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Role of impurities in the formation of point defects in Ti-Al alloys

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Abstract. The effect of impurities on the point defect formation energies in Ti-Al alloys was studied by the projector augmented-wave method. The grand canonical formalism was applied to calculate the formation energies of several kinds of defects. It was shown that the formation energy of Al-vacancy decreases by \( \approx 1.3 \) eV with increasing its content in the series of alloys Ti\textsubscript{1−x}Al–Ti\textsubscript{x}, whereas the formation energy of Ti-vacancy changes insignificantly. In general, the formation of Ti-vacancies is more preferred in Ti-Al alloys rather than the formation of Al-vacancies. We demonstrate that Nb, Mo, Tc, Ru, Rh, Pd lead to increase of the formation energy of Al-vacancy if they occupy the Al sites, whereas only Mo and Tc increase the formation energy of Ti-vacancy. All 4\textit{d} elements, if they substitute for Ti, reduce the formation energies of Al-vacancy. The influence of impurities on elastic constants is discussed.

1. Introduction

Intermetallic Ti-Al alloys are very attractive as high-temperature structural materials for aerospace, automotive, marine and other applications. These alloys have unique mechanical properties such as a high specific strength, advanced creep characteristics and relatively good oxidation/corrosion resistance. The development of new alloys based on these compounds, whose properties are between nickel-based superalloys and advanced ceramics, is a challenging problem of modern materials science. One of the methods that allows one to improve the functional properties of alloys is their doping. Atomic diffusion mechanisms and mechanical properties of alloys strongly depend on impurities. It is well-known that all self-diffusion mechanisms require the existence of vacancies or complexes of point defects. Although the formation energy of different defects and their complexes in binary alloys has been intensively studied, this topic remains in focus of numerous theoretical studies [1]. The formation energies of some defects in TiAl and Ti\textsubscript{3}Al alloys were calculated earlier in [2] using embedded-atom potentials. It was shown that in both alloys antistructural defects strongly dominate over vacancies. However, the information about the influence of impurities on the defect formation energy in Ti-Al alloys is insufficient. In this work we study the effect of 4\textit{d} impurities and Ga, Ge, In, Sn, etc. on the point defect formation energies in the series of alloys Ti\textsubscript{1−x}Al–Ti\textsubscript{x}–TiAl\textsubscript{3}.

2. Method of calculation

The calculations of atomic and electronic structure of binary alloys were performed by the projector augmented-wave method (PAW) method [3] implemented in the VASP code [4]. The generalized gradient approximation (GGA-PBE) [5] was used for the exchange-correlation functional. The full
optimization including volume and shape of crystal structures was carried out until the forces at atoms were smaller than 0.01 eV/Å. A k-point mesh of 7×7×7 obtained according to the Monkhorst–Pack scheme was used for integration over the Brillouin zone in (2×2×2) supercell of γ-TiAl and in (2×2×1) supercell of TiAl. In case of Ti3Al, the (2×2×2) supercell was used alongside with the 3×3×4 Γ-centered k-point mesh. The formation energy of defects was calculated using the following equation:

\[ E_i = E_{\text{def}} - E_{\text{id}} + n_A \mu_A + n_B \mu_B \]  

where \( E_{\text{def}} \) and \( E_{\text{id}} \) are the total energies of the supercell with defect and the ideal one (the difference between these energies (\( E^{\text{raw}} \)) is called “raw” energy), \( \mu_A \) and \( \mu_B \) – the chemical potentials of binary alloy \( A_xB_y \) components, \( n_A \) and \( n_B \) – the number of atoms of A and B added to \( n < 0 \) and/or removed \( n > 0 \) from the perfect crystal to form the defect. In order to calculate \( E_i \), the approach suggested in [6] for an alloy of equiatomic composition was used.

