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Interactions between interstitial oxygen and substitutional niobium atoms in Ti–Nb–O BCC alloys: First-principles calculations

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ABSTRACT
In this paper, the interactions between interstitial oxygen atoms and substitutional atoms in Ti–Nb–O alloys were investigated by first-principles calculations based on the density functional theory. The binding energies and formation energies of oxygen atoms sited were calculated in various interstices with different geometries, element species, and atomic arrangements. The calculation results showed that there was a strong repulsive binding energy between the interstitial oxygen and the substitutional niobium atoms. On this basis, the energetically favored sites and the distribution of interstitial oxygen atoms in Ti–Nb–O alloys were discussed and demonstrated by an electron energy loss spectroscopy method. Furthermore, the diffusion activation energies of interstitial oxygen atoms based on the formation energy results were presented, and the diffusion behaviors of interstitial oxygen atoms in Ti–Nb–O alloys were also discussed.

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I. INTRODUCTION
The interaction of interstitial atoms with substitutional atoms is indispensable information for understanding many basic physical performances and applications of solid solutions. A typical example is the development of the so-called Snoek-type high-damping ternary alloys (such as Ti–Nb–O, Nb–V–O, etc.). In these types of alloys, stress-induced redistribution of octahedral interstitial atoms can cause Snoek relaxation in body-centered-cubic (BCC) metals, that is, an interstitial atom moves from one octahedral site (O₁) to its adjacent octahedral site (O₂) via a tetrahedral site (T₁) between them during the relaxation process, as shown in Fig. 1. That is why these alloys usually exhibit high-damping performance. Since Snoek found this relaxation effect of carbon in α-Fe, many similar phenomena have been observed in binary and ternary BCC alloys, and various mechanisms have been put forward to explain the related experiment results. However, the deduced relaxation parameters, such as peak temperature and relaxation activation energy, exhibit qualitative consistency but quantitative disagreement. Notably, even very few numbers of interstitial atoms can have drastic influences on the relaxation process. Hence, it is essential to investigate the basic physical properties of interstitial atoms, including their interactions with substitutional atoms, their energy situations, and their diffusion activation energies in these alloy systems.

By now, some research on interatomic potentials has been carried out by different methods. Yu et al. calculated the interstitial–interstitial interaction in a ternary BCC system by a Fermi–Dirac statistics method, and the results showed that the repulsive O–O interaction effect was markedly influenced by the substitutional solute concentration. Ruda et al. described the formulation of carbon–metal interatomic potential by the embedded atom method (EAM), but it was proved that the EAM was just a good framework for the description of interstitial impurities rather than the best choice for the calculation of interatomic potential.

More recently, the first-principles density functional theory (DFT) method proved to be a powerful method to deal with these
important problems using the Vienna ab initio simulation package (VASP) 24,25. Domain and Becquart et al. 26,27 tried to find the energetically favored sites in the crystal lattices and compared the interactions of special pairwise atoms. Zhu and Wang et al. 28 studied the interaction between substitutional alloying atoms and interstitial oxygen in a Nb-based alloy. Olsson et al. 29 derived the interactions of Cr atoms with point defects in a complex ternary BCC Fe alloy. In addition, Sandberg et al. 30 explored the carbon impurity dissolution and migration in this system. Especially for titanium-based alloys, Boureau and Capron et al. 31 investigated the solutions of oxygen in titanium. Niu and Ping et al. 32 evaluated the quantitative suppression effect of O on the β to α transformation in Ti3NB. These investigations indicate that ab initio calculation based on the DFT is a more appropriate tool to evaluate fine interactions and can interpret the fundamental phenomena better at an atomistic level. Despite this, no consensus has been reached about some key points. For example, the Snoek relaxation parameters derived by different methods are not consistent or even contradictory, and there is no unified understanding of the Snoek relaxation mechanism, especially in the ternary system.

The main purpose of this paper is to clarify the behaviors of interstitial oxygen atoms interacting with substitutional atoms in ternary Ti–Nb–O alloys in detail through calculating binding energies, formation energies, and diffusion activation energies by first-principles calculations based on DFT. The binding energies are used to analyze the possible effects of interstitial oxygen atoms on intrinsic substitutional point defects in Ti–Nb–O alloys. The formation energies of different configurations are discussed to evaluate the difficulty of configuration formations and then determine the energetically favored sites in Ti–Nb–O alloys. The diffusion activation energy can reveal the effects of the distribution of substitutional niobium atoms on saddle points during the diffusion process of interstitial oxygen atoms, which provides helpful information for describing and understanding the diffusion behaviors of interstitial atoms in Ti–Nb–O alloys.

