METHOD FOR CALCULATION OF BONDING ENERGIES IN TERNARY OFF-STOICHIOMETRIC INTERMETALLIC COMPOUNDS TO PREDICT THEIR DEFECT TYPES, SITE PREFERENCE, AND ANTIPHASE BOUNDARY ENERGY

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ABSTRACT

Methods for modelling and prediction are presented for the defect
structure and the occupation site of a ternary element in off-stoichiometric
intermetallic compounds with such ordered structures as B2 and $L1_2$. The
criterion for a particular type of defect or the site preference to be
favorable against the others is based on the relative magnitude of the total
interatomic bonding energies of the possible structures taking only the
first nearest neighbors into account. Then the calculation of the antiphase
boundary(APB) energy is carried out using the same method and criterion in
B2, $L1_0$, $L1_2$ and DO_{19} type compounds. It is shown that the results of the
prediction is in good agreement with the experimental evidences found in
literatures.

INTRODUCTION

Alloy design of intermetallic compounds has become of significant
importance in the development of new structural materials particulary for
the application to the heat resisting components. In many cases to pursue
the improvement and the optimization in properties of a compound, alloying
additions are made resulting in breaking up of the stoichiometry. For an
effective stratergy for the alloy design, such information is necessary as
to the type of defect structure at offstoichiometry and the substitution
behavior of an alloying element. However, since it is a matter of atomistic
configuration, tedious experimental procedures are generally required to
reveal them such as a sophisticated X-ray diffraction method[1,2], ALCHEMI
combined with electron microscope[3], determination on the extent of
solubility lobe for a compound in ternary phase diagrams[4].

In the present work, the modelling of defect structure caused by the
substitution by a ternary element has been conducted in selected ordered
structure and an attempt is made to predict the stable atomic configuration.
Also by using the present method for calculation, it is possible to evaluate
the anti-phase boundary energy(APBE) of a compound at any composition within
its off-stoichiometry because it can also be established by calculating the

total bonding energy across the APB of a certain atomic cofiguration. The result for the APBE calculation is of importance in predicting plastic behavior of the compound because the dislocation configuration is strongly affected by its magnitude. The method described herein is applicable to most of the intermetallic compound and provides a useful foresight in carrying out a practical alloy design.

ASSUMPTIONS AND METHODS

For the modelling of defect structures , site preference of each element and APB energy, the total interatomic bonding energy is calculated based on the following assumptions.
   (1) A single phase compound is always formed at a given composition.
   (2) Temperature being considered is near zero kelvin and therefore entropy term is not taken into account.
   (3) An atomic configuration involving a ternary element or a vacancy is stable when the total binding energy for the defect structure is minimum.
   (4) Only the nearest neighbor bondings are considered for the calculation of the total binding energy.
   (5) Bonding energy H_{ij} being defined for i, j = A, B, and C, where A and B are the components of a compound, and C ternary element, is given by,

$$H_{ij} = (H_{ii} + H_{jj})/2 + V_{ij}, \tag{1}$$

where H_{ii} or H_{jj} denotes boning energy of a pure element given by heat sublimation reported on literature[5]. V_{ij}, being ordering energy, can be calculated using Miedema's semiempirical formula[6]. Note that bonding energy between an atom and a structural vacancy(v) is estimated as

$$H_{iv} = 0.35H_{ii} \text{ or } 0.35H_{ij}, \tag{2}$$

depending on whether the vacancy is at A-site or B-site.
   (6) No lattice distortion is considered upon formation of APB.
   (7) For $L1_0$ and DO_{19} compounds, an ideal c/a is assumed in each case.

In the following treatment we denote a binary compound consisting of A and B atoms as AB or A_3B. A ternary element, C, and a structural(not thermal) vacancy, v, are introduced as defined above. For a particular ordered structure, the following three patters of compositional conditions are considered. For each pattern, possible defect structures and associated site preferences can be written accordingly.

