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ON THE SITE PREFERENCES OF TERNARY ADDITIONS TO TRIPLE DEFECT B2 INTERMETALLIC COMPOUNDS

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Abstract

Knowledge of the site preference of ternary solute additions is essential to developing an understanding of how these solutes affect the properties of B2 intermetallic compounds. A quasichemical model will be presented which is able to predict the site preferences of dilute solute additions to triple defect B2 compounds. The only parameters required are enthalpies of formation at the stoichiometric composition. General equations are developed which can be used to determine site occupations and defect concentrations for dilute as well as non-dilute solute additions. These equations use atom pair bond enthalpies as the parameters. It is found that the site preferences of dilute additions are not always in agreement with predictions based on the solubility lobes in ternary Gibbs isotherms. Predictions for dilute additions to NiAl and FeAl are compared to experimental results found in the literature. Satisfactory correlation is found between the model and the experimental results. In addition, the predictions from the model on vacancy concentrations in Fe doped NiAl are compared to recent experimental results by the authors.

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1.0 Introduction

Intermetallic compounds with the B2 crystal structure such as NiAl and FeAl have been investigated recently for possible use as structural materials in high temperature, oxidizing and/or corrosive environments. The major limiting property of these materials has been a lack of sufficient room temperature ductility. Attempts to improve the ductility have often been made through ternary or higher order alloying. For B2 compounds, substitutional alloying additions can occupy either of the two sublattices and this site occupancy can be crucial in determining how the alloying addition affects the properties of the alloy. In this manuscript we will discuss the use of thermodynamic modeling to predict the site occupancies of ternary alloying additions in B2 compounds with the triple defect structure.

The B2 (or CsCl) phase has an ordered bcc structure with one element occupying the cube corners and the other occupying the cube center. The defect structure of these compounds generally fall into two categories, the anti-structure defect structure and the triple defect structure.[1] In this manuscript we will be considering only compounds with the triple defect structure such as NiAl, CoAl, and FeAl. In a B2 compound AB, where B is the larger atom, the triple defect model stipulates that the majority defect types are A atoms on β sites and vacancies on α sites (where we have defined α as the sublattice on which A atoms normally sit and β as the sublattice where B atoms normally sit). These defects are generated either thermally or constitutionally. Thermal defects arise from entropic effects at temperatures above absolute zero, while constitutional defects are present in compositions away from stoichiometry. In an A-rich triple defect compound the constitutional defect is the anti-site A atom on the β sublattice, while at B-rich compositions the constitutional defect is the α-site vacancy.

Quasichemical models, which are essentially extensions of the Braggs-Williams model, have been developed for binary B2 intermetallic compounds.[1-11] These models consider first nearest neighbor bond energies for the enthalpy term and assume random mixing on each sublattice. The models can be used to describe the defect concentrations, as well as various thermodynamic properties of the compounds. Ipser *et al.* extended the quasichemical model to ternary triple defect B2 compounds.[12] However, their model made the assumption that the A to C ratio (where C is the third element) is the same on both sublattices. This assumption is justified only in a few special cases. A more general model which makes no such assumption was developed by Kao, Pike, Chen, and Chang.[13] It is this model which will be utilized in the present manuscript to predict the site occupancies in real B2 triple defect systems. An even

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2.0 Quasiche

2.1 Definitions of Terms

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(a) The total numbers of A
N_C respectively. The total num
number of vacancies is $N_\square$.

(b) There are equal numbe
normally occupied by A atoms
number of sites, N_S, is $N_S = N$

(c) Composition will be des
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(d) The relative mole fracti

$$y^\alpha = \frac{}{N}$$

for the α and β sublattices resp
etc.

(e) The vacancy concentrat

more general model which can be used for systems with an arbitrary number of elements, an arbitrary number of sublattices, and several types of defects, including vacancies, was developed by Chen.[14] It can be shown that the previous models can be derived from this model if certain simplifying assumptions are made.

In the following section the model of Kao *et al.*[13] will be presented in detail. In Section 3 the application of the model to the prediction of the site preferences of ternary alloy additions will be described. In Section 4 this methodology will be applied to the case of ternary additions to the NiAl and FeAl systems.

2.0 Quasichemical Model for Triple Defect B2 Compounds

2.1 Definitions of Terms

The definitions of symbols are given below. Superscripts α and β represent sublattices, while subscripts A, B, C and $\Box$ (vacancy) represent species.

(a) The total numbers of A, B, and C atoms in the crystal are represented by N_A, N_B, and N_C respectively. The total number of atoms in the crystal, N, is then $N = N_A + N_B + N_C$. The number of vacancies is $N_\Box$.

