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# Site occupation behavior of sulfur and phosphorus in NiAl, TiAl and FeAl

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ABSTRACT

The site occupation behavior of sulfur and phosphorus in the binary NiAl, TiAl and FeAl alloys is investigated by first-principles calculations. Using a supercell approach, the enthalpies of formation of vacancies, antisites, and substitutional defects are calculated for the three binary alloys. The distributions of S and P in the three alloys and their dependence on Al composition are investigated based on a thermodynamical model. The predicted existence of the dominant defects agrees well with available experimental results and theoretical results. At 1273 K, P atoms occupy exclusively the Al sites in the three alloys, and S atoms occupy exclusively the Al sites in FeAl alloys. However, the concentration of S atoms occupying Ni (Ti) sites increases and that located at Al sites decreases as the Al content increases in NiAl (TiAl). These results cannot be determined from considering only the effects of atomic size and electronegativity on the site occupations. Instead, these results can be understood in terms of differences between the enthalpies of formation for impurity I occupying different sublattices coupled with the configurational entropy differences.

## 1. Introduction

Many binary intermetallic compounds, such as NiAl and TiAl, have attracted considerable interest for applications in advanced terrestrial and aerospace components [1–3] owing to their high melting temperature, good oxidation resistance, and excellent (metallic) electrical and thermal conductivities. Among them, the transition metal (TM) aluminides NiAl, TiAl and FeAl are the most promising candidates for high-temperature structural materials. Various dilute solutes in the three binary alloys, such as metallic (e.g., Fe or Cr) and nonmetallic solutes (e.g., S and P), play important roles in affecting the alloy performance such as the phase stability, oxidation resistance and mechanical properties [1–8]. Understanding the solute-related phenomena, especially the site occupation behavior of the solutes in binary alloys from both theory and experiment, is indispensable to the design of novel intermetallics with desirable properties.

Although a number of investigations have been carried out for metal solutes in certain binary alloys [8–19], few studies have been devoted to understanding the site occupation behavior of nonmetallic elements in NiAl, TiAl and FeAl alloys. Djajaputra et al. found that oxygen atoms prefer to occupy nickel sites over aluminum sites from a calculation of the site selection energy [20], which was determined by the difference between the total energies of supercells with an oxygen atom on the two sublattices in NiAl. The replaced Ni or Al atoms by oxygen were assumed to merge into the pure Ni or Al bulk state in the model. The assumption is a very rude approximate, as discussed by Legoas et al. [16].

There exists a large number of nonmetallic solute-related phenomena that require further investigation. For example, both Cao et al. [21] and Guo et al. [22] found that a proper amount of P in Ni-based alloys could improve the life time of deformed alloys. However, the presence of P was previously considered to be harmful to the structural stability of the alloy [21,22]. To understand these effects, information on the site preference of P in these alloys is crucial. In another example, Hou pointed out that no impurity S could segregate to an intact NiAl/$\alpha$-$Al_2O_3$ interface when the chemistry of the NiAl alloy is nearly stoichiometric, although S was often found at many NiAl-related interfaces when the alloys are nonstoichiometric [23]. In order to understand the segregation behavior of impurities such as S and P in alloy–oxide interfaces ensembles [24–26], the site occupation of those impurities in bulk alloys also has to be clarified, especially for quantitatively rationalizing segregation energies. Experimentally, work on binary

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alloys often provides incomplete answers to many issues [27], partially owing to the fact that even a slight composition deviation from ideal stoichiometry in an alloy may change the stable defect structures as well as the solute distribution and further affect the physical and chemical properties of the alloy. In this regard, accurate information on the site occupation of nonmetallic solutes in binary AB alloys is expected to be valuable for further design and optimization of advanced alloy materials.