Pattern 1: Concentration of A is higher than its stoichiometric composition.
 <P1-1> A and C at A site, and B and v at B site
 <P1-2> A and C at A site, and B and A at B site
 <P1-3> A at A site, and A, B and C at B site
 <P1-4> A at A site, and B, C and v at B site

Pattern 2: Concentration of B is higher than its stoichiometric composition. <P2-1> through <P2-4> are defined as above by just replacing A with B and vice versa.

Pattern 3: Concentrations of both A and B are less than their stoichiometric compositions.
<P3-1> A and C at A site, and B and v at B site
<P3-2> A and C at A site, B and A at B site
<P3-3> A and C at A site, and B and C at B site
<P3-4> A and B at A site, and B and C at B site
<P3-5> A and v at A site, and B and C at B site

The total bonding energy of a compound can then be calculated for each possible case listed above and then by judging from the relative magnitude the structure that is energetically favorable can be determined.

RESULTS AND DISCUSSIONS

Substituion Behavior and Occupation Site for a Ternary Element

By defining the H_{ij} to be the bonding energy between i and j atoms(i,j = A, B, C, and v), the total bonding energy associated with a particular defect structure with partial substitution by a ternary element and/or a vacancy, H, can be calculated for which the examples are shown hereafter.

(1) AB type compounds(B2 and $L1_0$)
For the equi-atomic phase such as B2 and $L1_0$, the Patterns 1 and 2 are equivalent and therefore only <P1>s and <P3>s are considered. The difference in the analysis between B2 and $L1_0$ is in the number of like or unlike atom pairs for each lattice site. An example of the results on the possible atomic configuration and the associated total bonding energy is shown below for the case of B2 structure.

(a) When the composition is given as $A_{x+1}B_{x-2}C_1$(Pattern 1), possible site occupancy is limited in the following 4 cases and the total binding energy can be expressed as;

<P1-1> A_{x+1} and C_1 at A site, and B_{x-2} and v_4 at B site

$$H = (8x-24)H_{AB} + 8H_{BC} + 32H_{Av} \qquad (3)$$

<P1-2> Location of atoms $(A_{x-1}, C_1$ at A site) $(B_{x-2}, A_2$ at B site)

$$H = (8x-24)H_{AB} + 8H_{AC} + 16H_{AA} \qquad (4)$$

<P1-3> Location of atoms $(A_x$ at A site) $(B_{x-2}, A_1, C_1$ at B site)

$$H = (8x-16)H_{AB} + 8H_{AC} + 8H_{AA} \qquad (5)$$

<P1-4> Location of atoms (A_{x+1} at A site) (B_{x-2}, C_1, v_2 at B site)

$$H = (8x-16)H_{AB} + 8H_{AC} + 16H_{Av} \qquad (6)$$

(b) When the composition is $A_{x-1}B_{x-1}C_2$ (Pattern 3), the possible atomic configurations are the followings.

<P3-1> A_{x-1} and C_2 at A site, and B_{x-1} and v_2 at B site

$$H = (8x-24)H_{AB} + 16H_{BC} + 16H_{Av} \qquad (7)$$

<P3-2> A_{x-2} and C_2 at A site, and B_{x-1} and A_1 at B site

$$H = (8x-24)H_{AB} + 16H_{BC} + 8H_{AA} \qquad (8)$$

<P3-3> A_{x-1} and C_1 at A site, and B_{x-1} and C_1 at B site

$$H = (8x-24)H_{AB} + 8H_{AC} + 8H_{BC} \qquad (9)$$

<P3-4> A_{x-1} and B_1 at A site, and B_{x-2} and C_2 at B site

$$H = (8x-24)H_{AB} + 16H_{AC} + 8H_{BB} \qquad (10)$$

<P3-5> A_{x-1} and v_2 at A site, and B_{x-2} and C_2 at B site

$$H = (8x-24)H_{AB} + 16H_{AC} + 16H_{Bv} \qquad (11)$$

The site occupation with the lowest H is favored, which can be determined by comparison of eq.(3) for the case (a) and eqs,(7) through (11) for the case (b).