(b) There are equal numbers of α and β sites, N^α and N^β. The α sublattice sites are normally occupied by A atoms, while β sites are normally occupied by B atoms. The total number of sites, N_S, is $N_S = N + N_\Box$.

(c) Composition will be described by the two variables, χ and ζ. χ is defined as $\chi = x_B - 0.5$, while $\zeta = x_A/x_C$ (where x_A is the mole fraction of A, i.e. $x_A = N_A / N$, etc.).

(d) The relative mole fractions of A and C atoms on the α and β sublattices are defined by

$$y^\alpha = \frac{N_C^\alpha}{N_A^\alpha + N_C^\alpha} \qquad \text{and} \qquad y^\beta = \frac{N_C^\beta}{N_A^\beta + N_C^\beta}$$

for the α and β sublattices respectively, where N_A^α is the number of A atoms on the α sublattice, etc.

(e) The vacancy concentration is defined as $z = N_\Box / N$.

2.2 Assumptions of the Model

(a) The majority defects are A atoms on the β sublattice, N_A^β, and vacancies on the α sublattice, $N_\square^\alpha$. The number of vacancies on the β sublattice, $N_\square^\beta$, and B atoms on the α sublattice, N_B^α, are considered to be negligible. The vacancy concentration thus becomes z = $N_\square$ / N = $N_\square^\alpha$ / N.

(b) The C atoms can go to the α sublattice as well as the β sublattice.

2.3 Development of Model

The relationships between the quantities defined above are shown in Table I. It can be seen that all of these quantities can be expressed in terms of the four variables N, y^α, y^β, and z. At a fixed temperature, T, pressure, P, and composition, χ and ζ , the total Gibbs free energy, G, is a function of these same four variables. That is

$$G = G(N, y^\alpha, y^\beta, z) = H - TS \tag{1}$$

where H and S are enthalpy and entropy, etc. H and S are in turn a function of these four variables as will be discussed later. At a fixed composition, y^α, y^β, and z are constrained by the following equation

$$\zeta = \frac{N_C}{N_A} = \frac{y^\alpha(1-z) + y^\beta(z-2\chi)}{(1-y^\alpha)(1-z) + (1-y^\beta)(z-2\chi)} \tag{2}$$

which can be derived from the information given in Table I.

Table I Distribution of Atoms and Vacancies on the α-sublattice and β-sublattice

Species	α-sublattice	β-sublattice	Total species (sum of each row)
A atoms	$N_A^\alpha = \frac{N}{2}(1-y^\alpha)(1-z)$	$N_A^\beta = \frac{N}{2}(1-y^\beta)(z-2\chi)$	$N_A = \frac{N}{2}[(1-y^\alpha)(1-z)+(1-y^\beta)(z-2\chi)]$
C atoms	$N_C^\alpha = \frac{N}{2}y^\alpha(1-z)$	$N_C^\beta = \frac{N}{2}y^\beta(z-2\chi)$	$N_C = \frac{N}{2}[y^\alpha(1-z)+y^\beta(z-2\chi)]$
B atoms	$N_B^\alpha = 0$	$N_B^\beta = \frac{N}{2}(1+2\chi)$	$N_B = \frac{N}{2}(1+2\chi)$
Vacancies	$N_\square^\alpha = \frac{N}{2}2z$	$N_\square^\beta = 0$	$N_\square^\beta = 0$
Total sites (sum of each column)	$N^\alpha = \frac{N}{2}(1+z)$	$N^\beta = \frac{N}{2}(1+z)$	$N_S = N(1+z)$

N_A^β, and vacancies on the α

$N_\square^\beta$, and B atoms on the α

centration thus becomes z =

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Total species sum of each row)
$-y^\alpha)(1-z)+(1-y^\beta)(z-2\chi)]$
$^\alpha(1-z)+y^\beta(z-2\chi)]$
$+2\chi)$
$+z)$

The requirement for thermodynamic equilibrium is that the total Gibbs free energy is a minimum. Thus the equilibrium defect concentrations and C atom distribution at a given temperature, pressure, and composition can be determined by minimizing G with respect to the variables y^α, y^β, and z under the constraint of Eq. (2). In order to do this we will first derive expressions for H and S in terms of y^α, y^β, and z and substitute these into Eq. (1).

