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Rare earth elements in α-Ti: A first-principles investigation

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ABSTRACT

The interaction energies between substitutional rare earth (RE) atoms, between RE and interstitial C, N, O, H atoms, as well as between RE and vacancies in α-Ti are calculated via first-principles density-functional theory with projector augmented-wave (PAW) pseudopotentials. The results show that the RE–vacancy and RE–RE interactions are attractive due to the weaker RE–Ti bond than the host Ti–Ti bond. All of the RE atoms investigated in this paper are repulsive to C and N, but attractive to H. RE–O interactions are repulsive for the light RE atoms, though the interactions are very weak for the heavy RE atoms. The mechanism underlying the interactions and their possible influence on the properties of Ti alloys are discussed.

1. Introduction

Titanium alloys are increasingly used in aerospace and marine engineering, as well as medical devices, mainly due to their excellent specific strength and outstanding corrosion resistance [1]. However, the applications of titanium are restricted due to some inherent shortcomings, such as the drop of ductility at low temperatures and inadequate high temperature creep resistance. In order to obtain an appropriate combination of properties of Ti alloys, various alloying procedures have been adopted. A great deal of research [2–6] shows that fracture toughness, creep resistance, room temperature ductility and strength may be improved with the addition of rare earth (RE) elements. Bulanova et al. [7] have studied the Ti–5%Dy alloy and found that it possesses high plasticity compared with pure Ti. They suggested that such an alloy with addition of a RE metal can be taken as a basis for multi-component alloys with improved high temperature strength. It was believed that the beneficial effects of RE on the properties of titanium alloys are mainly ascribed to (a) the refined grain size; (b) the dispersion strengthening of the RE-rich phase in the form of fine particles; (c) the purified matrix since impurities such as interstitial O atoms can be 'scavenged' by RE so as to form RE oxide. However, the fundamental physics underlying these effects is still far from clear. It is well established that the phase segregation or ordering in an alloy is closely related to the interaction between the alloying atoms: an attractive interaction indicates phase segregation whereas a repulsive interaction leads to ordering [8]. Therefore, an investigation of the RE atoms in titanium will help us to understand the Ti–RE phase diagram and the formation of a RE-rich phase. To gain insight into the formation of the RE oxide also demands knowledge of the interaction between the RE and O atoms.

Besides the segregation of the RE-rich and the RE oxide phase, there remain some solid solution RE atoms in titanium. From the Ti–RE binary phase diagrams it can be seen that for most of RE their equilibrium solubilities are quite low [9]. But technically increasing the solubilities is still possible. Rapid solidification treatment has shown the capability of increasing the concentration of the solid solution RE [10]. The creep resistance relates closely to the diffusion of the RE atoms and, therefore, may depend on the behavior of the RE–vacancy pair. Hu et al. [11] have calculated the interaction energy between vacancies and 3*d*/4*d* transition

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metal as well as some simple metal alloying atoms in α-Ti. By examining the calculated interaction energies and experimental creep resistance of the alloys, they found that alloying elements attracting vacancies generally improve the creep resistance but those repelling vacancies do not. In this regard, it is interesting to study the RE–vacancy interaction in titanium alloys.

The purpose of the present work is to investigate the interaction between RE and vacancies, between RE and RE, as well as between RE and interstitial atoms such as O, C, N, and H. The method adopted is a first-principles plane-wave pseudopotential method based on density-functional theory. The alloying effects of RE elements on the properties of Ti alloys are discussed. Most of the lanthanide elements, except for Tm, Yb and Lu, are investigated in this work. This paper is arranged as follows. In Section 2 we describe the calculation details. The results of the calculations are presented and discussed in Section 3. We summarize our main conclusions in Section 4.

2. Methodology

The first-principles calculations are performed by the use of the plane-wave pseudopotential method implemented in VASP [12,13]. In order to describe the RE elements accurately, we adopt projector augmented-wave pseudopotentials (PAW) [14,15] as supplied with VASP. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation is used to the electronic exchange-correlation functional [16]. Gao et al. [17] have carefully investigated the reliability of the PAW RE pseudopotentials, and according to their discussion, we ignore the effects of spin polarization and magnetization in our system. There are three kinds of PAW potentials available for RE metals: standard, soft, and divalent or trivalent versions, which treat the 4*f* electrons in different ways: the standard and soft versions treat the entire set of *f* levels as valence orbitals (the difference between the two versions is that the semi-core *s* states are treated as valence states only in the standard potentials); the divalent or trivalent version keeps some 4*f* electrons frozen in the core and treats the rest of 4*f* electrons as valence ones. There are only standard and soft versions for La because it has no occupied *f* levels in its elemental state and there is only a trivalent version of potential available for Tb, Dy, Ho and Er with VASP. For consistency and comparability the trivalent or divalent version potentials are used in our calculations for all RE elements except for La, for which a standard version is used.