(2) A_3B type (L1$_2$, DO$_{19}$, DO$_{22}$)
In a A_3B type compound, the ratio of A/B is 3 at stoichiometry. Therefore we have to treat all the patterns listed in section 2. An example of the analysis is shown for a L1$_2$ compound but it is also applicable to DO$_{22}$ and DO$_{19}$ because the first nearest coordinations are identical among them.

(a) Concentration of A is higher than 75 at% and the compound is expressed as $A_{3x+3}B_{x-15}C_{12}$.

<P1-1> $H = (12x-36)H_{AA} + (12x-228)H_{AB} + 96H_{AC} + 48H_{BC} + 240H_{Av}$ (12)

<P1-2> $H = (12x+84)H_{AA} + (12x-228)H_{AB} + 96H_{AC} + 48H_{BC}$ (13)

<P1-3> $H = (12x+36)H_{AA} + (12x-180)H_{AB} + 144H_{AC}$ (14)

<P1-4> $H = (12x+12)H_{AA} + (12x-180)H_{AB} + 144H_{AC} + 48H_{Av}$ (15)

(b) Concentration of B is higher than 25 at% and the compound is expressed as $A_{3x-15}B_{x+3}C_{12}$.

<P2-1> $H = (12x-156)H_{AA} + (12x-60)H_{AB} + 96H_{AC} + 48H_{BC} + 98H_{Av} + 48H_{Bv}$ (16)

<P2-2> $H = (12x-120)H_{AA} + 12H_{BB} + (12x-36)H_{AB} + 96H_{AC} + 48H_{BC}$ (17)

<P2-3> $H = (12x-120)H_{AA} + 60H_{BB} + (12x-84)H_{AB} + 144H_{AC}$ (18)

<P2-4> $H = (12x-300)H_{AA} + (12x-204)H_{AB} + 144H_{AC} + 480H_{Av} + 240H_{Bv}$ (19)

(c) Concentration of A is less than 75 at% and at the same time that of B is less than 25 at%. The compound is then expressed as $A_{3x-9}B_{x-3}C_{12}$.

<P3-1> $H = (12x-84)H_{AA} + (12x-84)H_{AB} + 96H_{AC} + 48H_{BC} + 48H_{Av}$ (20)

<P3-2> $H = (12x-60)H_{AA} + (12x-84)H_{AB} + 96H_{AC} + 48H_{BC}$ (21)

<P3-3> $H = (12x-72)H_{AA} + (12x-72)H_{AB} + 108H_{AC} + 36H_{BC}$ (22)

<P3-4> $H = (12x-72)H_{AA} + 36H_{BB} + (12x-108)H_{AB} + 144H_{AC}$ (23)

<P3-5> $H = (12x-180)H_{AA} + (12x-180)H_{AB} + 144H_{AC} + 288H_{Av} + 144H_{Bv}$ (24)

In each case of (a) through (c), a pattern with the lowest total bonding energy can be determined by substituting the value for H_{ij} using Miedema's formula for a choice of A, B and C elements. Examples of the result on the substitution site of a ternary element are shown for a $L1_2$ compound Ni_3Al in Fig. 1 through 3. The results shown are consistent with the experimental evidence in which the defect type of $L1_2$ Ni_3Al is known to be substitutional(or antistructure) because of the linear composition dependence of lattice parameter across stoichiometry[6]. From the figures, it is shown that Be is the only element to substitute Al-site regardless of the composition, which is in good agreement with the experimental data available[8]. Also the present results agree well with the published experimental evidence for example on Hf, Fe, Ta[9-11].

Calculation of APBE

Upon formation of APB, a bonding between A and B sites(A-B site bonding) is considered to be replaced by 1/2 A-A and 1/2 B-B site bondings in the unit area containing a A-B site bonding, being defined as S. Then the energy required for the process can be defined as APBE, E_{APB}, i.e.,

$$E_{APB} = \{(\text{A-A site bonding energy} + \text{B-B site bonding energy})/2$$
$$- (\text{A-B site bonding energy})\}/S \qquad (25)$$

If the probability for the site occupancy of each element is obtained, site bonding energy can be calculated which is then subsituted into eq.(25) to yield the APBE. The site occupancy is actually given by the same consideration made in the earlier section for the site preference and the substitution behavior.