The enthalpy term, which is obtained by considering only nearest neighbor interactions, is $H=\sum_{i,j} n_{ij}H_{ij}$ where n_{ij} is the number of nearest-neighbor pairs i-j and H_{ij} is the corresponding interaction enthalpy (i and j can be A, B, C, or □). It is further assumed that H_{ij} for the case of i on α and j on β is the same as when i is on β and j is on α. The n_{ij} terms can be derived from the information given in Table I with the coordination number of the B2 crystal structure (eight). The enthalpy can then be expressed as:

$$\begin{aligned} H=\frac{4N}{1+z}[&(1-y^\alpha)(1-y^\beta)(1-z)(z-2\chi)H_{AA}+(y^\alpha+y^\beta-2y^\alpha y^\beta)(1-z)(z-2\chi)H_{AC}\\ &+(1-y^\alpha)(1-z)(1+2\chi)H_{AB}+(1-y^\beta)(2z)(z-2\chi)H_{A\square}+y^\alpha(1-z)(1+2\chi)H_{CB}\\ &+y^\beta 2z(z-2\chi)H_{C\square}+2z(1+2\chi)H_{B\square}+y^\alpha y^\beta(1-z)(z-2\chi)H_{CC}] \end{aligned} \quad (3)$$

Since χ and z are small numbers, all terms in Eq. (3) that contain the product of (z-2χ) and z will be considered negligible. That is, the $H_{A\square}$ and $H_{C\square}$ terms will be dropped from Eq. (3).

For the entropy term we will consider only the configurational entropy, which can be obtained from the Boltzmann relationship. Using Table I and Stirling's approximation the following expression is obtained for the entropy term:

$$\begin{aligned} S=\frac{Nk}{2}[&(1-y^\alpha)(1-z)\ln\frac{(1+z)}{(1-y^\alpha)(1-z)}+y^\alpha(1-z)\ln\frac{(1+z)}{y^\alpha(1-z)}+2z\ln\frac{(1+z)}{2z}\\ &+(1-y^\beta)(z-2\chi)\ln\frac{(1+z)}{(1-y^\beta)(z-2\chi)}+y^\beta(z-2\chi)\ln\frac{(1+z)}{y^\beta(z-2\chi)}+(1+2\chi)\ln\frac{(1+z)}{(1+2\chi)}] \end{aligned} \quad (4)$$

where k is the Boltzmann constant.

Substituting Eqs. (3) and (4) into Eq. (1) we now have G expressed in terms of y^α, y^β, and z. It is now possible to minimize G with respect to y^α, y^β, and z under the constraint of Eq. (2). This can be done by means of a Lagrange multiplier. For reasons of brevity the details of this computation are not given here (refer to Kao *et al.* for details[13]). The results of the minimization are the following two equations:

$$\frac{(2z)^2(1-y^\beta)(z-2\chi)}{(1-y^\alpha)(1-z)(1+z)^2} = \exp\{\frac{-8}{kT(1+z)^2}\{[(1-2z+4\chi-z^2)(1-y^\alpha)(1-y^\beta)$$
$$-(1+z)(z-2\chi)y^\alpha(1-y^\beta)+(1+z)(1-z)y^\beta(1-y^\alpha)]H_{AA} + [(1-2z+4\chi-z^2) \quad (5)$$
$$(y^\alpha+y^\beta-2y^\alpha y^\beta)-(1+z)(1-z)y^\beta(1-2y^\alpha)+(1+z)(z-2\chi)y^\alpha(1-2y^\beta)]H_{AC}$$
$$-[2(1+2\chi)(1-y^\alpha)+(1+z)(1+2\chi)y^\alpha]H_{AB} - (1-z)(1+2\chi)y^\alpha H_{CB}$$
$$-(1-z)(z-2\chi)y^\alpha y^\beta H_{CC} + 2(1+2\chi)H_{B\square}\}\}$$

and

$$\frac{(2z)^2 y^\beta(z-2\chi)}{y^\alpha(1-z)(1+z)^2} = \exp\{\frac{-8}{kT(1+z)^2}\{-(1-z)(z-2\chi)(1-y^\alpha)(1-y^\beta)H_{AA}$$
$$+[(1-2z+4\chi-z^2)(y^\alpha+y^\beta-2y^\alpha y^\beta)+(1+z)(1-z)(1-y^\beta)(1-2y^\alpha)$$
$$-(1+z)(z-2\chi)(1-y^\alpha)(1-2y^\beta)]H_{AC} - (1-z)(1+2\chi)(1-y^\alpha)H_{AB} \quad (6)$$
$$-[2(1+2\chi)y^\alpha+(1+z)(1+2\chi)(1-y^\alpha)]H_{CB}$$
$$-[(1-z)(z-2\chi)y^\alpha y^\beta+(1+z)(z-2\chi)y^\beta-(1-z)(1+z)y^\alpha]H_{CC}$$
$$+2(1+2\chi)H_{B\square}\}\}$$

If the six interaction enthalpy terms (H_{AA}, H_{AC}, H_{AB}, H_{CB}, H_{CC}, and $H_{B\square}$) are known, Eqs. (5) and (6) can be solved simultaneously with Eq. (2) for y^α, y^β, and z. These terms uniquely determine the site ocupancies.

