Point defects and mechanical behavior of titanium alloys and intermetallic compounds

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Abstract. First principles calculations were carried out to investigate the energetics of point defects, including solute atoms, vacancies, and antisite defects, in titanium solid solution and intermetallics. Their influence on the mechanical behavior of titanium alloys and intermetallic compounds were discussed. The self consistent procedure proposed by the authors was applied to TiAl intermetallic compounds. The ordering parameter was redefined to include the contribution of vacancies to the disordering of intermetallic compounds, so that the new approach can be applied to both strongly and weakly ordered compounds. Concentrations of point defects of various kinds can be estimated for intermetallics of different composition at different temperature. The solid solution strengthening of alloying elements through short range ordering was studied for titanium alloys and the solid solution hardening rate was estimated for various alloying elements. The solute-vacancy interaction in titanium alloys was calculated and its influence on the diffusion and creep behavior was discussed. These calculations provided some useful information for the selection of alloying elements in designing new titanium alloys.

1. Introduction

Point defects of various kinds, such as vacancies, alloying or impurity atoms in alloys and antisite defects in intermetallic compounds, influence not only the physical properties (e.g., electronic, magnetic, and optical properties [1]), but also the mechanical properties (e.g., strength [2, 3], ductility and creep resistance [4]) of materials. The high concentration of point defects and its ordering on the lattice in intermetallic compounds were found to relate closely to lattice stability, phase equilibrium, strength and ductility etc [5]. The alteration of the mechanical properties can be directly the result of the change of atomic bonding around point defects. For example, the formation of a vacancy breaks some bonds, meanwhile strengthens the neighboring bonds through the redistribution of charge density. The alteration of bonds changes the lattice resistance, and therefore, the deformation behavior. Alternatively, point defects may change indirectly the mechanical properties of materials by interacting with other lattice defects (e.g., dislocations and grain boundaries) that closely related to the mechanical properties. As demonstrated in [6], the behavior of dislocations (sliding and dissociation,
etc.) can be altered significantly by the disordering of lattice due to antisite defects and segregation of alloying or impurity atoms to dislocations. The segregation of alloying or impurity atoms to grain boundary or other interface can influence strongly the strength and fracture properties of materials. In some intermetallic compounds, slight deviation from stoichiometry (therefore point defects introduced) may cause great change of mechanical properties (so called off-stoichiometry effects) due to the composition change and reconstruction of interfaces and grain boundaries [7].

Although the behavior of the point defects is critical to the mechanical properties of materials, it can hardly be accessed experimentally. First principles electronic structure calculation provides an ideal approach to study the details of point defects theoretically. The electronic structure, formation energy, interaction energy, and concentration of, and atomic relaxation around point defects, can be easily obtained through first-principles calculations [8]. In the present paper, we will discuss, on the basis of our recent first-principles calculations, the point defect behavior in titanium alloys and titanium based intermetallic compounds, including: (1) thermal equilibrium point defects concentrations and long range order (LRO) as a function of temperature and composition in intermetallic TiAl; (2) the site occupation behavior of alloying atoms in Ti$_3$Al; (3) the interaction energies between the point defects (vacancy-alloying atom as well as alloying atom-alloying atom) in α-Ti alloys have been calculated and their implications to the creep resistance and short-range order strengthening of the alloys. The results of these investigations helped our understanding and provide a theoretical basis for the selection of alloying elements when designing new alloys.

2. Electronic structure and energetics calculation

For the calculation of electronic structure and energetics of point defects, the CASTEP (Cambridge Serial Total Energy Package), DVM (Discrete Variational Method) and LMTO (Linearized Muffin-Tin Orbital) methods were employed. The details of these methods can be found in refs. [9-12]. Figure 1 shows some supercells and clusters used in the calculation. The supercell with vacancies or antisite defects was formed by removing one atom or replacing an A atom with B from the supercell or cluster of the perfect lattice. Two atoms as the nearest neighbors were replaced by two alloying atoms or an atom and a vacancy to study the interaction between alloying atoms or between alloying atom and vacancy. Total energy was calculated and defect formation energy and binding energy were calculated from the total energy. These energetics data were used as ‘raw energy’ input to calculate the point defect concentration and to analyze the site occupancy and interaction between the defects.