II. COMPUTATIONAL DETAILS AND METHODS

The calculations based on the DFT method have mostly been performed by using the VASP. The exchange and correlation functionals were described in the scheme of the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE), 33 and ultrasoft pseudopotentials (USPPs) 34 were chosen to describe the electron–ion interaction. A plane–wave basis set with an energy cutoff of 260 eV was employed. The valence electronic configurations for niobium, titanium, and oxygen atoms are 4d5s2, 3d24s2, and 2s2p4, respectively. A 4 × 4 × 4 β-Ti supercell of optimized lattice parameters and optimized oxygen positions was adopted, and the Brillouin zone was sampled using a 3 × 3 × 3 k-point grid. The calculated lattice parameters for β-Ti are \(a = b = c = 3.26 \text{ Å}\). For all geometry and oxygen position optimizations, all the internal coordinates were relaxed until the Hellmann–Feynman forces were less than 0.01 eV/Å.

The binding energy \(E_{\text{bind}}(S, I)\) between substitutional atoms (S, i.e., Nb atoms in Ti–Nb–O alloys) and interstitial atoms (I, i.e., O atoms in Ti–Nb–O alloys) is defined as the system energy of an S–I cluster at a certain distance, which is the first nearest neighbor, the second nearest neighbor, and so on, relative to the system energy without the interaction between S and I. 29,30 It is almost impossible to make sure that S and I do not interact with each other even if they are as far as possible in the scope of the supercell. 27 In that case, the binding energy is calculated as

\[
E_{\text{bind}}(S, I) = E_{\text{tot}}^{\text{S}}(I) + E_{\text{tot}}^{\text{S}}(S) - [E_{\text{tot}}(S, I) + E_{\text{ref}}],
\]

where \(x\) is the position of the interstitial oxygen atom, \(E_{\text{ref}}^{\text{S}}\) is the energy of the supercell without S and I atoms, \(E_{\text{tot}}^{\text{S}}(S)\) [respectively, \(E_{\text{tot}}^{\text{S}}(I)\)] is the energy of the supercell only with S [respectively, I], and \(E_{\text{ref}}^{\text{S}}(S, I)\) is the energy of the supercell with both S and I. All the supercells presented in this paper contain the same number of lattice points and have the same size. According to Eq. (1), the reference state of the binding energy is the energy of a perfect supercell without any defects. Thus, a positive binding energy indicates an attractive interaction between S and I atoms, whereas a negative one indicates a repulsive interaction.

For an interstitial atom sitting at position \(x\) of a BCC supercell, the formation energy \(E_{\text{form}}\) for a configuration containing N atoms with \(n\) matrix atoms (M), \(k\) substitutional atoms (S), and an interstitial atom (I) is defined as

\[
E_{\text{form}}^{\text{S}}(M_n, S_k, I) = E_{\text{tot}}^{\text{S}}(M_n, S_k, I) - nE(M) - kE(S) - EM_{\text{isolated}},
\]

where \(E_{\text{form}}^{\text{S}}(M_n, S_k, I)\) is the total energy of the configuration, \(E(M)\) [respectively, \(E(S)\)] is the energy per atom of the M(S) supercell with the same size, and \(EM_{\text{isolated}}\) is the energy of a single interstitial atom alone in the same supercell. Therefore, the formation energy is calculated by taking an isolated atom rather than the stable state of interstitial atoms as the reference in order to evaluate the difficulty of configuration.

Under a given condition (e.g., pressure), interstitial oxygen may diffuse from site x to site y through certain mechanisms, e.g., the so-called Snoek relaxation process. The activation energy in this process can be expressed as

\[
E_{\text{diff}}(x-y) = E_{\text{barrier}} - E_{\text{form}}^{\text{S}},
\]
where $E_{\text{barrier}}^{x-y}$ is the energy barrier of an interstitial oxygen atom moving from site $x$ to site $y$, and $E_{\text{for}}^x$ is the energy of the initial position. The diffusion barriers of two stable states $E_{\text{barrier}}^{x-y}$ are obtained from nudged-elastic band (NEB) calculations.\textsuperscript{35}

The distributions of the substitutional niobium and interstitial oxygen atoms are detected by electron energy loss spectroscopy (EELS) using a 200-kV transmission electron microscope in the Ti–25Nb–1.5O at. % alloy.

III. RESULTS AND DISCUSSIONS

Six nearest lattice sites can be replaced by substitutional atoms in the BCC octahedral structure. Therefore, different configurations $\delta^{u-v}$ can be distinguished by the number and arrangement of substitutional sites ($u$ is the number of substitutional atoms from 0 to 6, and $v$ represents the different configurations of substitutional atoms). Some configurations shown in Fig. 2 are examples of $u = 0$, 1, 2, and 5. In the following part, the behaviors of interstitial oxygen atoms in octahedral configurations of Ti–Nb–O alloys will be presented in detail.