2.4 Simplified Model for the Dilute Alloying Additions

Unfortunately, the interaction enthalpy terms are rarely known for most systems. It is possible to simplify Eqs. (5) and (6) if it is assumed that the ternary alloy addition is dilute (on the order of one atomic percent or less). By examining the right hand side of the two equations and dropping terms with the small numbers, z, χ, and y^α, we get the following two equations:

$$\frac{(2z)^2(1-y^\beta)(z-2\chi)}{(1-y^\alpha)(1-z)(1+z)^2} = \exp[\frac{-8}{kT}(H_{AA}-2H_{AB}+2H_{B\square})] = \exp(-\frac{\Delta H_i}{RT}) \quad (7)$$

and

$$\frac{(2z)^2 y^\beta(z-2\chi)}{y^\alpha(1-z)(1+z)^2} = \exp[\frac{-8}{kT}(H_{AC}-H_{AB}-H_{CB}+2H_{B\square})] \quad (8)$$

$-z^2)(1-y^\alpha)(1-y^\beta)$

$[(1-2z+4\chi-z^2)$ (5)

$)y^\alpha(1-2y^\beta)]H_{AC}$

$2\chi)y^\alpha H_{CB}$

$y^\alpha)(1-y^\beta)H_{AA}$

$-2y^\alpha)$

$y^\alpha)H_{AB}$ (6)

ccc

H_{CC}, and $H_{B\square}$) are known,
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$) \ ] = \exp(-\frac{\Delta H_t}{RT})$ (7)

] (8)

where $\Delta H_t \equiv 8N(H_{AA}-2H_{AB}+2H_{B\square})$ has been defined as the enthalpy of formation of a mole of triple defects in a binary AB compound[15]. Further, dividing Eq.(8) by Eq.(7) we obtain

$$\frac{(1-y^\alpha)y^\beta}{(1-y^\beta)y^\alpha} = \exp[\ \frac{2}{RT}(\Delta H_{CB}-\Delta H_{AB}-\Delta H_{AC})\ ] = \exp[\frac{2K}{RT}] \qquad (9)$$

where K is defined as $\Delta H_{CB}-\Delta H_{AB}-\Delta H_{AC}$. Here we have defined $\Delta H_{ij} = 4N[\ H_{ij}-1/2(H_{ii}+H_{jj})\ ]$. ΔH_{ij} can be interpreted as the enthalpy of formation of the compound i-j with the bcc form of the elements used as the standard states. Usually the enthalpies of formation found in the literature have the stable phase of the pure element as the standard state. The following equation may be used to convert the standard states:

$$K = (\Delta H_{CB}-\Delta H_{AB}-\Delta H_{AC}) = (\Delta H^f_{CB}-\Delta H^f_{AB}-\Delta H^f_{AC}) - \Delta H_A^{bcc\to\gamma} \qquad (10)$$

where the superscript f denotes that the stable phases of the pure elements are used as the reference states. $\Delta H_A^{bcc\to\gamma}$ is the enthalpy of transformation for A from bcc to γ. The symbol γ denotes the stable phase for the element A. The corresponding enthalpies of transformation for B and C are canceled in Eq. (10).

It can be seen that if K and ΔH_t are known, Eqs (2), (7), and (9) can be solved simultaneously for y^α, y^β, and z, which uniquely determine site occupancies for the case of a dilute addition.

3.0 Discussion of the Model's Implications

3.1 Direct Solution of the Model's Equations

In the previous section we derived equations (Eqs. 2, 5, and 6) that can be used to determine the site occupancies in the case of a ternary B2 triple defect compound. These equations required the knowledge of six interaction enthalpy terms. Since the knowledge of these terms is often not available, simplified equations for the case of a dilute ternary addition were derived (Eqs. 2, 7, and 9). Only two parameters are required to solve these equations, ΔH_t and K. ΔH_t is the enthalpy of formation of triple defects in the matrix binary B2 compound AB to which the dilute addition C is added. Values of ΔH_t for several binary B2 compounds can be found from Chang and Neumann.[1] ΔH_t for NiAl and FeAl are 183 and 101 kJ/(mol of defects), respectively. The value of K depends on both the matrix compound, AB, and the ternary addition, C. Values of K for various ternary additions to NiAl and FeAl are listed in Tables II and III, respectively. Due to the simplifying assumptions made in deriving the equations for the dilute addition case, calculations based on these equations should be used for qualitative interpretation only. Two examples are: 1) determining whether more C atoms go to the α or to

the β sublattice, and 2) whether the addition of C atoms increases or decreases the vacancy concentration.

