V$^{(a)}$ and Al$^{(a)}$ or In$^{(a)}$ in Al-rich side as shown in Fig. 11.

5. Conclusions

The Pt diffusion in NiAl has been investigated in NiAl compound with compositions of 43.7–51.9 at% Al at 1373–1673 K by the diffusion couple method. The diffusion coefficients of Pt at each temperature have the minimum values quite near the stoichiometry and they increase with the deviation from the stoichiometry. The diffusion coefficients satisfy the Arrhenius type equation and fall on straight lines. The activation energies evaluated by the temperature dependence show the maximum about at the stoichiometry and decrease in the off-stoichiometry.

The experimental and evaluated activation energies and the diffusion coefficients suggest the followings: The TDs mechanism mainly operates at stoichiometry. In the Ni-rich region, the diffusion of Ni atoms and Pt atoms occurs randomly by the anti-site atom bridge mechanism, while the In and Al atoms diffuse by the combination of Ni-ASB and nnn-Al-jump with vacancy. On the other hand, the Ni and Pt atoms diffuse by the nnn exchanges mainly with structural Ni vacancies, and the diffusion of Al and In atoms occurs by the nnn-Al jumps with divacancy and by the nnn-jumps of anti-site atoms of Al and In to Ni vacancies.

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research of the Japanese Minister of Education, Science and Culture (C-2-09650717). The authors express their appreciation for the support.

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