A. Binding energy

Figure 2 shows the binding energies in different configurations with various numbers of niobium atoms in Ti–Nb–O alloys. As mentioned, the interstitial oxygen sites include the octahedral sites (O$_1$ and O$_2$) and the tetrahedral site (T$_1$) (as given in the schematic diagram in Fig. 1). Obviously, not all the sites are in the stable states. The calculated binding energies (as shown in Fig. 2) between oxygen

![Diagram showing binding energies and formation energies of different configurations (O$_1$, O$_2$, and T$_1$) with various numbers of niobium atoms in Ti–Nb–O alloys. The different configurations $\delta^{u-v}$ can be distinguished by the number and arrangement of substitutional atoms, where $u$ (u = 0, 1, 2, and 5) is the number of substitutional atoms, and $v$ represents the various distributions of substitutional niobium atoms. The black, red, and gray balls in the configuration sketch images represent interstitial oxygen atoms, niobium atoms, and titanium atoms, respectively.](image-url)
and niobium atoms in Ti–Nb–O alloys are all negative, indicating repulsive interactions. Such interactions may prevent the oxygen atom from sitting around niobium atoms. These results reflect the intrinsic property of oxygen and niobium, which may affect the position of interstitial oxygen atoms in the lattice of Ti–Nb–O alloys.

Figure 3 presents binding energies of $O_1$, $O_2$, and $T_1$ configurations with various numbers of niobium atoms, according to Fig. 2. The higher binding energies of configurations $O_1$ and $O_2$ of $\delta^{2-3}$ and $\delta^{5-1}$ reveal that the binding energies increase drastically with the increase in the number of substitutional atoms. Especially, when substitutional niobium atoms have a better symmetry around interstitial oxygen atoms (e.g., $O_2$ of $\delta^{2-1}$ and $\delta^{5-3}$), the interstitial atoms will suffer stronger repulsive interactions and cannot stay there stably. Hence, much weaker binding energies in $O_1$ and $O_2$ of $\delta^{1-1}$ indicate that the configurations with one substitutional niobium atom are more stable than other configurations in Ti–Nb–O alloys. This may be the reason that many Snoek-type main damping peaks are generated by the interaction between the interstitial atom and a single substitutional atom. \cite{7,15} In addition, Fig. 3 shows that the binding energies of $T_1$ configurations are higher than those of $O_1$ configurations in all cases. It demonstrates that the niobium substitutional atoms in the tetrahedral configurations have stronger influences on the interstitial atoms than those in the octahedral configurations. This result may imply that the tetrahedral interstitials are less stable than the octahedral ones.

In brief, the binding energy describes the essential interactions between the interstitials and substitutions. These interactions may affect the formation of some clusters, e.g., tetrahedral, octahedral, and so on, which may influence the distribution and diffusion behaviors of the interstitial atoms.\cite{3}

### B. Formation energy

According to the definition in Eq. (2), the level of difficulty to form different configurations can be evaluated based on the
formation energy. Moreover, the formation energy has closer relations with the diffusion activation energy. Therefore, it is helpful to make some detailed investigation to illustrate the diffusion behaviors of interstitial atoms during the relaxation process (Subsection III C).

The formation energies of different configurations in Ti–Nb–O alloys are also provided in Fig. 2. In general, the repulsive interaction can baffle the formation of all configurations. First, for configurations with the same number of substitutional niobium atoms, the stronger the repulsive interaction, the higher the formation energy.

**FIG. 5.** The diffusion energy barrier pathway diagrams of different configurations: (a) δ²⁻¹, (b) δ¹⁻¹, (c) δ²⁻¹, (d) δ²⁻², (e) δ³⁻⁰, and (f) δ⁵⁻¹. O₁, O₂, and T₁ are shown with the energy barriers between the initial and final states.
and vice versa. Consequently, tetrahedral sites of a given configuration have much higher formation energy than octahedral sites (e.g., \(O_1\) and \(T_1\) of \(\delta^{1-1}\) and \(\delta^{1}\)). Second, for configurations with different numbers of substitutional niobium atoms, a lower symmetry results in a lower difficulty level of configuration formation (e.g., \(O_1\) and \(O_2\) of \(\delta^{1-1}\) and \(\delta^{1-2}\)). This implies that the formation of \(O_1\) and \(O_2\) of \(\delta^{1-2}\) is much easier than that of other configurations. Third, due to the quite high binding energy, it is more difficult to form configurations with more substitutional atoms (e.g., \(O_1\) and \(O_2\) of \(\delta^{1-2}\)) than those with less substitutional atoms.