Table II Calculated Values for K and exp[2K/RT] for Dilute Additions (C) to NiAl (AB)

The reference states for the enthalpies are pure stable solid elements

Dilute Addition C	ΔH^f_{CAl} (kJ/g-atom)	ΔH^f_{NiC} (kJ/g-atom)	K (kJ/g-atom)	exp[2K/RT] (at T= 1300 K)	Site Preference of Infintesimal Addition (at T=1300 K)
Pd	-94 ± 8 [1]	-0.5 ± 1.3 [16]	-23.0 ± 12.3	0.014	α
Co	-60 ± 5 [1]	0.0 ± 0.4 [16]	10.5 ± 8.4	7	α if > 42.8% Al
Cr[a]	-17 ± 3 [17]	6.4 ± 0.3 [16]	47.1 ± 6.3	6100	α if > 50.4% Al
Cu[b]	-20 ± 3 [16]	1.8 ± 0.4 [16]	48.7 ± 6.4	8200	α if > 50.4% Al
Fe	-25 ± 2 [1]	-4 ± 0.5 [16]	49.5 ± 5.5	9500	α if > 50.5% Al
Mn[a]	-22 ± 2 [16]	-14 ± 5 [16]	62.5 ± 10	105300	α if >51.8% Al
Ti[c]	-37 ± 3 [16]	-34 ± 2 [16]	67.5 ± 8	265600	α if >52.9% Al
V[a]	-20 ± 4 [17]	-20 ± 10 [18]	70.5 ± 17	462800	α if > 53.8% Al
ΔH^f_{NiAl} = -63 ± 3 KJ/g-atom from Reference 1 $\Delta H^{bcc \rightarrow fcc}_{Ni}$ = -7.5 KJ/g-atom from Reference 19					

a. The compounds "CrAl" and "VAl" are not stable B2 compounds. The stability of B2 MnAl is in dispute.
b. The compound CuAl has a centered orthorhombic structure.
c. The compound TiAl has the $L1_0$ structure.

3.2 Relative Site Preference of Dilute Ternary Additions

It is possible to determine whether a dilute alloying addition, C, has a stronger preference for the β sublattice than does A. From Eq. (9) we see that if K < 0 then $y^\alpha > y^\beta$, which implies that C atoms have a stronger preference for the α sublattice than do A atoms. Conversely, if K > 0 then $y^\beta > y^\alpha$, which implies C atoms have a stronger preference for the β sublattice than do A atoms. If K = 0 then $y^\beta = y^\alpha$, and the ratio of A atoms to C atoms is the same on both sublattices.

Table III Calculated Values for K

The reference stat

Dilute Addition C	ΔH^f_{CAl} kJ/g-atom	Δ kJ
Pd	-94 ± 8 [1]	-9 ±
Ni	-63 ± 3 [1]	-4.0 ±
Co	-60 ± 5 [1]	-10.3
Cu[b]	-20 ± 3 [16]	12 ±
Cr[c]	-17 ± 3 [17]	4.3 ±
Mn[c]	-22 ± 2 [16]	-4.3 ±
Ti[d]	-37.3 ± 3 [16]	-20
V[c]	-20 ± 4 [17]	-8.7 ±
ΔH^f_{FeAl} = -25 ± 2 KJ/g-atom from $\Delta H^{bcc \rightarrow fcc}_{Fe}$ = 0.90 ± 0.04 KJ/g-atom		

a. The reference state for Fe in has been converted to Fe (bc
b. The compound CuAl has a
c. The compounds "CrAl" and of B2 MnAl is in dispute.
d. The compound TiAl has the

3.3 Absolute Site Preference of Dil

Of more interest than the relative si dilute ternary element, C, is added, answer this Eq. (9) can be rewritten

$$\frac{N^\alpha_A N^\beta_C}{N^\beta_A N^\alpha_C} = \exp\left[\frac{2K}{RT}\right]$$

From this equation it can be seen th than N^β_A for a given composition, th more C atoms on the α sublattice th still greater than N^β_C. Thus, when preference for the α sublattice.

For the case of K > 0 no direct preference of C. To determine the solve the governing equations as de

- decreases the vacancy

is (C) to NiAl (AB)

olid elements

]	Site Preference of Infintesimal Addition (at T=1300 K)
	α
	α if > 42.8% Al
	α if > 50.4% Al
	α if > 50.4% Al
	α if > 50.5% Al
	α if >51.8% Al
	α if >52.9% Al
	α if > 53.8% Al

ls. The stability

a stronger preference for
$^{\alpha} > y^{\beta}$, which implies that
ms. Conversely, if K > 0
he β sublattice than do A
oms is the same on both

Table III Calculated Values for K and exp[2K/RT] for Dilute Additions (C) to FeAl (AB)

The reference states for the enthalpies are pure stable solid elements.

