Phase Separation of the B2 Structure Accompanied by an Ordering in Co-Al and Ni-Al Binary Systems

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The phase separation of the B2 structure in the Co-Al and Ni-Al binary systems has been studied by combining ab initio energetic calculations with the CALPHAD approach. The total energies of the ordered phases based on the bcc lattice were obtained using first-principle band-energy calculations. The cluster expansion method was applied to the results, and the free energies at finite temperatures were calculated for the bcc solid solution. The Co-Al and Ni-Al binary systems were analysed thermodynamically by considering the estimated metastable free energy of the bcc phase. The descriptions of the lattice stability parameters for each pure element were obtained chiefly from the Scientific Group Thermodata Europe (SGTE) database. The optimized parameters reasonably reproduced the characteristic features of these binary phase diagrams. The metastable (A2+B2) two-phase field forms in the Co-Al phase diagram, and this equilibrium is closely related to the anomaly in the phase boundaries of the binary system. On the other hand, the phase separation of the A2 and B2 structures are hindered by the presence of the D00 phase in the Ni-Al system. Ground state analysis was performed to clarify the difference in the behaviour of the B2 phase.

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1. Introduction

Various changes in the physical properties of alloys are indirectly reflected in the equilibrium phase diagrams. For example, it is well known that a magnetic transition is manifested in an abnormal behaviour at the phase boundaries in some alloy systems. The phase boundaries in the Co-Al binary system may be classified as such a category. The Co-Al phase diagram consists of liquid, two fcc solid solutions γ (Co) and γ (Al), hcp Co (ε), β with CsCl structure, and the intermetallic phases Co₂Al₄, CoAl₂, Co₂Al₃, and Co₂Al₄. There exist one eutectic reaction concerning the liquid phase and six invariant reactions between the solid phases. The B2 (β) phase has a large homogeneity range at higher temperatures, but the range decreases remarkably in the lower temperature region. It has been confirmed experimentally that the two-phase region for the A1 (γ)/B2 (β) phases extends over a wide composition range with decreasing temperature.¹ Owing to a sudden drop in the homogeneous region, these experimental values are debatable, and are not adopted in the assessment of the binary phase diagrams.² This judgement originates in the unusual shape of the phase boundary. Our preliminary analysis has shown that a phase separation, accompanied by an order-disorder transition of the B2 phase, plays an essential role in the anomaly at the phase boundary.

The Ni-Al binary system has almost the same phase constitutions as the Co-Al system. The system is composed of liquid, two fcc solid solutions γ (Ni) and γ (Al), β with CsCl structure, and the intermetallic phases L1₂ (γ’), Ni₅Al₃, Ni₃Al₂, NiAl, and NiAl₃. However, the features of the two phase diagrams are quite different, as shown in Fig. 1. In Fig. 1, the stable γ’ phase (L1₂ structure) is omitted in the Ni-Al binary system to allow for a direct comparison with the Co-Al system. Although the presence of an order-disorder transition of the bcc structure is known, the phase equilibria for the A1 (γ)/B2 (β) composition appears differently for the two binary systems.

Thus, in the present study, the difference in the behaviour of the B2 structure in the Co-Al and Ni-Al binary systems was studied using a thermodynamic analysis incorporating ab initio energetic calculations. Furthermore, the phase separation of the B2 structure is discussed in connection with the interaction energies between unlike atoms.

2. Calculation Procedures

2.1 Ab initio calculations of the Gibbs free energy

To clarify the thermodynamic properties of the bcc-based structure over the entire composition range, the formation energy was estimated by incorporating band-energy calculations using the cluster variation method. An outline for deriving the Gibbs free energies of the bcc-based structures is described as follows.

First, a set of superstructures {A-A2, A3-B-D03, AB-B2, AB-B32, AB3-D03, and B-A2} was selected to be representative of a series of bcc-based ordered phases. The total energies were calculated using the WIEN2k³ software package, based on the Full Potential Linearized Augmented Plane Wave (FLAPW) method within the generalized gradient approximation (GGA).⁴ Muffin-tin radii of 2.0 au (0.106 nm) for Co, Ni, and Al were assumed, and RKₘₐₓ was fixed at 9.0, which almost corresponds to the 20 Ry (270 eV) cut-off energy.

