On the modelling of the point defects in the ordered B2 phase of the Ti–Al system: Combining CALPHAD with first-principles calculations

H. Wang, R.C. Reed, J.-C. Gebelin, N. Warnken

Department of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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ABSTRACT

First-principles calculations are performed in order to calculate the energies of formation of different point defects in the ordered B2 phase of the Ti–Al system. The dominant point defects in the sublattice of the B2-TiAl structure are determined to be either substitutional vacancies or anti-site defects. Based on the results of first-principles calculations, substitutional vacancies are considered in the sublattice for the CALPHAD assessment (Al,Ti,VA)_{0.5} : (Al,Ti,VA)_{0.5}. A self-consistent set of thermodynamic parameters is obtained. Phase equilibria in the Ti–Al binary system are reproduced using these thermodynamic parameters.

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1. Introduction

High strength β-Ti alloys were developed specifically for aerospace applications. The Boeing 777 aircraft for example was the first commercial airplane for which the volume of β alloys outnumbered the volume of Ti–6Al–4V [1]. The high strength of these alloys is affected by the α precipitation during the aging process, which is commonly related with the concentrations of thermal vacancies induced by the ordered structure—B2 [2,3]. The B2 structure has been found in many β alloy systems, such as Ti–25V–15Cr–6Al [4], Ti–Al–Nb [5], Ti–Al [6]. The present work treats the modelling of point defects (substitutional vacancy and anti-site defect) in the B2 structure of the Ti–Al system. First-principles calculations are used to study which are the predominant point defects, which then leads to a revised CALPHAD assessment of the B2 phase in the Ti–Al system.

2. Background

In recent thermodynamic descriptions of the Ti–Al binary system, the B2 phase is modelled using either a two-sublattice model (Al,Ti)_{0.5} : (Al,Ti)_{0.5}, or a three-sublattice one ((Al,Ti)_{0.5} : (Al,Ti)_{0.5} : VA) which takes into account anti-site defects only [6–8]. This treatment differs from a previously proposed thermodynamic model for the B2 phase (Al,Ni,VA)_{0.5} : (Al,Ni,VA)_{0.5} in Ni–Al binary system, which considers both anti-site defects and substitutional vacancies [9]. Since the thermodynamic model of the B2 phase should reflect sound physical background, it is necessary to re-consider the model of the B2 phase on the basis of its known crystal structure.

Experimental studies of point defects in the B2 phase in the Ti–Al systems are hampered by the fact that bcc phase is not stable on the Al-rich side of the system. First-principles calculations are one way to overcome this limitation and to provide useful hints about the substitutional vacancy. Of course, results are limited, as calculation can only be done for the ground state. In order to overcome this limitation Hagen and Finnis [10] developed a method to study the point defects in the ordered alloys at finite temperatures which was then successfully applied to the B2 phase in the Ni–Al system. This method was used in the present work to calculate the concentration of different point defects located in different sites. The results of which were used to improve the thermodynamic model in the CALPHAD assessment of the Ti–Al binary system.

3. Methodology

3.1. First-principles calculations

The energies of various types of point defects were calculated by first-principles density functional theory, using a supercell approach which contains one defect (vacancy or antisite) in a large supercell (54-atom 3 × 3 × 3). The all-electron Blöchl's
projector augmented wave approach [11,12] was used in the calculations within the generalized gradient approximation potpaw_GGA, as implemented in the VASP software [13]. The Perdew–Burke–Ernzerhof (PBE) parameterisation [14,15] was used for the potpaw_GGA exchange-correlation functional. The valence configurations used for Ti are 4s3d, and those for Al are 3s3p. All the atoms were fully relaxed to the equilibrium positions. The other settings included plane-wave energy cutoff (450 eV), forces convergence cutoff (0.01 eV/Å) and Monkhorst k-point meshes for Brillouin zone (10 × 10 × 10).