3. Results and discussion

The main problem of the calculations of defect formation energies is connected with the determination of the chemical potentials of the alloy components. In most works the chemical potentials of bulk constituent elements are used. Another approach for the estimation of \( \mu_A \) and \( \mu_B \) was suggested in [6], in which the grand canonical formalism was used. It was shown that the chemical potential of component \( i = A, B \) in the linear approximation can be expressed as follows

\[ \mu_i = \mu_i^0 - T \tilde{\mu}_i(x) , \]  

where \( x \) is a deviation of the alloy composition from the stoichiometric \((A_{x+y}B_{x+y})\), \( \mu_i^0 \) is the chemical potential at zero temperature, \( \tilde{\mu}_i(x) \) is the coefficient of the linear temperature dependence of the chemical potential, \( T \) – temperature. Since antisites are the constitutional defects in Ti-Al alloys, their concentrations are much higher than those of the vacancies. The following expressions for \( \mu_i^0 \) and \( \tilde{\mu}_i \) were obtained in case of Ti\(_{x+y}\)Al\(_{x+y}\) alloy by modification of the equations (A3-A6, A11-A14) from [6]:

for Ti-rich \( (x > 0) \)

\[ \begin{align*}
\mu_{\text{Ti}}^0 &= e_0 + \beta E^{\text{raw}}(\text{Ti}_{\text{Ti}}), \\
\tilde{\mu}_{\text{Ti}} &= \beta k_B \ln(1/2x), \\
\mu_{\text{Al}}^0 &= e_0 - \alpha E^{\text{raw}}(\text{Ti}_{\text{Ti}}), \\
\tilde{\mu}_{\text{Al}} &= -\alpha k_B \ln\left(4(0.5 - x)^2/2x\right)
\end{align*} \]  

and

for Al-rich \( (x < 0) \)

\[ \begin{align*}
\mu_{\text{Ti}}^0 &= e_0 - \beta E^{\text{raw}}(\text{Al}_{\text{Ti}}), \\
\tilde{\mu}_{\text{Ti}} &= -\beta k_B \ln\left(-4(0.5 + x)^2/2x\right), \\
\mu_{\text{Al}}^0 &= e_0 + \alpha E^{\text{raw}}(\text{Al}_{\text{Ti}}), \\
\tilde{\mu}_{\text{Al}} &= \alpha k_B \ln(-1/2x)
\end{align*} \]  

where \( e_0 \) is the total energy per atom for the ideal supercell, \( E^{\text{raw}}(\text{Ti}_{\text{Ti}}) \) and \( E^{\text{raw}}(\text{Al}_{\text{Ti}}) \) are the raw energies of Ti and Al antisites, respectively. In case of the stoichiometric composition, the chemical potential \( \tilde{\mu}_i \) equals 0 and \( \mu_i^0 \) is calculated as an average of two values for \( x > 0 \) and \( x < 0 \) [2].

The obtained values of the formation energies of vacancies and antisites for Ti\(_3\)Al, TiAl and TiAl\(_3\) alloys are shown in Figure 1. It is seen that vacancies have higher formation energies than antisites in all considered compounds. The difference in \( E_i \) is the largest in Ti\(_3\)Al alloy but it decreases with increase of Al content. In general, the defect formation energies are more sensibly affected by the alloy composition in TiAl\(_3\) than in both TiAl and Ti\(_3\)Al alloys. It is seen from Figure 1 that Ti vacancies form easier than Al ones in the alloys of the stoichiometric composition. The difference in \( E_i \) for Al and Ti vacancies in stoichiometric alloy TiAl reaches 0.39 eV that is in agreement with the value of 0.41 eV [7] obtained by \textit{ab-initio} method, but it is slightly larger than that of 0.25 eV obtained by EAM [2]. At the same time, the calculated values of \( E_i \) in case of Ti-vacancy in Ti\(_{48.5}\)Al\(_{51.5}\) and Ti\(_{65.6}\)Al\(_{34.4}\) alloys are 1.63 eV and 2.10 eV that are larger than corresponding experimental values.
1.41±0.06 eV [8] and 1.55±0.2 eV [9] obtained by the positron lifetime spectroscopy for the alloys of the same compositions and at the same temperature. It is known that ab-initio methods within DFT overestimate the defect formation energy in alloys. However, the trend in increase of the formation energy of Ti-vacancy with increase of Ti content in alloy is in line with the experiment.