The supercell of α-Ti we used here contains 54 atoms, i.e., a $3 \times 3 \times 3$ hexagonal close packed (hcp) unit cell. The *k*-point mesh and plane-wave cut-off energy are carefully tested. Finally, we choose $5 \times 5 \times 4$ for the *k*-point mesh and 500 eV for the cut-off energy so as to make sure that the energy converges to an accuracy of a few meV per atom. All structural parameters (both lattice parameters and atomic coordinates) are fully relaxed.

According to the definition given in the Refs. [18–21], the interaction energy between two point defects is calculated as the energy difference between two lattice configurations: one includes two defects interacting with each other, and in the other configuration these two defects have an infinite distance in between and, therefore, do not interact with each other. The energy of the second configuration cannot be calculated directly with the supercell method due to the limited supercell size. However, we may equally express the energy difference as follows:

$$\Delta E = E[N, I_1, I_2] + E[N] - E[N, I_1] - E[N, I_2] \quad (1)$$

with N denoting the number of the lattice sites in the supercell. I represents a point defect, i.e. a vacancy, a substitutional atom or an interstitial. $E[N, I_1, I_2]$ is the total energy of the system with two point defects interacting with each other. $E[N]$ is the energy of the supercell without defect. $E[N, I_1]$ is the energy of the supercell containing only one I_1 defect, and $E[N, I_2]$ has a similar meaning. A positive ΔE means these two point defects repel each other, while a negative value means that they are attractive mutually. Since we are interested in the energy differences, all the total energies of the four configurations are calculated with identical setups in order to minimize the systematical error. As shown in Refs. [8,22], usually the nearest neighbor interaction dominates. Therefore in the present work, only the interactions between two nearest neighboring point defects are taken into account.

3. Results and discussion

3.1. Atomic volume of pure RE metals

In order to get an idea of the reliability of the RE PAW pseudopotential, we first calculate the lattice parameters of the pure RE metals. The RE metals are calculated for their low-temperature stable states [17,23]: dhcp structure for early RE metals La, Pr, Nd, and Pm, fcc for Ce, hcp for Gd, Tb, Dy, Ho, Er, Tm, Lu and Yb, and bcc for Eu. Fig. 1 compares the predicted atomic volumes to the experimental values [23].

The calculated atomic volumes agree well with the experimental values (except for Ce) as well as the theoretical results by Gao et al. from VASP calculations [17]. The predicted values are slightly larger than experimental values for early RE metals, but smaller for most of the late ones. The calculated volumes of Eu and Yb are respectively about 11% and 5% smaller than the corresponding experimental values. However, the discrepancy is acceptable, and the trend of the volume with respect to the atomic number is reasonable. The decreasing atomic volume with increasing atomic number (mostly for trivalent RE metals except Ce), the so called "lanthanide contraction", is well reproduced. The abnormally large atomic volume of Eu/Yb compared to those of other REs is due to their half/fully occupied 4*f* orbitals. Such an electronic configuration is of low-energy and very stable. Therefore, the interaction between the Eu/Yb atoms is quite weak since the interaction will disturb these stable electronic configurations through charge transfer or chemical bonding [17].

The trivalent PAW potentials for Ce used in the present work seem unable to reflect its real inner electronic structure correctly, in agreement with the result of Gao et al. [17]. If the standard Ce PAW potential is used, the anomalous volume collapse can be correctly predicted (25.69 Å^3), but drops too far from the experimental value (28.52 Å^3). As suggested in Ref. [24], the special characteristic of Ce may be attributed to its fractional valence.

3.2. RE–vacancy interactions

There are two configurations for a supercell containing a nearest neighbor RE atom and a vacancy: one with a substitutional

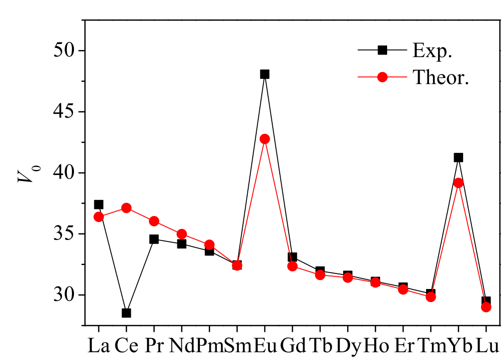

Fig. 1. Theoretical atomic volume of RE metals in comparison with experimental values (unit: Å^3/atom).