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1993 J. Phys.: Condens. Matter 5 6653

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Site preference of alloying additions in intermetallic compounds

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Received 7 December 1992, in final form 24 May 1993

Abstract. A general method is suggested in this paper to determine the site preference of alloying additions in intermetallic compounds with either stoichiometric or non-stoichiometric compositions, by first-principles binding-energy calculations using cluster models. The relationships of the site preference of alloying additions with the compositions of the host elements and with the concentrations of the additions themselves in the host are established. The validity and reliability of the method are tested by applying it to the site preference study of some ternary additions (Sc, Ti, V, Fe, Co, Cu, Nb, Mo and Pd) in γ' -Ni₃Al. The results obtained are in complete agreement with the experimental data, which proves that our method is successful.

1. Introduction

As one of the most promising types of high-temperature structural material, intermetallic compounds (ICs) have been the subject of widespread investigations [1–5]. ICs usually have quite complicated structures and, because of the strong interactions between their atoms, they are characterized by many attractive properties, such as a low density, high melting point and high bulk modulus. Aluminides and silicides are also characterized by good oxidation resistance. Unfortunately, ICs suffer from poor ductility at room temperature, which has so far prevented practical use. Recently, some alloying elements added to ICs have been reported to result in increased ductility [6–9].

For a long time, there has been an attempt to correlate the mechanical properties of materials with their electronic structures [10–13]. To obtain the results of electronic structure calculations, as the first step, one must know the microscopic structures of materials. Thus, in order to understand the effects of alloying additions in improving the ductility of ICs from the electronic structure theory, it is important to determine their occupation sites in the host. Generally speaking, the site preference of additions in an IC can be determined directly by experimental means, such as the ternary phase diagram, x-ray diffraction, Mössbauer

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spectroscopy and the technique of atom location by channelling microanalysis, but only a few experimental results have been reported [9, 14, 15]. Theoretically, there has not been a first-principles approach to study this problem up to now, while all the previous approaches [16–18] are empirical or semi-empirical. In this paper, we present a first-principles method with cluster models to determine the site preference of alloying additions in ICs and apply it to the site preference study of some ternary additions in γ' -Ni₃Al. The method is described in section 2. The calculation for γ' -Ni₃Al is presented in section 3 and our conclusion is given in section 4.

2. General method

2.1. Site preference

The site preference of alloying additions depends on their local structures in ICs, so we can adopt cluster models in our study, which have been used successfully to study the electronic structure of impurities in metals and alloys [19–21]. Let us consider a stoichiometric IC of the compositional formula A_nB_m (hereafter denoted A_nB_m(s)) which has two kinds of inequivalent site (A sites and B sites) in its lattice, and assume that each A atoms has n_1 A atoms and m_1 B atoms as its nearest neighbours (NNS), and each B atom has n_2 A atoms and m_2 B atoms as its NNS. Then, if we take into account only the NN interactions, we can choose the clusters AA_{n₁}B_{m₁} and BA_{n₂}B_{m₂} to represent the local structures for the A and B sites, respectively. When the ternary additions of M atoms are alloyed in A_nB_m(s), the local structure of an M atom will be represented by the substitutional cluster MA_{n₁}B_{m₁} if M occupies the A site, or by the cluster MA_{n₂}B_{m₂} if M is located in the B site.

We can obtain the binding energies E_b of the clusters from the first-principles approach which will be described in section 2.2 and then define two energy parameters ΔE_i ($i = 1, 2$) for each M as follows:

$$\Delta E_1 = E_b(\text{MA}_{n_1}\text{B}_{m_1}) - E_b(\text{AA}_{n_1}\text{B}_{m_1}) \quad (1)$$

$$\Delta E_2 = E_b(\text{MA}_{n_2}\text{B}_{m_2}) - E_b(\text{BA}_{n_2}\text{B}_{m_2}). \quad (2)$$

ΔE_i here is somewhat like the formation energy of an impurity in the host [22]. According to the lowest-energy principle, we can determine the site preference of each M in A_nB_m(s) by comparing the values of ΔE_1 and ΔE_2 as follows.

- (i) If $\Delta E_1 > \Delta E_2$, then M atoms prefer the A sites.
- (ii) If $\Delta E_1 < \Delta E_2$, then M atoms prefer the B sites.
- (iii) If $\Delta E_1 \simeq \Delta E_2$, then M atoms can occupy both A and B sites.