Dilute Addition C	ΔH^{f}_{CAl} kJ/g-atom	ΔH^{f}_{FeC} kJ/g-atom	K kJ/g-atom	exp[2 K/RT] (at T=1300 K)	Site Preference of Infintesimal Addition (at T=1300 K)
Pd	-94 ± 8 [1]	-9 ± 1 [16][a]	-60.0 ± 11.0	1.5×10^{-5}	α
Ni	-63 ± 3 [1]	-4.0 ± 0.5 [16][a]	-34.0 ± 5.5	1.9×10^{-3}	α
Co	-60 ± 5 [1]	-10.3 ± 0.2 [20]	-24.7 ± 7.2	0.01	α
Cu[b]	-20 ± 3 [16]	12 ± 2 [21][a]	-7 ± 7.0	0.3	α
Cr[c]	-17 ± 3 [17]	4.3 ± 1.3 [16]	3.7 ± 6.3	2	α
Mn[c]	-22 ± 2 [16]	-4.3 ± 1.7 [16][a]	7.3 ± 5.7	4	α if > 38% Al
Ti[d]	-37.3 ± 3 [16]	-20 ± 2 [16]	8.0 ± 7.0	4	α if >38% Al
V[c]	-20 ± 4 [17]	-8.7 ± 0.6 [22]	13.7 ± 6.6	13	α if > 47% Al
ΔH^{f}_{FeAl} = -25 ± 2 KJ/g-atom from Reference 1 $\Delta H^{bcc \rightarrow fcc}_{Fe}$ = 0.90 ± 0.04 KJ/g-atom from Reference 16					

a. The reference state for Fe in the original Reference is Fe (fcc). The reference state has been converted to Fe (bcc), by using $\Delta H^{bcc \rightarrow fcc}_{Fe}$.
b. The compound CuAl has a centered orthorhombic structure.
c. The compounds "CrAl" and "VAl" are not stable B2 compounds. The stability of B2 MnAl is in dispute.
d. The compound TiAl has the $L1_0$ structure.

3.3 Absolute Site Preference of Dilute Ternary Additions

Of more interest than the relative site preference is the absolute site preference. That is, when a dilute ternary element, C, is added, do more C atoms go to the α or to the β sublattice? To answer this Eq. (9) can be rewritten as

$$\frac{N^{\alpha}_{A} N^{\beta}_{C}}{N^{\beta}_{A} N^{\alpha}_{C}} = \exp[\frac{2K}{RT}] \qquad (11)$$

From this equation it can be seen that if $K < 0$ then $N^{\alpha}_{A} N^{\beta}_{C} < N^{\beta}_{A} N^{\alpha}_{C}$. Since N^{α}_{A} is always greater than N^{β}_{A} for a given composition, then N^{α}_{C} is always greater than N^{β}_{C}. That is, there are always more C atoms on the α sublattice than the β sublattice. If $K = 0$ then $N^{\alpha}_{A} N^{\beta}_{C} = N^{\beta}_{A} N^{\alpha}_{C}$, and N^{α}_{C} is still greater than N^{β}_{C}. Thus, when $K \leq 0$ the dilute ternary addition, C, has an absolute site preference for the α sublattice.

For the case of $K > 0$ no direct conclusion can be drawn as above for the absolute site preference of C. To determine the absolute site preference in this case it is necessary to directly solve the governing equations as described in Section 3.1.

3.4 Absolute Site Preference of Infinitesimal Ternary Additions

When the ternary addition is of an infinitesimal quantity, additional conclusions on the absolute site preference can be drawn. In the previous section we saw that if $K \leq 0$ then C has an absolute site preference for the α sublattice. We will now consider the case of $K > 0$. From Eq. (11) we find that in order for C to have an absolute site preference for the β sublattice then K must satisfy:

$$\exp[\frac{2K}{RT}] > \frac{N_A^\alpha}{N_A^\beta} \qquad (12)$$

The ratio N_A^α/N_A^β is strongly dependent on the composition of the alloy. We define an infinitesimal addition as one small enough not to affect the overall stoichiometry of the alloy. That is, N_A^α/N_A^β can be taken to be the same as that of the binary AB compound. N_A^α/N_A^β for AB compounds can be calculated with the binary quasichemical model of Chang and Neumann.[1] Values of this ratio for NiAl and FeAl at 1300 K are shown in Fig. 1. Values of exp[2K/RT] for various ternary additions to NiAl and FeAl are found in Tables II and III. With this information the absolute site preference of an infinitesimal ternary addition can be determined via Eq. (12). This determination has been performed for additions to NiAl and FeAl. The results are given in Tables II and III.