3.2. CALPHAD assessment

Ti-rich part of the Ti–Al phase diagram was re-optimised, while the Gibbs energies of all phases in the Al-rich part remained the same as the author’s previous work [8]. Based on the results of the present work, the ordered bcc phase B2 and the corresponding disordered A2 phase are modelled as (Al,Ti,VA)0.5 : (Al,Ti,VA)0.5 and (Al,Ti,VA)1, respectively. The hcp and Ti3Al phases are modelled in accordance with the previous optimisation as (Al,Ti)1 and (Al,Ti)0.25 : (Al,Ti)0.25. Parameters were optimised using the Thermo-Calc software [16].

4. Results and discussion

4.1. The site preference of point defects

In order to calculate the energies of formation of different point defects, and thus to determine the thermodynamic model for the ordered B2 phase, the total energy $E_{\text{pure}}$ of the perfectly stoichiometric TiAl was calculated first. After that the deviation from stoichiometry was taken into account by introducing four different point defects—one vacancy in Ti sublattice $E_{\text{VaTi}}$, one Al atom in Ti sublattice $E_{\text{AlTi}}$, one vacancy in Al site $E_{\text{VaAl}}$, and one Ti atom in Al site $E_{\text{TiAl}}$. All calculations were performed in the ground state, i.e., at zero temperature ($T=0$) and zero pressure ($p=0$).

With these energies, it is still not possible to determine the preference of any sort of point defect, since it is not appropriate to simply compare the difference between the cases of substitutional alloys containing anti-site defects and structural vacancies respectively. Point defects with lower enthalpy of formation are unambiguously more stable. Thus for Ti-rich alloys, the anti-site Ti defect is more stable than the vacancy, while in Al-rich alloy, the vacancy in the Ti sublattice is slightly more stable than the anti-site Al defect. This indicates that the preferred type of point defect is different on the Ti and Al side of the stoichiometric composition, with antisite atoms on the Ti side and structural vacancies respectively.

Concentrations of the point defects (note: the concentrations in the present work refer to concentrations per site, or site fraction). These four branches can be divided into two sets, one on each side of the perfect stoichiometric composition, corresponding to substitutional alloys containing anti-site defects and structural vacancies respectively.

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Table 1

| Values (kJ/mol) | Methods | Sources |
|----------------|---------|---------|
| – 26.9         | PBE/GGA | Present work |
| – 26.1         | EAM     | [24]    |
| – 28.0         | LAPW/GGA| [24]    |
| – 25.1         | FLASTO/LDA| [25] |
| – 25.9         | US-PP/GGA | [19] |
| – 39.4         | CALPHAD | [26]    |
| – 37.2         | CALPHAD | [6]     |

For simplicity, the standard states of the two elements (fcc-Al and hcp-Ti) are used as reference states [17]. The calculated enthalpy of formation of the B2-TiAl is listed in Table 1 compared to various sources. Good agreement can be found between the present work and previous theoretical results. In Fig. 1, the calculated enthalpies of formation of the five blocks given above are plotted as four different branches. The point defects are sufficiently dilute in the calculations thus the enthalpies of formation of the alloys scale linearly with the atomic concentrations of the point defects (note: the concentrations in the present work refer to concentrations per site, or site fraction). These four branches can be divided into two sets, one on each side of the perfect stoichiometric composition, corresponding to substitutional alloys containing anti-site defects and structural vacancies respectively. Point defects with lower enthalpy of formation are unambiguously more stable. Thus for Ti-rich alloys, the anti-site Ti defect is more stable than the vacancy, while in Al-rich alloy, the vacancy in the Ti sublattice is slightly more stable than the anti-site Al defect. This indicates that the preferred type of point defect is different on the Ti and Al side of the stoichiometric composition, with antisite atoms on the Ti side and structural vacancies on the Al side. This preference is confirmed by the calculation of point defect concentrations at finite temperature, as will be shown later. Some calculated enthalpies of formation are given in Table 2, such as those of isolated point defects (using Eqs. (6)–(9), complex concentration-conserving defects and interbranch excitation.