It has been generally accepted that trace amounts (ppm) of nonmetallic impurities like S and P are uncontrollable in binary alloys [28]. In order to provide fundamental understanding of the effects of those impurities on the properties of many alloy-based systems as mentioned above, first-principles calculations based on density-functional theory (DFT) are performed to evaluate the site occupation of S and P atoms in NiAl, TiAl and FeAl alloys in this work. The paper is organized as follows. First, the theoretical model for the site occupation analysis is introduced in Section 2. Secondly, the technique details of the first-principles computations are given in Section 3. Test calculations for the bulk properties of impurity-free NiAl, TiAl and FeAl alloys are also described in this section. Thirdly, the enthalpies of formation for various defects are presented, and the results of site distributions for S and P atoms in the three binary alloys and their dependence on alloy composition are also discussed in Section 4. Finally, by scrutinizing the correlation of the results with atomic radii and metal activities, the difference between the enthalpies of formation for impurity I occupying different sublattices, [i.e.,$H^{\mathrm{I}}_{\beta} - H^{\mathrm{I}}_{\alpha}$ (β = Al, α = Ni, Ti, or Fe)], coupling with the configurational entropy difference, is found to play an important role in determining the distribution characteristics of nonmetallic substitutional impurities in binary (AB) alloys at high temperature.

## 2. Thermodynamic model for analyzing solute distribution

A thermodynamic model is adopted to determine the distribution of substitutional solutes in AB alloys [29]. The basic assumption of the model is that an AB alloy can be regarded as a canonical ensemble in a thermodynamic equilibrium state. The A or B sublattice in an AB alloy is denoted by α or β, respectively. Each site in the sublattice α or β can be occupied by its own atom type ($A_\alpha$ or $B_\beta$), antisite ($B_\alpha$ or $A_\beta$), an impurity atom I (I = S or P), or a vacancy (V).

The *atomic concentration* can then be represented by

$$x^{\eta}_{\mathrm{sub}} = \frac{n^{\eta}_{\mathrm{sub}}}{N}, \tag{1}$$

in which $N$ is the total number of atoms in an alloy system, and $n^{\eta}_{\mathrm{sub}}$ is the number of the specified species $\eta$ ($\eta$ = A, B, I, V) in a sublattice sub (sub = α, β). For NiAl, TiAl, and FeAl alloys, α designates the Ni, Ti, or Fe sublattice, and β indicates the Al sublattice. Only the site occupation behavior of the substitutional S and P impurities is investigated because earlier experimental and theoretical work proved the dominant presence of this type of impurities in those alloys [11,13,14,16–20]. Our DFT calculations also confirmed that substitutional S is the most stable state in a strain-free bulk Ni with a similar metallic environment, 0.15 eV lower in energy than the interstitial S [30].

Correspondingly, the *site concentration* of one species $\eta$ at a given sublattice can be expressed as

$$c^{\eta}_{\mathrm{sub}} = \frac{n^{\eta}_{\mathrm{sub}}}{M}. \tag{2}$$

Here, $M$ is the number of total lattice sites in the system. Infact, $M$ is usually greater than $N$ due to the existence of vacancies. Therefore, there exists a correlation between the *site concentration* and the *atomic concentration*, i.e.,

$$c^{\eta}_{\mathrm{sub}} = x^{\eta}_{\mathrm{sub}} \Big/ \left(1 + x^{\mathrm{V}}_{\alpha} + x^{\mathrm{V}}_{\beta}\right). \tag{3}$$

In the canonical ensemble, the ratio of lattice sites α to β is also fixed to 1:1 [Eq. (4b)] in studying the AB type of binary alloys. Although the total number of atoms is kept fixed [Eq. (4a)], the total lattice sites could change as temperature or alloy compositions vary due to the annihilation or creation of vacancies. In this regard, such an alloy system satisfies the following two constraints:

$$x^{\mathrm{A}}_{\alpha} + x^{\mathrm{B}}_{\alpha} + x^{\mathrm{I}}_{\alpha} + x^{\mathrm{B}}_{\beta} + x^{\mathrm{A}}_{\beta} + x^{\mathrm{I}}_{\beta} = 1, \tag{4a}$$

$$\left(x^{\mathrm{A}}_{\alpha} + x^{\mathrm{B}}_{\alpha} + x^{\mathrm{I}}_{\alpha} + x^{\mathrm{V}}_{\alpha}\right) \Big/ \left(x^{\mathrm{B}}_{\beta} + x^{\mathrm{A}}_{\beta} + x^{\mathrm{I}}_{\beta} + x^{\mathrm{V}}_{\beta}\right) = 1. \tag{4b}$$