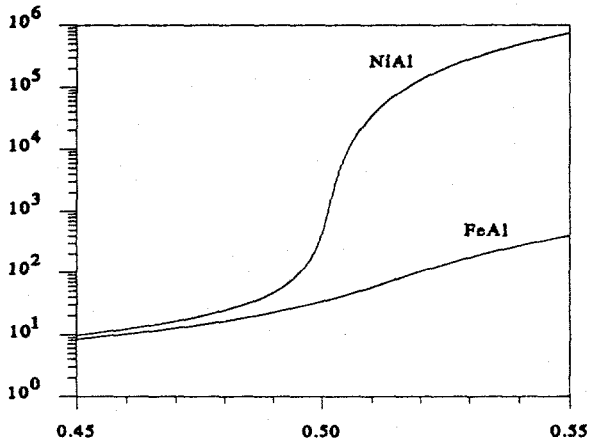

Figure 1 - The Ratio N_A^α/N_A^β for NiAl and FeAl at 1300 K Calculated as a Function of Composition by Using the Model of Chang and Neumann. [1]

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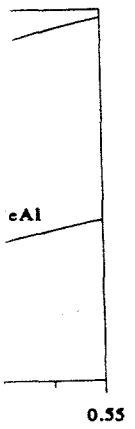

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The three factors which control whether a ternary addition prefers a given sublattice are K, ΔH_t, and stoichiometry. As can be seen from Eq. (12), the larger the value of K the more likely C will prefer the β sublattice. From Fig. 1 we see that for matrix compounds with smaller values of ΔH_t, such as FeAl, the value of N_A^α/N_A^β is smaller. In turn, this implies that C atoms are more likely to prefer the β sublattice. The effect of stoichiometry can also be seen by considering Fig. 1. It is clear that on the A-rich side of stoichiometry the value of N_A^α/N_A^β is smaller. Thus, C atoms are more likely to prefer the β sublattice on the A-rich side of stoichiometry. A fourth factor, temperature, can also affect the site preference of C, as both sides of Eq. (12) are a function of temperature. Consideration of the effect of temperature on the site occupations will be reserved for a later study.

4.0 Comparison of the Model's Predictions with Experimental Data

4.1 NiAl

Table II contains useful information for estimating the site preference of ternary additions to NiAl. Of the ternary additions considered, only Pd shows a site preference for the α(Ni) sublattice relative to Ni. That is, $K < 0$ for the case of Pd in NiAl. The elements Co, Cr, Cu, Fe, Mn, Ti, and V show a relative site preference for the β(Al) sublattice ($K > 0$). Also given in Table II is the absolute site preference of infinitesimal ternary additions. Infinitesimal additions of Pd have an absolute site preference for the α sublattice. The rest of the elements considered show a change in the absolute site preference of an infinitesimal addition from the β to the α sublattice as the composition of the matrix compound moves toward Al rich compositions.

It is interesting to compare the predictions of our model to experimental evidence. Unfortunately, most experimental data found in the literature are of cases where the amount of ternary addition is too large to justify being called dilute. Nevertheless, we will make qualitative estimates on site occupations by directly solving Eqs. (2), (7), and (9). Experimental studies have been performed for Cr, Fe, and V additions to NiAl.[23-26] The values of K are strongly positive for all of these cases. The model predicts that these elements will have a relative site preference for the β sublattice, but the absolute site preference is a strong function of matrix stoichiometry. Atom location by channeling-enhanced microanalysis (or ALCHEMI) was used by Field, et al.[23] to determine the site preference of 1Cr-50Ni-49Al. They found Cr to have an absolute site preference for the Al sublattice. In another ALCHEMI study Cotton et al.[24] found

a similar result for 0.94Cr-49.7Ni-49.3Al (balance C and O). These results are in agreement with the estimates based on the calculations of our model. A recent ALCHEMI study by Anderson et al.[25] found that Fe preferred the Ni sublattice in a 2.2Fe-47.1Ni-50.7Al alloy and in a 10Fe-40Ni-50Al alloy. In contrast, they found Fe prefers the Al sublattice in 10Fe-50Ni-40Al. All of these results are consistent with the estimates based on our model. Finally, Munroe and Baker[26] did an ALCHEMI study of V added to NiAl. They found 94.5% of the V atoms on the Al sublattice in 3V-50Ni-47Al. This result is also consistent with our model. It is clear that satisfactory agreement can be found between the model and experimental data in cases where K is strongly positive.