The above scheme is valid only for ICs of stoichiometric compositions, where all A atoms are in the A sites and all B atoms in the B sites. However, many ICs can exist stably over a composition range around their stoichiometry with the structures unchanged. Such non-stoichiometric ICs may be either A poor or A rich. First we consider the A-poor IC with the compositional formula A_{n-x}B_{m+x} ($0 < x < 1$) (hereafter denoted A_nB_m(p)). As in A_nB_m(s), all A atoms in A_nB_m(p) are in the A sites, but B atoms in A_nB_m(p) can be located in two kinds of site: the majority in the regular B sites and the minority (with concentration x) in the A sites. As a result, the substitutional ways for ternary additions to occupy the same kind of site will be different in A_nB_m(s) and A_nB_m(p). In A_nB_m(s), the

ternary additions occupy the A(B) sites by substituting for A(B) atoms only. However, they can be located in the A sites of $A_nB_m(p)$ by substituting for either A or B atoms. Hence, the local structure for A sites in $A_nB_m(p)$ should be represented by the two clusters $AA_{n_1}B_{m_1}$ and $BA_{n_1}B_{m_1}$, and we need to define a third energy parameter, besides ΔE_1 and ΔE_2 as defined above, for each M as

$$\Delta E_3 = E_b(MA_{n_1}B_{m_1}) - E_b(BA_{n_1}B_{m_1}). \quad (3)$$

The site preference of each M in $A_nB_m(p)$ can then be determined by comparing the values of ΔE_1 , ΔE_2 and ΔE_3 , as follows.

- (i) If ΔE_1 is the largest, then M atoms prefer the A sites.
- (ii) If ΔE_2 is the largest, then M atoms prefer the B sites.
- (iii) If ΔE_3 is the largest and (a) $\Delta E_1 > \Delta E_2$, then M atoms prefer the A sites, or (b) $\Delta E_1 < \Delta E_2$, then M atoms can occupy A and (B) sites.

In the case of (iii)(b), the notation (B) means that it depends on the value of x and the concentration of the additions themselves whether M atoms will occupy the B sites, as will be explained in more detail in the case of γ' -Ni₃Al.

Similarly, in the A-rich IC with the compositional formula $A_{n+x}B_{m-x}$ ($0 < x < 1$) (hereafter denoted $A_nB_m(r)$), the additions can occupy the B sites by substituting for either A or B atoms, and the local structure for the B sites should be represented by the two clusters $BA_{n_2}B_{m_2}$ and $AA_{n_2}B_{m_2}$. Therefore, we have to define a fourth parameter for each M as

$$\Delta E_4 = E_b(MA_{n_2}B_{m_2}) - E_b(AA_{n_2}B_{m_2}) \quad (4)$$

and the site preference of each M in $A_nB_m(r)$ can be determined by comparing the values of ΔE_1 , ΔE_2 and ΔE_4 . One can extend this further in the same way as for $A_nB_m(p)$.

Obviously, the above scheme can be easily generalized to other ICs of more than two inequivalent sites or components.

2.2. Binding energy calculation

The discrete-variational (DV) local-density-functional (LDF) method is used to calculate the binding energies of the clusters in the above scheme. This method is a kind of molecular orbital calculational method, and its theoretical foundation is LDF theory. Since it has been described in detail elsewhere [23–25], here we only summarize its main steps and discuss the computational technique of the binding energies.

- (a) The one-electron Hamiltonian underlying the DV LDF method is

$$h(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_C(\mathbf{r}) + V_{xc}(\mathbf{r}) \quad (5)$$

where the first two terms are, respectively, the kinetic energy and the Coulomb potential given by

$$V_C(\mathbf{r}) = -\sum_{\nu} \frac{Z_{\nu}}{|\mathbf{r} - \mathbf{R}_{\nu}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6)$$

and $V_{xc}(\mathbf{r})$ is the local exchange–correlation potential, which we take to be of the von Barth–Hedin [26] form, with the parameters taken from Moruzzi *et al* [27]. \mathbf{R}_ν is the site of the ν th nucleus in the cluster.