(1) AB type compounds(B2 and $L1_0$)

Example of calculation is given for a composition, $A_{1+x}B_{1-x-y}C_y$, which is the case <P1-2>. Here x and y satisfiy the condition, $1> x > 0$, $1 > y > 0$, and $x + y < 1$. Probability for the site occupancy in this case is given in Table 1 and subsequently the fraction of particular atomic bonding for each site bonding can be listed as in Table 2. Then using eq. (25), the APBE is obtained as,

$$E_{APB} = \{y(1 - x - 2y)V_{AC} + (1 - x - y)(x + 2y - 1)V_{AB}$$
$$- y(1 - x - y)V_{BC}\}/S \qquad (26)$$

For B2 type compound with (111) APB, S is given as $\sqrt{2}\ a^2$, where a is lattice parameter. For $L1_0$ type compound with (110) APB, it is given as $\sqrt{3}\ a^2/2$. Such equation as (26) is deduced for all the cases from P1 through P3. The results of calculation are shown in Fig. 4 for B2 (Ni, Fe)Al and in Fig. 5 for $L1_0$ TiAl with V.

(2) A_3B type compound($L1_2$ and DO_{19})

Similar method is applied to $L1_2$ and DO_{19} compounds, where APB is regarded to be on (111) in the former case and (0001) in the latter. The results are shown in Fig. 6 for $L1_2$ Ni_3(Al,Ti) and in Fig. 7 for DO_{19} Ti_3Al with Nb.

To be noted is that the method of calculation developed in the present work agrees perfectly with what have been proposed by Flinn[12], by Marcinkovski[13] and by Umakoshi[14], although all the previous works have been done only at stoichiometry.

CONCLUSIONS

By the method of modelling and predictions developed by the present work, it is clearly shown that the substitution behavior of a ternary compound is generally dependent on composition, i.e. the occupation site generally differs depending on the side of deviation from the stoichiometry. It is also shown that the method is applicable to the calculation of APBE of a compound at any composition within its off-stoichiometry. It is highly tedious if the values are to be obtained experimentally.
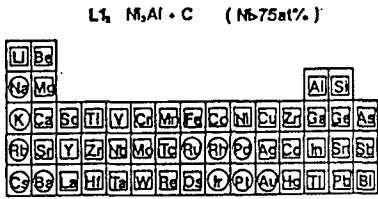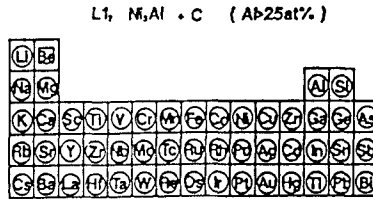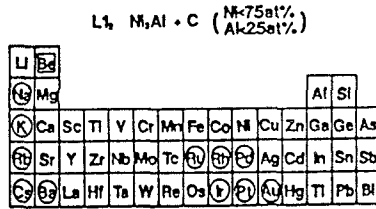
Fig.1

Fig.2

Fig.3

The results on prediction of occupation site for ternary elements
in $L1_2$ Ni_3Al compound with,
  Fig.1 Ni>75 at%, Fig.2 Ni>25 at%, and Fig.3 Ni<75at%, Al<25at%
Elements circled occupy Ni-site, those with a square Al-sites,
and unmarked both sites.