With the total energies known, the formation energy of the bcc-based superstructures, ΔEₜₜₜ, was defined by averaging the total energy of the elements with chemical compositions up to the segregation limit, as follows:

\[
\Delta E_{\text{form}}(\phi) = E_{\text{tot}}(\phi) - \sum_{M} x_{M}E_{\text{bccf}}^{M}(\phi) - (1 - x_{\text{Al}})E_{\text{bccAl}}^{\text{tot}}(\phi),
\]

where φ denotes the type of superstructure and φ is the lattice constant. M denotes an element, Co or Ni.

The resultant formation energy can be further fitted using a
Lennard–Jones type potential function, as shown in eq. (2).

$$\Delta E_{\text{form}}^\phi(a) = \left( \frac{p^\phi}{a} \right)^{2n} - \left( \frac{q^\phi}{a} \right)^{n} \phi$$  \hspace{1cm} (2)

Here, the exponent $n = 3.5$ is used to reproduce $\Delta E_{\text{form}}^\phi$ to the highest accuracy.

Then, the effective cluster interaction energies, $\{v_i(a)\}$, can be extracted from these formation energies using the Cluster Expansion Method (CEM) developed by Connolly and Williams.\(^5\) This leads to a set of composition-independent parameters from which, the energy of the set of superstructures can be reproduced in terms of a set of correlation functions $\{\xi_i\}$

$$\Delta E_{\text{form}}^\phi(a) = \sum_{i=0}^{\gamma} v_i(a) \cdot \xi_i, \hspace{1cm} (3)$$

where, $v_i(a)$ is the effective interaction energy of the $i$-point cluster, and $\xi_i$ is the correlation function for cluster $i$ in the phase $\phi$. $\xi_i$ is defined as the ensemble average of the spin operator, $\sigma(p)$, which takes values of $\pm 1$, depending on the atomic occupancy of the lattice site, $p$. The values of $\xi_i$ for the superstructures considered in this study are summarized in Table 1.

The upper limit of the summation in eq. (3), $\gamma$, specifies the largest cluster participating in the expansion. In this study, we considered a tetrahedron as being the largest cluster. Since in the bcc structure the tetrahedron is an irregular shape that contains both the first- and second-nearest-neighbour distances, the second pair interactions are also taken into account, which leads to the consequence that mathematically, five $\gamma$ should represent six types of cluster.

From Table 1, it can be seen that $\{\xi_i\}$ is a regular $6 \times 6$ matrix. Then, the matrix inversion of eq. (3) yields the effective interaction energies

$$v_i(a) = \sum_{i=0}^{5} (\xi_i^\phi)^{-1} \Delta E_{\text{form}}^\phi(a). \hspace{1cm} (4)$$

The formation energies to the segregation limit for the Co-Al and Ni-Al systems in the D0$_3$, B2, B32, and A2 structures in the ground state are summarized in Table 2. The Gibbs free energies of the metastable bcc-based phase in the Co-Al and the Ni-Al binary systems were evaluated using the effective cluster interaction energies up to the tetrahedron cluster, including the second pair interactions

$$\Delta E = \sum_{i=0}^{5} v_i \xi_i. \hspace{1cm} (5)$$

At a finite temperature, $T$, the free energy of a phase of interest, $\Delta G$, can be obtained by adding the configurational entropy term, $\Delta S$, to the internal energy, as follows\(^6,7\)

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>Molar fraction of Al</th>
<th>Structure</th>
<th>Formation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Al</td>
<td>0.25</td>
<td>D0$_3$</td>
<td>$-12.7$</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>B2</td>
<td>$-62.3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B32</td>
<td>$-23.7$</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>D0$_3$</td>
<td>$-18.3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D0$_3$</td>
<td>$-40.7$</td>
</tr>
<tr>
<td>Ni-Al</td>
<td>0.5</td>
<td>B2</td>
<td>$-69.5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B32</td>
<td>$-34.0$</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>D0$_3$</td>
<td>$-18.2$</td>
</tr>
</tbody>
</table>
\[ \Delta G = \Delta E - T \cdot \Delta S. \]  

(6)