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\[
H_{\text{Va}} = H_{\text{Al}} - H_{\text{pure}} \tag{6}
\]

\[
H_{\text{Ti}} = H_{\text{Va}} - H_{\text{pure}} \tag{7}
\]

\[
H_{\text{Al}} = H_{\text{Va}} - H_{\text{pure}} \tag{8}
\]
Table 2
The enthalpies of formation of isolated defects, complex concentration-conserving defects, and interbranch excitations in TiAl (hcp Ti – 7.8 eV/atom and fcc Al – 3.7 eV/atom are used as reference states (Wan, 2004)).

| Name                  | Designation or quasichemical reaction | \( \delta H_{i}^{f} \) (eV) |
|-----------------------|--------------------------------------|-----------------------------|
| Intrinsic point defects |                                      |                            |
| Ti in Al               | Ti\(^{ii}\)                           | 0.38                        |
| Vacancy in Al          | Va\(^{ii}\)                          | 1.54                        |
| Al in Ti               | Al\(^{ii}\)                          | 1.15                        |
| Vacancy in Ti          | Va\(^{ii}\)                          | 0.55                        |
| Concentration-conserving defect complexes |                      |                            |
| Triple Ti (TT)         | 0 – 2Va\(^{ii}\) + Ti\(^{ii}\)       | 1.40                        |
| Divacancy (DV)         | 0 – 2Va\(^{ii}\) + 2Al\(^{ii}\)     | 2.10                        |
| Volume (E)             | 0 – Ti\(^{iii}\) + Al\(^{iii}\)     | 1.53                        |
|Triple Al (TA)          | 0 – 2Va\(^{ii}\) + Al\(^{ii}\)     | 4.23                        |
| Interbranch excitation |                                      |                            |
| Interbranch Ti         | Ti\(^{ii}\) – 2Va\(^{ii}\)          | 2.70                        |
| Interbranch Al         | 2Va\(^{ii}\) – Al\(^{ii}\)          | 0.04                        |

Table 3
The enthalpies of formation of the point defects \( \delta H_{i}^{f} \) based on different reference states: on the Ti-rich site, TiAl and Ti\(_{3}\)Al (– 4.27 eV/atom for Al and – 7.80 eV/atom for Ti); on the Al-rich site, TiAl and Ti\(_{3}\)Al (– 3.28 eV/atom for Al and – 8.79 eV/atom for Ti) [19].

| Name                  | Point defects | \( \delta H_{i}^{f} \) (eV) |
|-----------------------|---------------|-----------------------------|
| Ti in Al               | Ti\(^{ii}\)   | –0.20                       |
| Vacancy in Al          | Va\(^{ii}\)   | 1.26                        |
| Al in Ti               | Al\(^{ii}\)   | –0.25                       |
| Vacancy in Ti          | Va\(^{ii}\)   | –0.15                       |
| Interbranch Ti excitation | Ti\(^{ii}\) – 2Va\(^{ii}\) | 2.70                        |
| Interbranch Al excitation | 2Va\(^{ii}\) – Al\(^{ii}\) | 0.04                        |

\[
\delta H_{i}^{f} = 54 \cdot (\delta H_{i}^{f} – H_{pure}) \tag{9}
\]