(b) The one-electron wavefunctions ψ_i for the cluster are expanded in a linear combination of $\chi_j(\mathbf{r})$:

$$\psi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r}) C_{ji} \quad (7)$$

where the $\chi_j(\mathbf{r})$ are the symmetrized atomic orbitals that transform as one of the irreducible representations of the point group of the cluster.

(c) The one-electron equation

$$(h - \epsilon_i)\psi_i(\mathbf{r}) = 0 \quad (8)$$

is approximately solved by the Rayleigh–Ritz variational method, which is achieved by using the expansion of ψ_i in (7) and minimizing certain error functions Δ_{ij} defined as

$$\Delta_{ij} = \langle \psi_i | h - \epsilon | \psi_j \rangle. \quad (9)$$

This procedure leads to the secular equation

$$(\mathbf{H} - \epsilon\mathbf{S})\mathbf{C} = 0. \quad (10)$$

(d) In the DV scheme, the matrix elements of the Hamiltonian matrix \mathbf{H} and the overlap matrix \mathbf{S} are obtained by a weighted summation over a set of sample points \mathbf{r}_k (diophantine points) [23], i.e.

$$H_{ij} = \langle \chi_i | h | \chi_j \rangle = \sum_k \omega(\mathbf{r}_k) \chi_i^*(\mathbf{r}_k) h(\mathbf{r}_k) \chi_j(\mathbf{r}_k) \quad (11)$$

$$S_{ij} = \langle \chi_i | \chi_j \rangle = \sum_k \omega(\mathbf{r}_k) \chi_i^*(\mathbf{r}_k) \chi_j(\mathbf{r}_k) \quad (12)$$

where the $\omega(\mathbf{r}_k)$ -values are appropriate integration weights.

(e) The calculation of Coulomb integrals is simplified by introducing the average self-consistent charge density ρ_{SCC} approximation [24]:

$$\rho(\mathbf{r}) = \sum_i f_i |\psi_i|^2 \simeq \rho_{SCC} = \sum_{\nu nl} f_{nl}^\nu |R_{nl}(\mathbf{r}_\nu)|^2 \quad (13)$$

where f_i is the Fermi–Dirac occupation number for the ψ_i orbital, f_{nl}^ν is the Mulliken population for the nl atomic shell of atom ν , and $R_{nl}(\mathbf{r}_\nu)$ is the corresponding radial function, with $\mathbf{r}_\nu = \mathbf{r} - \mathbf{R}_\nu$.

(f) The total energy of a cluster in the local-density approximation is written in standard notation [24] as

$$\begin{aligned}
 E_{\text{tot}} &= \sum_i f_i \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\
 &\quad + \int \rho(\mathbf{r})[\epsilon_{\text{xc}}(\mathbf{r}) - v_{\text{xc}}(\mathbf{r})] d\mathbf{r} + \frac{1}{2} \sum_{\mu} \sum_{\nu}' \frac{Z_{\mu}Z_{\nu}}{R_{\mu\nu}} \\
 &= \int e(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{\mu} \sum_{\nu}' \frac{Z_{\mu}Z_{\nu}}{R_{\mu\nu}} \quad (14)
 \end{aligned}$$

where ϵ_{xc} and v_{xc} are the exchange–correlation energy density and potential, respectively, and $e(\mathbf{r})$ is an energy density. The binding energy of the cluster is then defined with respect to some reference system, say the dissociated atoms, as

$$E_{\text{b}} = -(E_{\text{tot}} - E_{\text{tot}}^{\text{ref}}) \quad (15)$$

where

$$E_{\text{tot}}^{\text{ref}} = \int e^{\text{ref}}(\mathbf{r}) d\mathbf{r}. \quad (16)$$

In the DV scheme, the numerical error of E_{b} is minimized with the point-by-point error cancellation technique. In this technique, the reference system energy is computed with the same sampling grid as in the SCF and the cluster energy procedures by freezing the atoms at their respective lattice sites but are now assumed to be non-interacting [28–30], so that the numerical error of E_{b} can be partly cancelled out via point-by-point subtraction of $e(\mathbf{r}_k)$ and $e^{\text{ref}}(\mathbf{r}_k)$:

$$E_{\text{b}} = - \sum_k \omega(\mathbf{r}_k)[e(\mathbf{r}_k) - e^{\text{ref}}(\mathbf{r}_k)] - \frac{1}{2} \sum_{\mu} \sum_{\nu}' \frac{Z_{\mu}Z_{\nu}}{R_{\mu\nu}}. \quad (17)$$