We used the cluster variation method (CVM) with the tetrahedron approximation to calculate the configurational entropy. For the bcc-structure, the entropy formula is

\[ \Delta S = k_B \cdot \ln \left\{ \frac{\prod (N_{ij})!}{\prod (N_{ik})!} \right\}^{12} \cdot \frac{\prod (N_{ij})!}{\prod (N_{ik})!} \cdot \frac{\prod (N_{ijkl})!}{\prod (N_{ikl})!} \cdot \frac{\prod (N_{ijkl})!}{\prod (N_{iklm})!}, \]  

(7)

where \( x_{ij}, y_{ij}, z_{ijk} \) and \( w_{ijkl} \) are the cluster probabilities of finding the atomic configurations specified by the subscript(s) at a point, the nearest neighbour pair, the second-nearest neighbour pair, a triangle cluster, and a tetrahedron cluster, respectively, and \( N \) is the number of lattice points.

By minimizing the grand potential with respect to all the correlation functions, the Gibbs energy of mixing can be obtained as a function of composition at a constant temperature, \( T \).

\[ y_i^s = n_i^s / \sum_j n_j^s = n_i^s / n' \quad \text{with} \quad \sum_k n_k^s = n^s \quad \text{and} \quad \sum_s n^s = n, \]  

(9)

where \( n_j^s \) is the number of species \( j \) in sublattice \( s \), \( n' \) is the number of sites in sublattice \( s \), and \( n \) is the total number of sites. The quantity \( n' \) is related to \( n \) by \( n' = n(u^1 + u^2 + \ldots) \).

The \( \beta \) phase was described using a four-sublattice model, so as to reflect the results of the \textit{ab initio} calculations on the phase diagram computation as follows:

\[ \begin{pmatrix} Al^1 & M^1 \\ y_{Al}^1 & y_{M}^1 \end{pmatrix}_{0.25} \begin{pmatrix} Al^2 & M^2 \\ y_{Al}^2 & y_{M}^2 \end{pmatrix}_{0.25} \begin{pmatrix} Al^3 & M^3 \\ y_{Al}^3 & y_{M}^3 \end{pmatrix}_{0.25} \begin{pmatrix} Al^4 & M^4 \\ y_{Al}^4 & y_{M}^4 \end{pmatrix}_{0.25}. \]  

(10)

The number of each sublattice site is 0.25, and the four sites are therefore equivalent. The disordered state is described when the site fractions of the different species are the same in the four sublattices. For the ordered structures, if two sublattices have the same site fractions, as do the two others, but are different, then the model describes the B2 and B32 phases. If three sublattices have the same site fractions, and are different from the fourth, then D03 ordering is described.

The Gibbs energy of the \( \beta \) phase is expressed by the following equation:

\[ G_m = \sum_i \sum_j \sum_k \sum_m y_i^j y_j^k y_k^m d_i G_{ijkl} \]

\[ + \frac{RT}{4} \sum_{i=1}^4 \sum_j y_i^j \ln(y_i^j) \]

\[ + \sum_{i=1}^4 \sum_{j=1}^4 \sum_{k=1}^4 \sum_{m=1}^4 y_i^j y_j^k y_k^m y_m^l L_{ijkl}, \]  

(11)

where \( G_{ijkl} \) denotes the Gibbs energy of a compound \( ijk \), and terms relative to the same stoichiometry are identical, whatever the occupation of the sublattice. \( L_{ijkl} \) is the interaction parameter between unlike atoms on the same sublattice.

2.2 Thermodynamic models

The Co-Al binary system is composed of the liquid (L), fcc (\( \gamma \) Co, \( \gamma \) Al), B2 (\( \beta \)), hcp (\( \sigma \) Co), CoAl, CoAl, CoAl, and CoAl phases. On the other hand, the Ni-Al binary system consists of the liquid (L), fcc (\( \gamma \) Ni, \( \gamma \) Al), L12 (\( \gamma ' \)), B2 (\( \beta \)), Ni2Al, Ni2Al, Ni2Al, and NiAl phases.