![Figure 1. Supercells employed in the electronic structure calculation for (a) TiAl with L1$_0$ structure and (b) HCP titanium, as well as (c) cluster for Ti$_3$Al with D0$_{19}$ structure.](image)

For the calculation of the equilibrium point defect concentration, the grand canonical ensemble was employed, and concentrations of antisite defects and vacancies were derived by minimizing the grand potential [13]. Clearly, the energy difference between an atom at the right position and antisite position is the largest when the compound is completely ordered, so it is difficult to form an antisite defect. When the compound is completely disordered, there is no energy difference for an atom at different positions. Similar to the Bragg-Williams Approximation [14], we assume the antisite defect formation energy proportional to the degree of LRO of the lattice, while the vacancy formation energy
was kept constant.

For the site occupation criteria, it is difficult to compare the binding energy with different substitution, since the cluster environments are not identical. We draw a diagram using the binding energy of clusters with different occupancy for each alloying element as axis. Two straight lines with unity slope passing through the point of two constituent elements of the compound were used to classify the site occupancy into different groups.

The ordering tendency of solute atoms in titanium can be measured by the energy difference between the configurations with two solute atoms put together or apart in titanium host. It has been demonstrated that this energy difference is about twice that of the effective pair interaction. Similarly, the interaction between vacancy and alloying atom can be obtained by the energy difference between two configurations, one with vacancy and solute atom as the nearest neighbor, the other with the two separated.

3. Results and discussion

3.1. Equilibrium point defect concentration and long range ordering of TiAl

The degrees of LRO for different TiAl composition as a function of temperature are shown in Figure 2. It can be seen that for all the compositions, the degree of LRO reduces when the temperature is increased, while it is fairly steady at temperature below about 1000K. For off-stoichiometric compounds, the degree of order is lower due to the presence of antisite defects, and the decrease of LRO parameter at low temperature is approximately proportional to the deviation from stoichiometry. It should be noted that the LRO parameter for the off-stoichiometric TiAl reduces dramatically only at a higher temperature compared with the stoichiometric TiAl, say 1200K for Ti54Al, as shown by the pink line in figure 2. The disordering will influence the dislocation dissociation, due to the change of energy of the antiphase boundaries bounding the superpartials. The separation between the partials is expected to increase due to the reduction of the fault energy, therefore affecting the deformability of the compounds. It is worth noting that the lower degree of LRO due to off-stoichiometric composition decreases slower with the increase of temperature, and this may help us identify suitable composition for high temperature application.

Figure 3 shows the point defect concentrations of 4 kinds of defect, i.e., vacancy on Ti sublattice, vacancy on Al sublattice, Ti atom on Al sublattice and Al atom on Ti sublattice, as a function of composition, at 1073K, which corresponding to the application temperature. At such a high temperature, the antisite defect concentration is much higher (more than 4 orders of magnitude) than that of vacancies on different sublattice. This is in agreement with the experimental results that TiAl is an antisite defect type of intermetallics. The antisite defect concentration shows an X shaped change when the compound composition changes, almost symmetrically. This suggests that the difficulty of forming antisite defects on the two sublattices is similar, and the concentration of A type of antisite defect increases when component A becomes rich. The Ti sublattice has a much higher vacancy concentration than the Al sublattice; this is a reflection of the lower formation energy of vacancy on Ti sublattice. The difference is larger for Al rich TiAl, and become smaller when Ti content increases, since the vacancy concentration on the Ti sublattice is larger for Ti lean compositions while vacancy concentration on Al is larger for Ti rich compositions.

Figure 4 shows that the 4 types of point defect concentration of stoichiometric TiAl increase with temperature. The overlap of the two antisite defect concentrations is due to the limitation of the stoichiometry and the small vacancy concentration compared with that of antisite defect.
Figure 2. LRO parameter for different TiAl composition as a function of temperature. Ti48 here means the mole fraction of Al is 0.48 in TiAl.