3. Site preference of ternary additions in γ' -Ni₃Al

γ' -Ni₃Al is known as one of the most important nickel-based alloys and has excellent high-temperature strength properties, but its application as a high-temperature structural material is restricted owing to the ductility in its polycrystalline form. Extensive investigations have been made concerning its ductilization [30–34] and considerable experimental data on the substitution behaviours of ternary additions in it are available [16, 34]. Here we shall perform a first-principles calculation on the site preference of some ternary additions in γ' -Ni₃Al with our general method, in the hope of providing a theoretical basis for understanding the experimental data and meanwhile providing a test of our method.

γ' -Ni₃Al is an IC of $L1_2$ -type structure ($a = 3.566 \text{ \AA}$). This type of structure is based on an ordered FCC unit cell in which Ni and Al atoms are located in the face-centred sites and the cube corners, respectively (figure 1(a)). Each Ni site is surrounded by eight NN

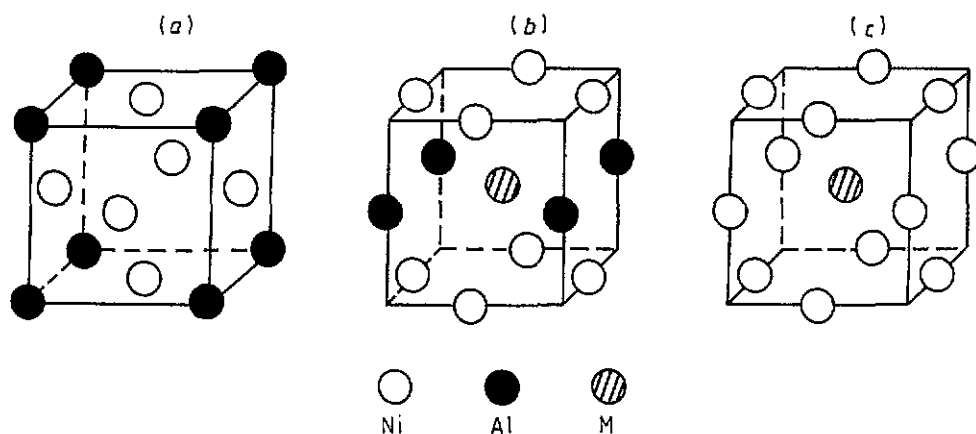


Figure 1. Cluster models: (a) the unit cell of γ' -Ni₃Al; (b) MNi₈Al₄ cluster; (c) MNi₁₂ cluster.

Ni atoms and four NN Al atoms, and each Al site by 12 NN Ni atoms. Hence we choose the substitutional clusters MNi₈Al₄ with D_{4h} point group symmetry (figure 1(b)) and MNi₁₂ with O_h symmetry (figure 1(c)) to represent the local structure of an atom M in the Ni and Al sites, respectively, where M stands for an Ni(Al) atom or ternary additions. In the notation of the general method, we have A \equiv Ni, B \equiv Al, $n = 3$, $m = 1$; $n_1 = 8$, $m_1 = 4$; $n_2 = 12$, $m_2 = 0$ and M \equiv Al, Sc, Ti, V, Fe, Co, Ni, Cu, Nb, Mo and Pd.

The spin-restricted scheme is adopted in our DV LDF binding-energy calculations. The numerical atomic basis functions are chosen as the variational basis set, which are obtained from the self-consistent atomic LDF calculations [35]. We choose the 1s- np of an M atom (M \equiv Al, $n = 3$, M \equiv Sc, Ti, V, Fe, Co, Ni and Cu, $n = 4$; M \equiv Nb, Mo and Pd, $n = 5$) as the basis set in our calculations (hereafter called the basis set I). That is, we choose 1s-2p, 3s, 3p for Al, 1s-3p, 3d, 4s, 4p for the first-row transition-metal atoms and 1s-4p, 4d, 5s, 5p for the second-row transition-metal atoms. The lower-energy orbitals are treated as frozen cores. 300 sample points per atom are adopted in our numerical integrations.