The B2 structure (\( \beta \)) in the Co-Al and Ni-Al binary systems exhibits a range of non-stoichiometric alloys, and it was modelled using a multi-sublattice model, by considering its ordering behaviour. The general formula of the model was

\[ \left( \begin{array}{cccc} \text{Al}^1 & \text{M}^1 \\ y_{Al}^1 & y_{M}^1 \\ \text{Al}^2 & \text{M}^2 \\ y_{Al}^2 & y_{M}^2 \\ \text{Al}^3 & \text{M}^3 \\ y_{Al}^3 & y_{M}^3 \\ \text{Al}^4 & \text{M}^4 \\ y_{Al}^4 & y_{M}^4 \end{array} \right). \]  

(8)

\( M \) denotes Co or Ni in eq. (8). The subscripts \( u^1, u^2 \ldots \) are the numbers of the sublattice sites that are within the brackets, and \( \text{Al}^1, \text{M}^1 \ldots \) and \( \text{Al}^2, \text{M}^2 \ldots \) denote the elements in the corresponding sublattice sites. The quantities \( y_i^1 \) and \( y_i^2 \) are the site fractions of the elements \( i \) and \( j \) in their respective sublattice, designated by the numbers 1 and 2. If the relationship \( u^1 + u^2 + \ldots = 1 \) holds, then the thermodynamic quantities are referring to one mole of the sites. For each sublattice, \( s \), the site fraction of species \( i \) is equal to

\[ y_i^s = n_i^j / \sum_j n_j^s = n_i^s / n' \quad \text{with} \quad \sum_k n_k^s = n^s \quad \text{and} \quad \sum_s n^s = n, \]  

(9)

where \( n_j^s \) is the number of species \( j \) in sublattice \( s \), \( n' \) is the number of sites in sublattice \( s \), and \( n \) is the total number of sites. The quantity \( n' \) is related to \( n \) by \( n' = n(u^1 + u^2 + \ldots) \).

The following regular solution approximation was applied to the disordered fcc (\( \gamma \) Co, \( \gamma \) Ni, \( \gamma \) Al), hcp (\( \sigma \) Co), and liquid phases

\[ G_m^p = x_{Al} G_{Al}^p + x_{M} G_{M}^p \]

\[ + RT(x_{Al} \ln x_{Al} + x_{M} \ln x_{M}) \]  

(12)

\[ + x_{Al} x_{M} L_{ALM} + G_{mag}, \]

where \( G_m^p \) denotes the Gibbs energy of element \( i \) in the phase. This quantity is called the lattice stability parameter, and is described by the formula

\[ G_m^p - H_{ref}^p = A + BT + CT \ln T + DT^2 \]

\[ + ET^3 + FT^4 + IT^5 + JT^6, \]  

(13)

where \( H_{ref}^p \) denotes the enthalpy of the pure element \( i \) in its stable state at 298.15 K. The parameter \( L_{ALM} \) denotes the interaction energy between Al and M, and has a compositional dependency following the Redlich–Kister polynomial as

\[ L_{ALM}^p = \frac{L_{ALM}^p_0 + (x_{Al} - x_{M}) \cdot 1 L_{ALM}^p_0}{1 + (x_{Al} - x_{M})^2 \cdot 2 L_{ALM}^p}. \]  

(14)

The magnetic contribution to the Gibbs free energy, \( G_{mag} \), is given by the expression
The variable $\tau$ is defined as $T/T_c$, where $T_c$ is the Curie temperature and $\beta$ is the mean atomic volume expressed in Bohr magnetons, $\mu_B$. The value of $p$ depends on the structure, and $p = 0.28$ for the fcc phase.

The L1$_2$ ($\gamma'$) phase in the Ni-Al system is an ordered structure based on the fcc phase. Therefore, it is also possible to treat the $\gamma'/\gamma$ equilibrium as an order-disorder transition.

However, to avoid a complication of the parameters, a different thermodynamic model was applied to the $\gamma'$ phase, and the Gibbs energy was represented using the two-sublattice model as

$$G_m = RT \cdot f(\tau) \ln(\beta + 1),$$

where

$$f(\tau) = 1 - \frac{1}{A} \left\{ \frac{79}{140p} + \frac{474}{497} \frac{(1 - p)}{(1 - p) - 1} \right\} \tau^2 + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}, \quad \text{for } \tau < 1$$

and

$$f(\tau) = -\frac{1}{A} \left\{ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right\}, \quad \text{for } \tau \geq 1,$$

and

$$A = \frac{518}{1125} + \frac{11692}{15975} \left( \frac{1}{p} - 1 \right).$$

The Gibbs energy for one mole of the phase is given by the following equation.