	A site	B site
A	$1-y$	$x+y$
B	0	$1-x-y$
C	y	0

Table 1 Probabilites for the occurence of A, B and C atoms
         on A and B sites in the case for above defined P1-2
         in A-rich AB compound.

bond	A site-A site	B site-B site	A site-B site
A-A	$(1-y)^2$	$(x+y)^2$	$(1-y)(x+y)$
A-B	0	$2(x+y)(1-x-y)$	$(1-y)(1-x-y)$
A-C	$2(1-y)y$	0	$y(x+y)$
B-B	0	$(1-x-y)^2$	0
B-C	0	0	$y(1-x-y)$
C-C	$(y-x)^2$	0	0

Table 2 Probabilites for the occurence of atomic bonds on
         the A-A, B-B and A-B site-bonds in the case for
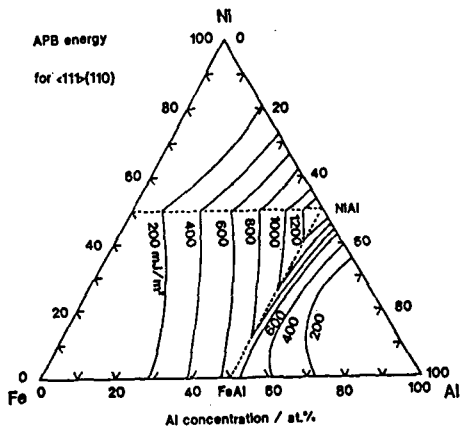   above defined P1-2 in A-rich AB compound.

Ni
APB energy
for <11b(110)

Al concentration / at.%

Fig.4 The counter for calculated
APB energy of B2 (Ni,Fe)Al
in Ni-Fe-Al system.

V
APB energy
for <110>(111)

Al concentration / at.%
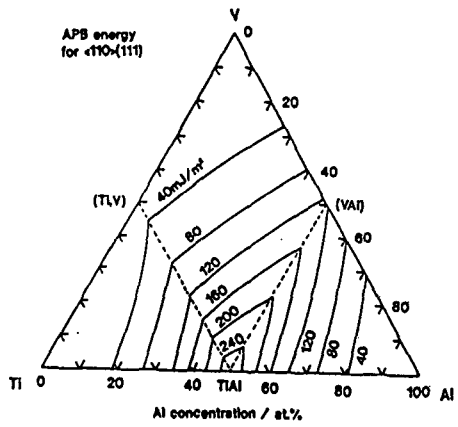
Fig.5 The counter for calculated
APB energy of $L1_0$ TiAl with V
in Ti-Al-V system.

Ni
APB energy
for <110>(111)

Al concentration/ at.%
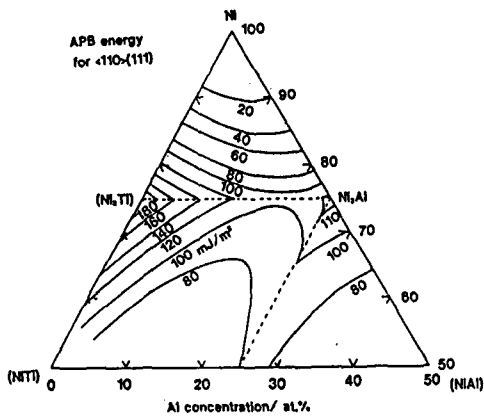
Fig.6 The counter for calculated
APB energy of $L1_2$ Ni_3(Al,Ti)
in Ni-Al-Ti system.

Nb
APB energy
for <1120>(0001)
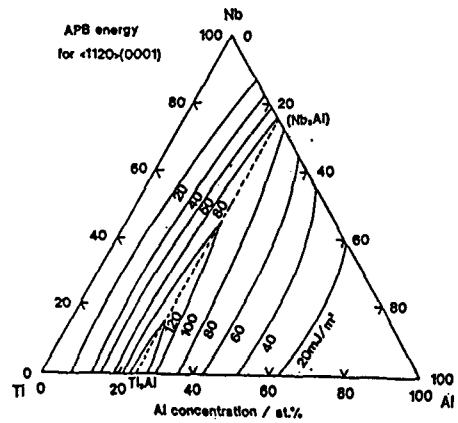
Al concentration / at.%

Fig.7 The counter for calculated
APB energy of DO_{19} Ti_3Al with
Nb in Ti-Al-Nb system.

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