Table 1 lists the binding energies of the clusters. Using the results of this table, we obtain the values of ΔE_i , as presented in table 2. Comparing the values of ΔE_1 and ΔE_2 , we can determine the site preference of each M in Ni₃Al(s) (table 3). From table 3, we find that there are three fundamental site preference behaviours for ternary additions in Ni₃Al(s). Sc, Co, Cu and Pd atoms prefer the Ni sites, Ti, V, Nb and Mo atoms prefer the Al sites, while Fe atoms can occupy both the Ni and the Al sites. We see that all the calculated results for Ni₃Al(s) are in complete agreement with the experimental data, which proves our method to be successful.

Table 3 also lists the ternary site preference in Ni₃Al(p) and Ni₃Al(r). The three types of occupation behaviour for ternary additions exist too in Ni₃Al(p) and Ni₃Al(r), but given M additions may occupy different sites in Ni₃Al(s), Ni₃Al(p) and Ni₃Al(r). We can divide the ternary additions into two groups. The first group contains Ti, V, Cu, Nb, Mo and Pd. Their site preference remains unchanged irrespective of whether the host is Ni₃Al(s), Ni₃Al(p) or Ni₃Al(r). Experiment [14] indicated that Pd atoms strongly prefer the Ni sites regardless of the composition of the host. This is identical with our calculated result. The other ternary additions Sc, Fe and Co belong to the second group. Their site preference in Ni₃Al(p) remains the same as in Ni₃Al(s) but depends on the concentrations of the additions

Table 1. Binding energies of clusters in γ' -Ni₃Al.

M	E_b (MNi ₈ Al ₄) (eV)	E_b (MNi ₁₂) (eV)
Al	64.21	70.10
Sc	62.40	70.51
Ti	65.67	74.07
V	66.48	75.36
Fe	64.85	72.87
Co	63.66	71.22
Ni	62.06	69.41
Cu	62.51	66.58
Nb	68.52	77.28
Mo	68.57	77.63
Pd	63.05	65.96

Table 2. The values of ΔE_i ($i = 1, 2, 3, 4$) in γ' -Ni₃Al.

M	ΔE_1 (eV)	ΔE_2 (eV)	ΔE_3 (eV)	ΔE_4 (eV)
Al	2.15	0	0	0.69
Sc	0.34	-0.41	-1.81	1.10
Ti	3.61	3.97	1.46	4.66
V	4.42	5.26	2.27	5.95
Fe	2.79	2.77	0.64	3.46
Co	1.60	1.12	-0.55	1.81
Ni	0	-0.69	-2.15	0
Cu	0.45	-3.52	-1.7	-2.83
Nb	6.46	7.18	4.31	7.87
Mo	6.51	7.53	4.36	8.22
Pd	0.99	-4.04	-1.16	-3.45

Table 3. The site preference of some ternary additions in γ' -Ni₃Al.

M	Ni ₃ Al(s)			
	Present work	Experimental result [16]	Ni ₃ Al(p)	Ni ₃ Al(r)
Sc	Ni	Ni	Ni	Al, (Ni)
Ti	Al	Al	Al	Al
V	Al	Al	Al	Al
Fe	Ni, Al	Ni, Al	Ni, Al	Al, (Ni)
Co	Ni	Ni	Ni	Al, (Ni)
Cu	Ni	Ni	Ni	Ni
Nb	Al	Al	Al	Al
Mo	Al	Al	Al	Al
Pd	Ni	Ni	Ni	Ni

themselves in Ni₃Al(r). Such concentration dependence occurs when $\Delta E_4 > \Delta E_1 > \Delta E_2$ for a given M in Ni₃Al(r) (see table 2), corresponding to case (iii)(b) for A_nB_m (p). To show this, we take Sc as an example. The compositional formula for the host Ni₃Al(r) is written in atomic percentages as Ni_{75+x}Al_{25-x} ($x > 0$). In this formula, Ni atoms are divided into two parts: 75 at.% Ni are in the Ni sites and the rest x at.% Ni are in the Al sites. The condition