It is interesting to consider the case of Fe added to NiAl. As discussed earlier Fe has a preference for the Al sublattice relative to Ni. From Table III, it can be seen that an infinitesimal addition of Fe to Ni-50Al would prefer the Al sublattice. Since it is unlikely that Al atoms would be moved to the Ni sublattice, the site balance would require the generation of vacancies on the Ni sublattice. Keeping the Al concentration fixed at 50%, if more Fe was added it would eventually have to go to the Ni sublattice in order for the solid solution between NiAl and FeAl to exist. The transition of the absolute site preference of Fe from the Al to the Ni sublattice with increased Fe concentration is indeed predicted by the model. The tendency for a greater number of transition metal atoms (Ni and Fe) to occupy the Al sublattice than in binary NiAl continues, however. This necessitates the generation of vacancies. That is, as more Fe is added to NiAl (keeping the Al content fixed at 50%) the model predicts the vacancy concentration to increase. It is possible to measure the vacancy concentration of these alloys experimentally by a combination of x-ray lattice parameter determination and bulk density measurements. This has been done by the authors of this manuscript on samples quenched from 1000°C.[27] It was found that when 5 at.% Fe was added to NiAl (with the Al content fixed at 50 at.%) the vacancy concentration increased from 0.34% to 0.88%. This agrees well with the predictions of the model.

4.2 FeAl

Table III provides the data useful for making site preference estimates of ternary additions to FeAl. For Pd, Ni, and Co the value of K is strongly negative. We can therefore expect that these atoms will exhibit a relative as well as absolute site preference for the α(Fe) sublattice. For Cu, Cr, Mn, and Ti, the magnitude of K is quite small and is on the order of the experimental error. Therefore, estimates based on these numbers are suspect. V has a more

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positive K and most likely shows a relative site preference for the β(Al) sublattice. The absolute site preference of an infinitesimal addition of V changes the Al to the Fe sublattice as the Al concentration increases in the matrix compound.

As with NiAl, the experimental data in the literature is mostly for non-dilute cases, but qualitative estimates based on this assumption can be made. Ternary additions of Ni, Co, Cu, Cr, Mn, Ti, and V to FeAl have been investigated.[28-31] A synchrotron x-ray diffraction study by Khosla of Cr in Fe-rich FeAl found that Cr has a site preference for the Al sublattice.[28] An ALCHEMI study by Munroe and Baker revealed a similar result.[29] This is not in complete agreement with the model, which predicts Cr atoms to be relatively evenly distributed on the two sublattices. As mentioned earlier, the uncertainty of the value of K could easily explain this discrepancy. Mossbauer measurements were performed for ternary additions of Mn and Ti to Fe-rich FeAl by Li et al.[30] They found Mn on both Fe and Al sites, but Ti only on Fe sites. These results are not in complete agreement with the model, but again the uncertainty of the value of K could be responsible.

The most complete experimental study was performed by Kong and Munroe.[31] In that study ALCHEMI was used to determine the site preference of 1X-49Fe-50Al alloys where the ternary addition, X, was Ni, Co, Cu, Cr, Mn, Ti, or V. They found that Ni, Co, Cu, Mn, and Ti preferentially occupied the Fe sublattice, and V occupied primarily the Al sublattice. Cr occupied both sublattices approximately equally. In agreement, the model predicts Ni, Co, Cu, Mn, and Ti to preferentially occupy the Fe sublattice. However, the model disagrees with the experimental data on Cr, predicting Cr to occupy primarily the Fe sublattice. It is interesting that in Kong and Munroe's study the only element to strongly prefer the Al sublattice was V, as this is the element with the highest value for K as seen in Table III. The model predicts V to occupy both sublattices fairly equally. However, if K were slightly larger than the estimated value, the model would predict V to prefer the Al sublattice as the experimental data suggests.

In summary, the comparison of the model to experimental data is not as convincing for ternary additions to FeAl as it is for NiAl. In most cases, this is primarily due to the small values of K. The experimental evidence for additions which had strongly negative K values (i.e. Ni and Co) were in complete agreement with the model, but for additions where K was of a smaller magnitude the model proved to be insufficient for consistent predictions of site preferences.

5.0 Summary

(a) A quasichemical model was developed for ternary triple defect B2 compounds. The model is able to predict the site occupations and defect concentrations if the required six interaction enthalpy terms are known.

(b) Simplified equations that can estimate the site occupations and defect concentrations for the case of a dilute ternary addition to a binary triple defect B2 compound were derived. These equations require only two parameters: ΔH_t and K. ΔH_t is dependent only on the binary compound to which the third element is added. K depends on both the binary compound and the ternary element itself. Values for these parameters can be estimated from thermodynamic data.

(c) Comparisons of experimentally determined site preferences of ternary additions in NiAl and FeAl to the predictions of model were quite satisfactory for cases where K was either strongly negative or strongly positive. For cases where the magnitude of K was small the model was not always successful in making predictions of site preferences.

(d) The model was able to predict the experimental observation that as Fe is added to Ni-50Al (at a constant Al concentration of 50 at.%) the concentration of vacancies increases.

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