Figure 3. Point defect concentrations as a function of Ti mole fraction in TiAl at 1073K. A on B in the legend stands for the defect concentration of A on B sublattice.

Figure 4. Change of various point defect concentrations with temperature for TiAl. Note that the curves of the two antisite defect concentrations overlap because they are very close to each other.

3.2. Ordering of alloying elements in intermetallic compounds - site occupancy
In ordered intermetallic compounds, there are more than one sublattices. When a third element is
added into the compound, there is a problem of site selection. Variation in site occupancy may cause change of the properties of the material. Figure 5 shows the site occupancy prediction by the first principles calculation, using DVM [11]. The binding energy of clusters with two different site occupations was calculated for each element. Since the composition of each cluster for different occupation is different, it is meaningless to make direct comparison of the energy, so the binding energy was used to draw a diagram, as shown in Figure 5 [15]. The two straight lines pass through the point of the two constituent elements of the compound, with slopes of unity. These two lines separate the elements with different occupation behavior into 3 groups. Elements located below the lower line will occupy the Ti site, whereas those above the upper line will occupy the Al site, regardless of the matrix composition; elements in between the two lines has a smaller energy difference when occupying the two sites, so they have a weaker ordering tendency, and their site occupancy depends on the matrix composition as well as the concentration of the alloying element itself. These predictions agree with most of the site occupancy measurements by ALCHEMI and other methods reported in literature and our own results [16].

The difference of the energy of atoms occupying different sites is a measure of their site selection tendency, or ordering tendency of alloying elements on different sublattice. Due to the difference of their ordering tendency, there will be a site competition between different alloying elements when more than one alloying elements are added into the compounds. This site competition effect has been verified by our ALCHEMI measurements for elements Ga, Cr and Nb in Ti$_3$Al [17]. It was shown that Ga and Nb, located outside the two lines and with very strong tendency to occupy Al and Ti site respectively, can push Cr, located in between the two lines and with weaker ordering tendency, to the opposite sites, so that we can control the site occupancy of some elements by others which have stronger ordering tendency, and therefore control the alloying effects.

Another effect due to the difference of ordering tendency is that the elements with strong ordering tendency will remain ordered up to high temperature, while those elements with weaker ordering tendency would become disordered at relatively low temperature. We can thus adjust the ordering behavior of the compounds by adding different alloying elements. The minor change of ordering from perfect order or complete disorder caused by alloying additions will influence the dislocation dissociation and glide, and may also affect the antiphase domain growth behavior as well as the deformation properties.

![Figure 5](image_url)

**Figure 5.** Prediction of site occupancy of alloying elements in Ti$_3$Al [15].

### 3.3. Short range ordering and its strengthening effects

Near-$\alpha$ titanium is usually alloyed with Al, Si etc. to increase high temperature strength, but some long range ordered phases, such as $\alpha_2$, may form, which strengthen the material but decrease the ductility. It is therefore important to understand the mechanism governing the ordering and strengthening of the alloys. SRO may contribute significantly to high temperature strength, and it is
important both in practice and in theory to understand the strengthening effects of various alloying elements.

The ordering tendency in titanium can be evaluated using the solute-solute interaction, which can be calculated as the energy difference of two configurations with two alloying atoms as the first neighbors or placed apart. It is demonstrated that the solute interaction energy calculated this way is about twice the effective pairwise interaction (EPI) previously defined by Cowley [19].

Our calculated EPIs for various elements in titanium show that simple metals, such as Al, Si, Ga and Ge may have strong ordering tendency and, as the valence increases, the absolute value of EPI increases, so that the ordering tendency becomes stronger, while Mn, Fe, Co and Ni tend to clustering. These trends are in qualitative agreement with the binary phase diagram; for example, at certain temperature, the solubility of Al and Ga is larger than that of Si and Ge.