$\Delta E_4 > \Delta E_1 > \Delta E_2$ for Sc-doped $\text{Ni}_3\text{Al}(r)$ indicates that Sc in $\text{Ni}_3\text{Al}(r)$ will substitute for the Ni atoms in the Al sites prior to replacing the Ni atoms in the Ni sites. So, if we write the compositional formula for Sc-doped $\text{Ni}_3\text{Al}(r)$ as $\text{Ni}_{(75-y_2)+(x-y_1)}\text{Al}_{25-x}\text{Sc}_y$ with $x > 0$ and $y_1 + y_2 = y$, we have $y_1 = y, y_2 = 0$ when $y \leq x$, and $y_1 = x, y_2 = y - x \neq 0$ when $y > x$. That is to say, Sc atoms occupy only the Al sites when $y \leq x$ and is located in both the Al and the Ni sites when $y > x$. Also, it is worth noting that, for those additions occupying only the Al sites in $\text{Ni}_3\text{Al}(s)$, their site preference remains unaltered in $\text{Ni}_3\text{Al}(p)$ and $\text{Ni}_3\text{Al}(r)$.

Finally we discuss the accuracy of our method. The convergence of the basis set was examined by performing cluster calculations using the basis set II which includes the nd of an M atom based on the basis set I. We found that there is a small difference between E_b (basis set I) and E_b (basis set II), but the values of ΔE_i calculated by using E_b (basis set I) and E_b (basis set II), respectively, are almost the same. Because we are only interested in the comparison of the ΔE_i values, in this sense we can say that the basis set I used in our calculations is convergent. As for the number of integration points, it was found that 300 diophantine points per atom (or a total of 3900 numerical integration points for a cluster) in both the SCF and the energy procedures, with the use of the point-by-point error cancellation technique for E_b , were sufficient to produce an average relative precision of 0.05 eV in the binding energies [25] (at this moment, the absolute errors in the total energies [29] are of the order of 1 eV). With this degree of precision it is possible to compare the ΔE_i -values for a given M.

In order to test the effect of the cluster size, we extended our clusters to include the second-NN atoms. That is, we chose the 19-atom clusters $\text{MNi}_8\text{Al}_4\text{Ni}_4\text{Ni}_2$ and $\text{MNi}_{12}\text{Al}_6$ for the Ni and Al sites, respectively. With 19-atom clusters, the values of E_b and ΔE_i for some selected M ($M \equiv \text{Al}, \text{V}, \text{Fe}, \text{Co}$ and Ni) were calculated and presented in table 4. From this table, we found that, although the values of E_b and ΔE_i are changed by the increase in the cluster size, the relationships between the ΔE_i for a given M are not changed. For example, the relation $\Delta E_4 > \Delta E_2 > \Delta E_1 > \Delta E_3$ for V obtained from this table is the same as that from table 2. Thus, we can say that the cluster size has no influence on the final results of the paper.

Table 4. The values of E_b and ΔE_i for $M \equiv \text{Al}, \text{V}, \text{Fe}, \text{Co}$ and Ni with 19-atom clusters.

M	E_b ($\text{MNi}_8\text{Al}_4\text{Ni}_6$) (eV)	E_b ($\text{MNi}_{12}\text{Al}_6$) (eV)	ΔE_1 (eV)	ΔE_2 (eV)	ΔE_3 (eV)	ΔE_4 (eV)
Al	109.60	103.11	1.89	0	0	0.83
V	111.24	108.82	3.53	5.71	1.64	6.54
Fe	109.72	105.17	2.01	2.06	0.12	2.89
Co	108.73	103.66	1.02	0.55	-0.87	1.38
Ni	107.71	102.28	0	-0.83	-1.89	0

4. Conclusions

We have presented a general method to determine the site preference of alloying additions in ICs with either stoichiometric or non-stoichiometric compositions, by first-principles binding-energy calculations using cluster models. The validity and reliability of the method are

tested by applying it to the site preference study of some ternary additions in γ' -Ni₃Al. The calculated results completely reproduce the experimental data, which proves that our method is successful. The calculated results clearly show how the site preference of ternary additions changes with the compositions of the host elements and with the concentrations of the additions themselves in the host.

Since the method is of general applicability, we believe that it will become a promising tool for theoretical prediction of the site preference of alloying additions in other ICs, such as γ -TiAl [36]. Also, these results will provide a basis for further studying the effects of alloying additions in improving the ductility of ICs. Certainly, we should point out that the temperature effect has not been included in the present scheme for it has a very small influence on the site preference of alloying additions [16]. If necessary, however, we could use our method incorporating the cluster variation method [37] to study the site preference at finite temperatures.