$$G_m = \alpha^1 \cdot \gamma_{Al}^1 \cdot \gamma_{Ni}^1 \cdot (\text{Al}^1 \cdot \text{Ni}^1)_{0.75} \cdot (\text{Al}^2 \cdot \text{Ni}^2)_{0.25}.$$

The Gibbs energy one mole of the phase is given by the following equation.

$$G_m = \frac{1}{A} \left\{ \frac{79}{140p} + \frac{474}{497} \frac{(1 - p)}{(1 - p) - 1} \right\} \tau^2 + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}, \quad \text{for } \tau < 1$$

and

$$f(\tau) = -\frac{1}{A} \left\{ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right\}, \quad \text{for } \tau \geq 1,$$

and

$$A = \frac{518}{1125} + \frac{11692}{15975} \left( \frac{1}{p} - 1 \right).$$

The descriptions of the lattice stability parameters for each pure element were obtained chiefly from the Scientific Group Thermodata Europe (SGTE) data file, and are shown in Table 3. The evaluated parameters for the Co-Al binary system are shown in Table 4. The calculated Gibbs free energy of the bcc phases at 1000 K was compared with the results from the ab initio energetic calculations in Fig. 2. The calculated Co-Al binary phase diagram is compared with the experimental data in Fig. 3. The characteristic features of the binary phase diagram are well reproduced by the calculations. The dotted line shows the metastable two-phase separated region between the A2 (bcc Co) and the B2 ($\beta$) phases.

3.1 Thermodynamic analysis of the Co-Al and Ni-Al systems

3.1.1 Co-Al binary system

According to the critical assessments of McAlister and Dupin and Ansa, there exist one eutectic reaction concerning the liquid phase and six invariant reactions between the solid phases. The peritectic reactions of Co$_5$Al$_3$, Co$_3$Al$_2$, Co$_4$Al$_3$, and Co$_2$Al$_2$ were determined by thermal analysis and metallographic studies, and there were small discrepancies within experimental error. Several liquidus studies using melt analysis as well as thermal analysis have been reported, and the experimental data were adopted in this analysis. The B2 ($\beta$) phase that formed congruently from the melt at an almost equimolar composition has a homogeneity range extending from 22%Al to almost 50%Al at higher temperatures, but the range decreases remarkably in the lower temperature region. The phase boundary on the Co-rich side has been studied metallographically and using X-ray diffraction, EPMA, electromotive force measurements, lattice constant measurements, and EPMA and lattice parameter measurements. The present analysis attempted to reproduce the experimental data of Takayama et al., which locates the phase boundary nearest to the stoichiometric composition among the above measurement values.

3.1.2 Ni-Al binary system

With regard to this binary system, a large number of experimental data have been reported, and a critical assessment has been carried out by Nash et al. The liquidus lines have been measured mainly using thermal analysis and the microstructural observation, and the experimental data show good agreement with each other. The liquid phase undergoes five types of invariant reactions with the solid phases. The B2 ($\beta$) phase has an ordered structure, with a wide homogeneity range extending from about 31%Al to
and the mixing enthalpy of the liquid phase has been determined. Since the $L_1^2$ phase has $58\%$ Al, and it melts congruently at 1911 K. The phase boundary of Ni$_2$Al has been established using electron probe microanalysis,24-26 On the other hand, a slight difference in the experimental data can be observed in the acute point in the free energy curve in the $\beta$ phase. The two-phase separation, based on the bcc structure, closely resembles the Ni-rich side of the phase diagram, as can be seen in Fig. 3.

Table 3 Lattice stability parameters for Al, Co, and Ni.