It should be pointed out that an alternative way to subtract reference states is also presented as described by Zhang and Northrup [18]. On the Ti-rich site, the two defects Va\(^{ii}\) and Ti\(^{ii}\) are described with respect to TiAl and Ti\(_{3}\)Al: \( e_{Ti}^{ii} + e_{Al}^{ii} = E_{TiAl} \); \( 3 \times e_{Ti}^{ii} + e_{Al}^{ii} = E_{Ti_{3}Al} \). On the Al-rich site, the other two defects Va\(^{ii}\) and Al\(^{ii}\) are referred to TiAl and Ti\(_{3}\)Al: \( e_{Ti}^{ii} + e_{Al}^{ii} = E_{TiAl} \); \( 5 \times e_{Ti}^{ii} + 3 \times e_{Al}^{ii} = E_{Ti_{3}Al} \) (note the total energies of the compounds are taken from Ghosh and Asta [19]). The calculated enthalpies of formation of the defects are listed in Table 3. It is found that the values of the enthalpies of formation of the defects are different, but the interbranch excitation of Ti and Al defects does not depend on the choice of the reference states, which has been mentioned in the work by Hagen and Finnis [10]. It is also noteworthy that since the enthalpy of formation of the interbranch Al defect is small (this enthalpy of formation is also affected by the calculation errors and atomic relaxations), a competition between triple and interbranch Al defects on the Al-rich side can be expected. Nevertheless, considering the present calculations, constitutional vacancies need be taken into account in the CALPHAD optimisations and this can be confirmed by predicting concentrations of the thermal defects which follows.

4.2. Vacancies at finite temperature

In this section, the concentration of substitutional vacancies at finite temperatures are evaluated. The concentrations of point defects are determined by using the results of first-principles calculations.

A linear relationship between the enthalpy of formation of an alloy \( H_{i} (i = Al, Ti, Va, k = Al, Ti) \) and the concentrations of the point defects \( x_{j} (i = Al, Ti, Va, k = Al, Ti) \) is given by

\[
H_{i} = H_{pure} + \sum_{j} H_{j}^{f} x_{j} \tag{10}
\]

where \( H_{pure} \) corresponds to the enthalpy of formation of an alloy without point defects, and \( H_{j}^{f} (i = Al, Ti, Va, k = Al, Ti) \) is the enthalpy of formation of one point defect, either anti-site defect or substitutional vacancy. In order to introduce temperature dependency, entropy needs to be taken into account; for the sake of simplicity only configurational entropy of the alloy is considered, such that

\[
S = k \left( 1 + x_{Al}^{ii} + x_{Ti}^{ii} \right) \ln \left( \frac{1 + x_{Al}^{ii} + x_{Ti}^{ii}}{2} \right) - \sum_{j} x_{j} \ln x_{j} \tag{11}
\]

The equilibrium concentrations of the point defects are then calculated by combining minimisation of the Gibbs free energy \( (G = H – TS = \text{min}) \) with mass-balance constraints, consistent with

\[
x_{Al}^{ii} + x_{Ti}^{ii} + x_{Va}^{ii} = 1 \tag{12}
\]

\[
x_{Ti}^{ii} + x_{Al}^{ii} + x_{Va}^{ii} = 1 \tag{13}
\]

\[
x_{Al}^{ii} + x_{Ti}^{ii} = x_{Al} \tag{14}
\]

\[
x_{Ti}^{ii} + x_{Al}^{ii} = x_{Ti} \tag{15}
\]

where \( x_{Al} \) and \( x_{Ti} \) are the total mole fraction of Al and Ti in the alloy, respectively. An analytical solution of this model, as derived in Refs. [10,20,21], is used in the present work. This yields the concentrations of point defects as functions of alloy composition and temperature.

The predicted concentrations of various point defects at 627 °C are plotted against the mole fraction of Al in Fig. 2. It becomes clear that substitutional vacancies are the major point defects on the Al-rich side. On the Ti-rich side the major point defects are anti-site Ti atoms, but the concentration of substitutional vacancies on the Ti sublattice is still relatively high. Higher concentrations of vacancies can be expected at higher temperatures than 627 °C. The high concentration of substitutional vacancies is consistent with the experimental results, which indicates that ordering raises the vacancy concentration [2,3]. These results also illustrate the importance of including substitutional vacancies into the thermodynamic model for the B2 phase.