Acknowledgments

This work was supported by the National Science Foundation of China and by the Youth Natural Science Foundation of USTC.

References

- [1] McAndrew J B and Kessler H D 1956 *J. Met.* **8** 1348
- [2] Lipsitt H A 1985 *High-temperature Ordered Intermetallic Alloys I (Mater. Res. Soc. Symp. Proc. 39)* (Pittsburgh, PA: Materials Research Society) p 351
- [3] Chubb S R, Papaconstantopoulos D A and Klein B M 1988 *Phys. Rev. B* **38** 12120
- [4] Liu C T, Taub A I, Stoloff N S and Koch C C (ed) 1989 *High-temperature Ordered Intermetallic Alloys III (Mater. Res. Soc. Symp. Proc. 133)* (Pittsburgh, PA: Materials Research Society)
- [5] Huang S C and Hall E L 1991 *Metall. Trans. A* **22** 427
- [6] Liu C T 1984 *Int. Metall. Rev.* **29** 169
- [7] Hanamura T, Uemori R and Tanino M 1988 *J. Mater. Res.* **3** 656
- [8] Kim Y W 1989 *J. Met.* **41** 24
- [9] Huang S C and Hall E L 1991 *Acta Metall. Mater.* **39** 1053
- [10] Frisch H L and Patel J R 1967 *Phys. Rev. Lett.* **18** 784
- [11] Daw M S and Baskas M I 1983 *Phys. Rev. Lett.* **50** 1285
- [12] Painter G S and Averill F W 1987 *Phys. Rev. Lett.* **58** 234
- [13] Eberhart M E and Vvendsensky D D 1987 *Phys. Rev. Lett.* **58** 61; 1988 *Phys. Rev. B* **37** 8458
- [14] Chiba A, Shindo D and Hanada S 1991 *Acta Metall. Mater.* **39** 13
- [15] Babu V S and Seehra M S 1991 *J. Mater. Res.* **6** 339
- [16] Ochiai S, Oya Y and Suzuki T 1984 *Acta Metall.* **32** 289
- [17] Wu Y P, Tso N C, Scanzhez J M and Tien J K 1989 *Acta Metall.* **37** 2835
- [18] Nandy T K, Banerjee D and Gogia A K 1990 *Scr. Metall. Mater.* **24** 2019
- [19] Ellis D E, Benesh G A and Byrom E 1979 *Phys. Rev. B* **20** 1198
- [20] Yang Jinlong, Wang Kelin, Donà dalle Rose L F and Toigo F 1991 *Phys. Rev. B* **44** 4275, 10508
- [21] Guenzburger D and Ellis D E 1991 *Phys. Rev. Lett.* **67** 3832
- [22] Kajihara S A, Antenelli A, Bernholc J and Car R 1991 *Phys. Rev. Lett.* **66** 2010
- [23] Painter G S and Ellis D E 1970 *Phys. Rev. B* **1** 4747
- [24] Rosen A, Ellis D E, Adachi H and Averill F W 1976 *J. Chem. Phys.* **65** 3629
- [25] Delley B, Ellis D E, Freeman A J, Baerends E J and Post D 1983 *Phys. Rev. B* **27** 2132
- [26] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
- [27] Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (Oxford: Pergamon)
- [28] Khowash P K and Ellis D E 1989 *Phys. Rev. B* **39** 1908

- [29] Guenzberg D and Ellis D E 1992 *Phys. Rev. B* **45** 285
- [30] Flinn P A 1960 *Trans. Metall. Soc. AIME* **218** 145
- [31] Thornton P H, Davies R G and Johnson T L 1970 *Metall. Trans. A* **1** 207
- [32] White C L, Padgett R A, Liu C T and Yalisove S M 1984 *Scripta Metall.* **18** 1417
- [33] Baker I, Huang B and Schulson E M 1989 *Acta Metall.* **36** 493
- [34] Chiba A, Hanada S and Watanabe S 1991 *Acta Metall.* **39** 1799
- [35] Averill F W and Ellis D E 1973 *J. Chem. Phys.* **59** 6412
- [36] Yang Jinlong, Xiao Chuanyun, Xia Shangda and Wang Kelin 1992 *Phys. Rev. B* **46** 13709
- [37] Kikuchi R 1951 *Phys. Rev.* **81** 988