<table>
<thead>
<tr>
<th>Element (Al, Co, Ni)</th>
<th>Phase</th>
<th>Lattice stability parameter, J/mol</th>
<th>Temperature range, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>$G^{\text{Cu}}<em>{\text{Cu}} - G^{\text{hcp}}</em>{\text{Cu}}$</td>
<td>11005.029 - 11.841867T + 7.934 $\times 10^{-20}T^3$</td>
<td>$298 &lt; T &lt; 1768$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10482.382 - 11.253974T + 1.231 $\times 10^{-20}T^3$</td>
<td>$933.6 &lt; T &lt; 6000$</td>
</tr>
<tr>
<td>Al (bcc, B2)</td>
<td>$G^{\text{Al}}<em>{\text{Al}} - G^{\text{hcp}}</em>{\text{Al}}$</td>
<td>10083 - 4.813T</td>
<td>$298 &lt; T &lt; 2900$</td>
</tr>
<tr>
<td>Ni$_2$Al</td>
<td>$G^{\text{NiAl}}<em>{\text{NiAl}} - G^{\text{fct}}</em>{\text{NiAl}}$</td>
<td>5481 - 1.8T</td>
<td>$298 &lt; T &lt; 2900$</td>
</tr>
<tr>
<td>Ni</td>
<td>$G^{\text{Co}}<em>{\text{Co}} - G^{\text{hcp}}</em>{\text{Co}}$</td>
<td>15085.037 - 8.931932T + 2.19801 $\times 10^{-21}T^3$</td>
<td>$298 &lt; T &lt; 1768$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16531.056 - 9.683796T + 9.34888 $\times 10^{-20}T^3$</td>
<td>$1768 &lt; T &lt; 6000$</td>
</tr>
<tr>
<td>Co (fcc)</td>
<td>$G^{\text{Co}}<em>{\text{Co}} - G^{\text{hcp}}</em>{\text{Co}}$</td>
<td>427.59 - 0.615248T</td>
<td>$298 &lt; T &lt; 6000$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_\alpha = 1396, \beta = 1.35$</td>
<td></td>
</tr>
<tr>
<td>Ni$_2$Co</td>
<td>$G^{\text{CoCo}}<em>{\text{CoCo}} - G^{\text{hcp}}</em>{\text{CoCo}}$</td>
<td>2938 - 0.71387T</td>
<td>$298 &lt; T &lt; 6000$</td>
</tr>
<tr>
<td>Ni (L1$_2$)</td>
<td>$G^{\text{Ni}}<em>{\text{Ni}} - G^{\text{Co}}</em>{\text{Co}}$</td>
<td>16414.686 - 9.3977T - 3.82318 $\times 10^{-21}T^3$</td>
<td>$298 &lt; T &lt; 1728$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18290.88 - 10.5377T - 1.12754 $\times 10^{-21}T^3$</td>
<td>$1728 &lt; T &lt; 3000$</td>
</tr>
<tr>
<td>Ni (bcc, B2)</td>
<td>$G^{\text{Ni}}<em>{\text{Ni}} - G^{\text{hcp}}</em>{\text{Ni}}$</td>
<td>10464.1 + 1.255T</td>
<td>$298 &lt; T &lt; 3000$</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>$T_\alpha = 633, \beta = 0.52$</td>
<td></td>
</tr>
<tr>
<td>Ni$_2$Ni</td>
<td>$G^{\text{NiNi}}<em>{\text{NiNi}} - G^{\text{hcp}}</em>{\text{NiNi}}$</td>
<td>8715.084 - 3.556T</td>
<td>$298 &lt; T &lt; 6000$</td>
</tr>
<tr>
<td>Ni (L1$_2$)</td>
<td>$G^{\text{NiNi}}<em>{\text{NiNi}} - G^{\text{fct}}</em>{\text{NiNi}}$</td>
<td>0</td>
<td>$298 &lt; T &lt; 6000$</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>$T_\alpha = 633, \beta = 0.52$</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Effect of the phase separation of the B2 structure on the phase boundaries

A thermodynamic analysis of the Co-Al system shows the occurrence of the metastable (A2 + B2) two-phase region in the Co-rich side of the phase diagram, as can be seen in Fig. 3. The two-phase separation, based on the bcc structure, closely relates the anomaly in the phase boundaries in the Co-Al binary system. This situation is schematically illustrated in Fig. 6, where the Gibbs free energies of the B2 ($\beta$) and the A1 ($\gamma$ Co) phases are drawn. The two-phase separation of the $\beta$ phase does not occur at higher temperatures, $T_1$, mainly owing to the effect of the entropy of random mixing on the atomic arrangement. On the other hand, the tendency towards ordering becomes stronger at lower temperatures, $T_2$. In the B2 structure, the interaction between unlike atoms strengthens around the 50% Al composition, since the degree of order reaches a maximum at the equiatomic composition. The decrease in the enthalpy term due to the attractive interaction results in the acute point in the free energy curve in the vicinity of the 50% Al composition, and consequently, a two-phase separation in the $\beta$ phase forms. This situation yields a significant shift of the phase boundary for the ($\gamma$ Co + $\beta$)/$\beta$ composition to the equiatomic composition.