The increase of shear strength due to the SRO strengthening by addition of 5% of Si, Ge, Ga and Al were estimated using Flinn’s model and shown in Fig. 6 [18]. It can be seen that the shear strengthening due to SRO drops only slightly up to 900K, which is about the upper limit for the application of titanium alloys, so the SRO strengthening of these elements contributes substantially to high temperature strength of titanium alloys. The theoretical SRO hardening rate increases in the order Al < Ga < Ge < Si, which is in agreement with experimental results. The EPI energies of Ti–simple metal (SM) and Ti–transition metal (TM) solutions are dominated by different factors. In Ti–SM solutions, the EPI energy may be related to the repulsive interaction between the SM alloying atoms induced by the hybridization between the low-lying states of the SM atoms whereas in most Ti–TM solutions, it is dominated by atomic size effect. The calculated strengthening data of different solute atoms can be utilized as guidance for the selection of the alloying elements when developing new alloys.

![Figure 6. The change of SRO strengthening with temperature for different elements [18].](image)

### 3.4. Creep properties and solute-vacancy interaction in titanium alloys

Creep strength is essential to titanium alloys for high temperature use. It was recognized that the vacancy-solute interaction is closely related to the creep properties of alloys, so it is important to understand the interaction of various alloying atoms with vacancies in titanium, in order to identify the most effective alloying elements in alloy design.

The solute-vacancy interaction can be defined as the energy difference between two configurations of supercell with solute atom and vacancy as first neighbors and that with the two placed apart. These energies were calculated using the LMTO-ASA method for candidate elements in the third through fifth row of the periodic table, and the results are shown in Fig. 7 [20]. It can be seen that the simple metals and 4d transition metals have negative (attractive) interaction energy with vacancies, while the 3d metals are repulsive to the vacancies. On comparison of the calculation results with experimental information, a simple relationship between the solute-vacancy interaction and high-temperature creep properties of Ti alloys was found: solutes attractive to the vacancy can...
improve the creep resistance, while those repulsive to the vacancy have no beneficial effect on the creep resistance. These results indicate that solute-vacancy interaction may be an important factor related to the creep properties of the titanium alloys. In fact, most alloying elements presently used in high temperature titanium alloys, such as Al, Si, Zr, Nb, Mo, Sn etc., have negative interaction with vacancy, while Fe, which is repulsive to vacancy in our calculation, is detrimental to the creep properties, so that its content, as an impurity in high temperature titanium alloys, was usually strictly restricted.

The creep mechanisms of alloys at high temperature are dislocation climbing, dislocation viscous gliding and grain-boundary sliding. Some experiments show that formation of solute atmosphere around dislocations is the main reason for the improvement in the creep properties of \( \alpha \)-Ti. The formation of the solute atmosphere at dislocations was ascribed to the elastic interaction between the solute and dislocation due to the size difference between the substitutional solute atoms such as Al or Si and the Ti atom. This is the well-known Cottrell atmosphere strengthening. However, using only the elastic interaction may not explain why some solutes such as V, Cr or Ni cannot improve the creep resistance but others such as Al or Si can. Furthermore, the Cottrell atmosphere mechanism will fail at high temperature, due to the increase of diffusion rate. It is shown by experiment that dislocation is a major kind of sink of vacancy, so the atoms attractive to vacancy will be brought to the dislocation; the accumulation of these solute atoms will form a strong atmosphere or even precipitates around the dislocation, so that it will have a stronger pinning effect on the dislocation movement. Even at relatively high temperature, the dislocations can not overcome the large solute atmosphere or precipitates.

It can be seen from Fig. 7 that Ga, Ge, etc. are attractive to vacancy. These elements may improve the creep properties at high temperature, and thus may be candidate alloying elements for high temperature titanium alloys.

![Figure 7. Interaction between alloying elements with vacancy in titanium alloys, negative value here means attractive [20].](image)

4. Concluding remarks

The point defect concentration and degree of LRO in gamma TiAl for various compositions as a function of temperature were obtained using a proposed self-consistent procedure based on the first principle calculation and statistical mechanics; the solute-solute and solute-vacancy interaction in Ti alloys and site occupation in intermetallic compounds investigated have greatly improved our understanding of the mechanism underlying the SRO strengthening and creep behavior in titanium alloys; it is demonstrated that the first principles materials computation is becoming an important tool for guiding alloying element selection and design of heat treatment schemes of new titanium based materials, there is still much to be done.

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