It is also interesting to separate structural from thermal point defects. Structural point defects are induced by the deviation from
the exact stoichiometry. They are present at both 0 K and finite temperatures, while thermal point defects are present only at finite temperatures. In the following, only the major point defects obtained in Fig. 2 are considered (anti-site Ti defects on the Al sublattice and vacancies on the Ti sublattice). The concentrations of the thermal defects $x_{iT}^k$ ($i = Al, Ti, Va, k = Al, Ti$) can be obtained as described by Lozovoi et al. [20]:

$$x_{iT}^k = x_{i}^k - x_{i}^0$$

(16)

where $x_{i}^k$ and $x_{i}^0$ ($i = Al, Ti, Va, k = Al, Ti$) are the concentrations of various types of point defects at finite temperature and 0 K, respectively. At 0 K two cases need be considered, depending on which is the dominant point defect on the sublattice under consideration:

(i) anti-site defect:

$$x_{iT}^0 = 2x_{i} - 1$$

(17)

(ii) substitutional vacancy:

$$x_{iT}^0 = 1 - (1 - x_{i})/x_{i}$$

(18)

in which $x_{i}$ ($i = Al, Ti$) is the total mole fraction of $i$ atoms in the $i$-rich alloy. The calculated concentrations of thermal defects are shown in Fig. 3. Interestingly vacancies on the Ti sublattice are the main point defects on the Ti-rich side, at an increasing concentration towards the stoichiometric composition, i.e. increasing Al alloy compositions. Similar behaviour is observed for anti-site Ti, but at lower defect concentrations. Above the stoichiometric composition ($> 50$ at.% Al) the concentration of Ti vacancies steeply drops and thermal Ti vacancies are absent at any higher Al compositions. Similar behaviour is also found in the Ni–Al system, where it is attributed the interbranch Al excitation $2VaTi \rightarrow Alt$ (see Table 2) [20]. Anti-site Al atoms are the dominant thermally induced point defects on the Al-rich side of the stoichiometry. Anti-site Ti is predicted at similar concentration close to the stoichiometric composition, but quickly drops to much lower values at higher Al alloy compositions.

4.3. Phase diagram

The thermodynamic description of the Ti–Al binary system was revised, based on the information on point defects presented in this work. The revised description is largely based on a previously published assessment [22]. In order to reflect the influence of point defects, substitutional vacancies were added into the thermodynamic model of the ordered B2 phase—$(Al, Ti, Va_{0.5})$ and the model for the corresponding disordered A2 phase therefore becomes $(Al, Ti, Va_{0.5})$. These changes also affect the parameters of the $x$ and $x_2$ phases, the revised parameters of these are given in Table 4 and the corresponding phase diagram is shown in Fig. 4. Furthermore, Table 5 shows the temperatures and compositions of the two relevant peritectoid reactions in comparison to those found in other sources. Besides a sounder physical description, a better consistency with experimental data of phase equilibria is observed.

Fig. 5 shows the calculated Ti–Al phase diagram without the ordered B2 phase. In this case the bcc–hcp does not show the peculiar bending as seen in Fig. 4, and the $x_2$ phase (Ti3Al) forms congruently from the $x$ (hcp) phase at 1164 °C. The same diagram, calculated using the author’s previous description is also shown, using dotted lines [8]. It can be seen that the temperature of congruent formation of $x_2$ has increased after the re-optimisation. Taking the B2 phase into account will cause the bcc–hcp two phase region to bend sufficiently to form the $\beta + x \rightarrow x_2$ peritectoid reaction. However, the maximum temperature of this reaction cannot be higher than the temperature of congruent formation of $x_2$. The introduction of point defects into the A2/B2 model and the re-optimisation of the Ti rich part of the phase diagram did increase the temperature of congruent $x_2$ formation sufficiently, to raise the temperature of the peritectoid reaction from 1160 °C to 1198 °C. This is in very good agreement with the most recent assessment of the Ti–Al phase diagram by Schuster and Palm [23]. Fig. 6 shows the vacancy concentration in the B2 phase versus temperature as obtained from CALPHAD calculations for Ti–30 at% Al. This alloy shows a B2 single phase region between 1210 °C and 1490 °C. An increase of the vacancy concentration with temperature is found up to about 1200 °C followed by a