![Figure 1. Formation energies of point defects (vacancies and antisites) in Ti₃Al (a), TiAl (b) and TiAl₁₃ (c) as functions of composition near the stoichiometry.](image1)

The influence of impurities on $E_f$ in TiAl alloy is summarized in Figure 2. Note that the impurities were located in the first neighbors of defects. It is interesting that impurities such as Nb and Mo increase the formation energy of all point defects if they occupy Al-sublattice but this effect is less pronounced in case of Al antistructural defect. The impurities of groups IIIA and IVA (Si, Ga, Ge, In, Sn) on both Al and Ti sites provide an Al removal from their local environment. All these impurities lead also to reduce of $E_f$ for Al-vacancies and Ti-antisites but they increase of Al-antisite formation energy. Impurities of Ru, Rh, Pd and Ag substituting for Al atom affect the similar way in respect to titanium. It should be noted that a dramatic downfall of the vacancy formation energy at the addition of Y and Zr instead of Al is connected with a displacement of the impurity atoms from their positions towards vacancy. As a result, the final structure looks like complex of the interstitial impurity atom and two vacancies. All considered impurities, if they occupy the Ti sites, provide the decrease of the formation energy of Al-vacancy. Finally, it is necessary to emphasized that the site substitution behavior is found to be in agreement with earlier experimental and theoretical results [7,10,11].

![Figure 2. The change of point defect $E_f$ in TiAl due to impurities on both Ti (a) and Al (b) sites relative to undoped alloy.](image2)

Several words should be said about influence of impurities on the elastic moduli of γ-TiAl alloy. It is seen from Table 1 that calculated $C_{ij}$ are in good agreement with earlier available theoretical and experimental results. Note that the local density approximation for the exchange-correlation functional and pseudopotential approach was used in [7]. Modulus $C_{44}$, which reflects the resistance to shear in the (001) plane in the [010] or [100] direction, agrees well with the experimental data, whereas other
moduli demonstrate the deviations as compared to the other theoretical results. It is almost twice larger than the corresponding one in Ti3Al (55.5 GPa). Modulus $C_{66}$ related to the resistance to shear in the (010) plane in the [100] direction, also is smaller than that for Ti3Al (51.1 GPa). So, the Ti-rich alloy is elastically softer than $\gamma$-TiAl against shear modes. Impurities such as Nb, Mo and also Zr, Tc, Ru, Rh on Ti sites lead to increase of bulk modulus that is in line with conclusion from [10], whereas Young’s and shear moduli are decreased in doped alloy excepting the case of Mo. At the same time, Ga and Ge affect the B modulus slightly and their effects on $E$ and $G$ are opposite.

| Table 1. Calculated elastic ($C_{ij}$), bulk ($B$), Young’s ($E$) and shear ($G$) moduli (in GPa) for undoped and doped $\gamma$-TiAl alloy |
|-----------------|---|---|---|---|---|---|---|
| $\gamma$-TiAl   | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ | $B$ | $E$ | $G$ |
| [7]             | 168.0    | 89.2    | 90.4    | 171.8    | 113.3    | 84.1    | 116.4 | 175.4 | 70.2 |
| exp. [12]       | 177      | 99      | 93      | 181      | 111      | –       | 125   | 70.9  | 69.5 |
| Nb on Ti site   | 167.3    | 96.7    | 89.5    | 178.8    | 114.0    | 79.7    | 118.3 | 174.3 | 69.5 |
| Mo on Ti site   | 171.0    | 100.6   | 89.2    | 183.0    | 113.4    | 82.3    | 120.3 | 177.0 | 70.5 |
| Ga on Al site   | 168.0    | 91.8    | 89.9    | 172.5    | 112.6    | 73.2    | 116.9 | 171.2 | 68.2 |
| Ge on Al site   | 171.4    | 92.3    | 87.3    | 183.1    | 112.1    | 76.0    | 117.7 | 177.0 | 70.9 |

4. Conclusion
In summary, the influence of impurities on the formation energies of point defects and elastic moduli in Ti-Al alloys was performed within DFT method. We demonstrate that the formation energy of Al-vacancy depends strongly on Al content in the Ti-Al alloy, whereas the formation energy of Ti-vacancy changes insignificantly on alloy composition. In spite of all 4d impurities lead to decrease of the formation energies of Al-vacancy, if they substitute for Ti, only impurities of the beginning of 4d period prefer to be on Ti-sites. Besides, Nb and Mo increase the formation energy of Ti-vacancies. We established that impurities such as Tc, Ru, Rh, Pd, which prefer to occupy the Al sites, lead to increase of the formation energy of Al-vacancies. The calculations of elastic moduli allow to confirm that TiAl is stiffer than Ti3Al against shear modes. Impurities such as Nb and Mo, if they substitute for Ti, and also simple metals on the Al-sites lead to increase of bulk modulus.

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