3.3 Effective interaction energies of clusters

The variation in the effective interaction energy, $v_i(a)$, with the lattice constant calculated using eq. (4) is shown in
Table 4  The optimized thermodynamic parameters for the Co-Al and Ni-Al binary systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>Thermodynamic Parameter, J/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>$L^L_{\text{CoAl}} = 1950$</td>
<td>$-117500 - 33.2T - (x_{\text{Al}} - x_{\text{Co}}) \cdot (9900 + 25.45T)$</td>
<td>Present work</td>
</tr>
<tr>
<td>L</td>
<td>$L^L_{\text{NiAl}} = 24000$</td>
<td>$-178700 + 8.91T + (x_{\text{Ni}} - x_{\text{Al}}) \cdot (7100 + 13.3T) + (x_{\text{Al}} - x_{\text{Ni}}) \cdot (36500 - 17.5T)$</td>
<td>Present work</td>
</tr>
<tr>
<td>Ni-Al</td>
<td>$L^L_{\text{NiAl}} = 24000$</td>
<td>$-30000 + 1.113T$</td>
<td>Present work</td>
</tr>
<tr>
<td>Ni-Al</td>
<td>$L^L_{\text{NiAl}} = 24000$</td>
<td>$-70300 + 1.176T$</td>
<td>Present work</td>
</tr>
<tr>
<td>Ni-Al</td>
<td>$L^L_{\text{NiAl}} = 24000$</td>
<td>$-40600 - 1.34T$</td>
<td>Present work</td>
</tr>
<tr>
<td>Ni-Al</td>
<td>$L^L_{\text{NiAl}} = 24000$</td>
<td>$-10400 + 6.33T$</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Fig. 2  The calculated Gibbs free energy of the bcc phase in the Co-Al binary system at 1000 K compared with the results from the ab initio energetic calculations.

Fig. 3  A comparison of the calculated Co-Al binary phase diagram with previous work.
The positive numbers define the attractive force working between unlike atoms. The $i$-point effective interaction energy at the equilibrium lattice constant in these two binary systems can be compared using the data in Table 5. The equilibrium lattice constant of the B2 structure was 5.38 au (0.285 nm) for the Co-Al system, and 5.46 au (0.289 nm) for the Ni-Al system. There seems to be no remarkable difference in these values between the two binary systems.

Ino$^{33}$ proposed a pairwise interaction model to explain the coexistence of the ordering and the phase separation. This model requires an attractive first-nearest neighbour interaction and a repulsive next nearest neighbour interaction. However, the sign of the interaction energies may not play an essential role in the systems under investigation in this study, since both parameters show positive numbers in the binary systems.

3.4 Origin of the different behaviour of the B2 phase in the Co-Al and Ni-Al systems

The formation energies to the segregation limit for Co-Al and Ni-Al in the D0$_3$, B2, B32, and A2 structures in the ground state, as listed in Table 2, are plotted versus Al concentration in Fig. 8. In comparing the two systems, it can be seen that in the Co-Al system, the energy of the D0$_3$ structure at the 25% Al composition is located slightly above the straight line connecting the energy values at the 0% Al and 50% Al compositions, which results in a two-phase separation of the A2 (bcc Co) and B2 ($\gamma'$-Co) structures. On the other hand, the energy plot of the Ni-Al system shows the stabilization of the Ni$_3$Al-D0$_3$ structure compared with the two-phase separation of the A2 (bcc Ni) and B2 ($\beta$) structures, since the formation energy of the D0$_3$...
phase is lower than the straight line connecting the energy values at the 0%Al and 50%Al compositions. This energetic analysis suggests that a two-phase separation of the bcc-Co and B2 (\(\text{C}1\text{2}\)) phases occurs on the Co rich side in Co-Al system, while such a separation is not realized in the Ni-Al system.