### Table 4

| Thermodynamic parameters | Value (J/mol) |
|--------------------------|---------------|
| $G(BCC_A2_Alti;0)$        | $-121785 + 34.0aT$ |
| $G(BCC_A2_Alti;0)$        | $60 000$      |
| $G(BCC_A2_Alti;0)$        | $150 000$     |
| $G(BCC_A2_Alti;0)$        | $0$           |
| $G(BCC_A2_Alti;0)$        | $-21645 + 3.1aT$ |
| $G(BCC_A2_Alti;0)$        | $5000 - 0.5aT$ |
| $G(BCC_A2_Alti;0)$        | $-21645 + 3.1T$ |
| $G(BCC_A2_Alti;0)$        | $0$           |
| $G(BCC_A2_Alti;0)$        | $26645 - 3.6aT$ |
| $G(BCC_A2_Alti;0)$        | $5000 - 0.5aT$ |
| $G(BCC_A2_Alti;0)$        | $26645 - 3.1aT$ |
| $G(BCC_A2_Alti;0)$        | $0$           |
| $G(BCC_A2_Alti;0)$        | $-75 000$     |
| $G(BCC_A2_Alti;0)$        | $-75 000$     |
| $G(BCC_A2_Alti;0)$        | $-7080$       |
| $G(BCC_A2_Alti;0)$        | $-7080$       |
| $G(BCC_A2_Alti;0)$        | $-3150$       |
| $G(BCC_A2_Alti;0)$        | $-3150$       |
| $G(HCP_A3_Alti;0)$        | $-128189 + 35.2aT$ |
| $G(HCP_A3_Alti;0)$        | $16 034 - 12.2aT$ |
| $G(Ti3Al_Alti;0)$         | GALCHP         |
| $G(Ti3Al_Alti;0)$         | $32 363.6 - 8.25aT + 0.75\*GHSERAL + 0.25\*GHSERTI$ |
| $G(Ti3Al_Alti;0)$         | $G(Ti3Al_Alti;0)$ |
| $G(Ti3Al_Alti;0)$         | $G(Ti3Al_Alti;0)$ |
| $G(Ti3Al_Alti;0)$         | $G(Ti3Al_Alti;0)$ |
| $G(Ti3Al_Alti;0)$         | $G(Ti3Al_Alti;0)$ |
| $G(Ti3Al_Alti;0)$         | $G(Ti3Al_Alti;0)$ |

Fig. 3. The calculated concentrations of thermal defects at 627 °C: Ti anti-site defect, Al anti-site defect, Ti vacancy and Al vacancy.
decrease at higher temperatures. This is consistent with the creation of vacancies due to an increase in temperature, and their loss due to reduced degrees of ordering, which reflects a greater opportunity of random arrangement of atoms in the crystal lattice. Calculations of vacancy concentrations using CALPHAD can be very helpful to explain vacancy-related effects at high temperatures—such as rapid precipitate growth in quenched alloys—especially when extrapolated to more complex alloys.

5. Conclusions

The enthalpies of formation of different point defects in the B2 phase of the Ti–Al system are calculated using first-principles calculations. The preference of the point defects is predicted—Ti anti-site defect in the Al sublattice and vacancy in the Ti sublattice. The concentrations of various types of point defects were calculated at finite temperatures using first-principles calculations.
calculations. Substitutional vacancies were added into the thermodynamic model of the B2 phase, which is now modelled as (Al,Ti)\textsubscript{2}V\textsubscript{5} : (Al,Ti)\textsubscript{2}V\textsubscript{5}. The Ti–Al binary system was re-optimised, which resulted in a better reproduction of experimental phase equilibria.

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Appendix. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.calphad.2012.06.007.

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