Experimentally, it has been identified that there is, to a good approximation, a linear relationship between the enthalpy of formation (*EOF*) of an alloy and the composition in the Ni–Al, Ti–Al and Fe–Al systems [1,31]. This is consistent with the Wagner–Schottky approximation [32], applicable to the dilute defect limit to neglect the interactions between point defects. In this case, the *EOF* of the whole system can be reasonably formulated by a linear function of defect *atomic concentrations* to a good approximation, i.e.

$$\Delta H = \Delta H_{\mathrm{A}_{0.5}\mathrm{B}_{0.5}} + \sum_{\mathrm{d}} H_{\mathrm{d}} x_{\mathrm{d}}, \tag{5}$$

where $\Delta H_{\mathrm{A}_{0.5}\mathrm{B}_{0.5}}$ is the *EOF* (per atom) of the strictly stoichiometric AB alloy. The summation in Eq. (5) is over all defect types. $H_{\mathrm{d}}$ is then the enthalpy of formation of an isolated point defect with $H^{\mathrm{B}}_{\alpha}(H^{\mathrm{A}}_{\beta})$ for an antisite $B_\alpha$ ($A_\beta$), $H^{\mathrm{V}}_{\alpha}(H^{\mathrm{V}}_{\beta})$ for a vacancy in the α (β) sublattice, and $H^{\mathrm{I}}_{\alpha}(H^{\mathrm{I}}_{\beta})$ for a substitutional impurity I in the α (β) sublattice. $x_{\mathrm{d}}$ indicates the corresponding defect atomic concentration, i.e., the $x^{\eta}_{\mathrm{sub}}$ in Eq. (1). $H_{\mathrm{d}}$ for a given defect type d can then be calculated from first-principles as

$$H_{\mathrm{d}} = \left(\Delta H - \Delta H_{\mathrm{A}_{0.5}\mathrm{B}_{0.5}}\right) / x_{\mathrm{d}}. \tag{6}$$

In Eq. (6), the *EOF* $\Delta H$ of the alloy $\mathrm{A}_{1-x-y}\mathrm{B}_x\mathrm{I}_y$, can be calculated by a supercell approach, i.e.

$$\Delta H = E_{\mathrm{tot}}\left(\mathrm{A}_{1-x-y}\mathrm{B}_x\mathrm{I}_y\right) - (1-x-y)E(\mathrm{A}) - xE(\mathrm{B}) - yE(\mathrm{I}), \tag{7}$$

where $E_{\mathrm{tot}}(\mathrm{A}_{1-x-y}\mathrm{B}_x\mathrm{I}_y)$ is the first-principles total energy (per atom) of the alloy supercell. $E$(A), $E$(B) and $E$(I) are the total energies of the corresponding pure solid phases of A, B, and I (per atom), respectively. $x$ and $y$ are the atomic concentrations of B and I in the supercell.

In mean-field approximation, the configurational entropy (per atom) of a binary alloy system with defects can be expressed as

$$S = k\left(1 + x^{\mathrm{V}}_{\alpha} + x^{\mathrm{V}}_{\beta}\right)\ln\left(\frac{1 + x^{\mathrm{V}}_{\alpha} + x^{\mathrm{V}}_{\beta}}{2}\right) - k\sum_{\mathrm{sub}}\sum_{\eta} x^{\eta}_{\mathrm{sub}} \ln x^{\eta}_{\mathrm{sub}}, \tag{8}$$

where $k$ is the Boltzmann constant. Contribution to *EOF* from lattice vibration is not considered in this work. On the one hand, *EOF*s in Eqs. (6)–(8) refer to energy difference, and the vibration contributions are expected to cancel with each other in each case. According to our past work on the Sulfur segregation at the Ni/$\mathrm{Al_2O_3}$ in Ref. [30], we have found that the vibration contributions contributed little for the final analysis. On the other hand, lattice vibration usually was shown not to change the general trend of physical results on the site occupation behavior of additives in the binary NiAl, TiAl and FeAl alloys [11,13,14,16–20]. In those works, the predicted results for metal or nonmetal elements in binary alloys were all consistent with the experimental observations,