Figure 9 shows the density of states (DOS) of the B2 (\(\text{C}1\text{2}\)) structure in the Co-Al and Ni-Al alloy systems. In Fig. 9, \(E_F\) denotes the Fermi energy, where no electrons occupy the electronic states above this energy level. It can be seen that the distribution of the DOS of the B2 phase in the two systems is similar, with both showing a low DOS at the Fermi level. However, when observing the DOS of the D0\(_3\) phase for these two systems, as shown in Fig. 10, we observe a marked difference between these two systems, in that the Fermi level is located near the peak of the DOS for the Co\(_3\)Al-D0\(_3\) phase but decreases in a region with a very low DOS in the Ni\(_3\)Al-D0\(_3\) phase. This fact indicates that, from an energetic point of view, the stable D0\(_3\) structure of the Ni\(_3\)Al phase is highly preferred, while in the Co\(_3\)Al-D0\(_3\) phase is unstable with respect to separation of the A2 and B2 phases in the Co-Al system.

This difference in the density of states at the Fermi level might be considered to be the result of the extra d-electron in Ni versus Co. From the point of view of the rigid band approximation, this difference in the number of electrons for two neighbouring elements shifts the Fermi level towards the higher energy side in the Ni-Al system versus the Co-Al system. This raises the different relative positions of the Fermi level in the DOS curve, which consequently leads to the different structural stabilities.

The ground state analysis of the Ni-Al system suggests that the phase separation concerning the D0\(_3\) structure forms at absolute zero. When assuming that such a two-phase separation forms at a finite temperature, however, the agreement between the calculated phase boundaries and experimental data is insufficient. For example, Fig. 11 shows the phase diagram in the case that a two-phase separation between the metastable D0\(_3\) and B2 structures occurs around

<table>
<thead>
<tr>
<th>Effective cluster interaction</th>
<th>Co-Al (kJ/mol)</th>
<th>Ni-Al (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1)</td>
<td>15.6</td>
<td>33.9</td>
</tr>
<tr>
<td>(v_2)</td>
<td>52.5</td>
<td>63.2</td>
</tr>
<tr>
<td>(v_3)</td>
<td>5.7</td>
<td>9.1</td>
</tr>
<tr>
<td>(v_4)</td>
<td>4.8</td>
<td>-8.6</td>
</tr>
<tr>
<td>(v_5)</td>
<td>-2.9</td>
<td>-6.6</td>
</tr>
</tbody>
</table>

Fig. 8 Variation of the formation energies to the segregation limit for Co-Al and Ni-Al with concentration of Al.

Fig. 7 Variation of the effective interaction energy, \(v_i\), of the Co-Al and Ni-Al binary systems with lattice constant.
773 K. The homogeneity range of the B2 single phase is comparatively reduced owing to the influence of the metastable miscibility gap with decreasing temperature, and accordingly, the calculated phase boundaries deviate from the experimental data. Therefore, the phase separation of the D0\textsubscript{3} structure is not likely in the experimentally observable temperature range.

4. Conclusions

The phase separation behaviour of the B2 structure in the Co-Al and Ni-Al binary systems was studied using first-principle band-energy calculation and thermodynamic analysis, yielding the following results.

(1) The Co-Al and Ni-Al binary systems were analysed thermodynamically by considering the free energy of the bcc phase estimated from \textit{ab initio} calculations. The optimized parameters reasonably reproduced the characteristic features of these binary phase diagrams. The metastable (A2 + B2) two-phase field forms in the Co-Al binary system, and this metastable equilibrium relates closely to the anomaly seen in the phase boundaries in this system. On the other hand, the phase separation of the A2 and B2 structures is not likely in the Ni-Al system.

(2) The effective interaction energies for clusters were obtained using \textit{ab initio} calculations on the formation energies for the bcc-based ordered structures. However, there seems to be no marked difference in the values between these two binary systems.

(3) Ground state analysis showed that the D0\textsubscript{3} structure forms in the Ni-Al system, while two-phase separation between the ordered B2 and the disordered A2 phase occurs in the Co-Al system. The difference in the
stability of the D0₃ phase in these binary systems corresponds to a difference in the number of d electrons between Co and Ni.

Acknowledgments

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