Another important concern is the distribution of interstitial oxygen and substitutional niobium atoms in Ti–Nb–O systems. Due to the repulsive interaction of niobium atoms with interstitial oxygen atoms, the distribution of niobium atoms has drastic influences on the distribution of oxygen atoms. By comparing the formation energies of \(O_1\) and \(T_1\) in various configurations, the octahedral configurations are more likely to be the energetically favored sites among the interstitial positions, and this is because the octahedral configurations have a slighter repulsive binding energy and lower formation energy than the tetrahedral ones. According to the formation energies of \(O_1\) and \(O_2\) in various configurations, when the oxygen atoms are located at the \(O_2\) interstitial positions, the configurations have much stronger binding energies and higher formation energies than when the oxygen atoms are at the \(O_1\) interstitial positions. Hence, a weaker repulsive interaction and a lower formation energy are appropriate for the interstitial oxygen atoms in the \(O_1\) configuration. In fact, the distribution of interstitial and substitutional atoms in these ternary systems has been deemed as a highly disputed physical topic for a long time. Ruda explored the interatomic potentials for carbon interstitials in BCC Fe and considered the tetrahedral sites as the energetically favored ones, but there was a discrepancy between potentials and experiments. Therefore, Bécquart and Domain argued that Ruda’s viewpoint was in contradiction with what was commonly accepted or recognized. Here, the calculation results of formation energies can be used to discuss and clarify where the energetically favored sites are.

Due to the regularity of formation energy and the ubiquity of repulsive interaction between the interstitial oxygen and substitutional niobium atoms in Ti–Nb–O alloys, the niobium atoms tend to repel the interstitial oxygen atoms away so that the oxygen atoms may be rich at the niobium atom depleted area. Figure 4 exhibits the distribution of niobium and oxygen atoms in the Ti–25Nb–1.5O (at.%) alloy by EELS. As can be seen, the oxygen atoms tend to aggregate at the bright area of the zero-loss image, while the niobium atoms aggregate at the dark area. The EELS results shown in Fig. 4 demonstrate that the contrary distributions of the substitutional niobium and interstitial oxygen atoms agree well with the calculation results of binding energy and formation energy.

C. Diffusion energy barrier of interstitial oxygen atoms

Many important phenomena in materials science involve the diffusion of interstitial atoms. In this subsection, some details about saddle points and the influences of the diffusion path on the energy barrier are analyzed.

Figure 5 shows the diffusion energy barriers of different configurations. As can be seen, saddle points are not precisely at the tetrahedral sites, and position discrepancies are prominent. Traditionally, however, an oxygen atom moves from one octahedral to its neighbor octahedral via a tetrahedral site during the diffusion process, which is assumed as the saddle point between two octahedral sites. Figure 5(a) presents the diffusion path of the interstitial oxygen atom in pure BCC \(\beta\)-Ti. The obvious difference relative to other configurations indicates that the tetrahedral position without substitutional atoms is a metastable state. The calculated diffusion energy barrier is 2.30 eV, which is consistent with the values in some experiments (1.35–2.99 eV). Figures 5(b)–5(f) exhibit the energy barrier sites between \(O_1\) and \(O_2\) with different configurations. In some works, \(\delta^{1-2}\) tetrahedral sites are considered as the saddle points. However, as Fig. 5 shows, the saddle points shift toward the right side of tetrahedral sites to various degrees (e.g., \(\delta^{1-3}\), \(\delta^{2-1}\), and \(\delta^{2}\)), and the configurations \(\delta^{1-3}\) does not even have an energy barrier. This indicates that in different configurations, asymmetrical distributions of substitutional atoms can influence the saddle points. According to the formation energies of stable states and saddle states, it is obvious that both the number and the distribution of substitutional atoms have notable influences on the diffusion activation energy.

It should be noted that the energy barriers of the diffusion and inverse diffusion process for the interstitial atoms between two stable states \(O_2\) and \(O_2\) may be different. Taking \(O_1\) and \(O_2\) of the configuration \(\delta^{1-1}\) as an example, the energy barrier differences for the configuration with the same number and distribution of substitutional atoms are just the differences between these two stable states. Hence, the probability of the diffusion from \(O_2\) to \(O_2\) is not equal to that from \(O_1\) to \(O_2\). That is to say, under given conditions, an interstitial atom can migrate from \(O_2\) to \(O_2\), but cannot migrate back under the same thermal equilibrium condition. This diffusion behavior may influence some performances of the alloys. For example, the irreversible diffusion processes of the interstitial atoms may prevent the Snoek relaxation effect and reduce the damping performance of the so-called Snoek-type high-damping alloys. Other similar configurations may also influence the damping performance of these kinds of damping alloys during their service life.

IV. CONCLUSIONS

In summary, the interactions between interstitial oxygen atoms and substitutional atoms in Ti–Nb–O alloys were investigated by first-principles calculations based on the density functional theory, and conclusions can be drawn as follows:

1. There exists repulsive interaction between the interstitial oxygen atoms and the substitutional niobium atoms in BCC Ti–Nb–O alloys. As the number of substitutional atoms increases, the binding energies increase drastically.

2. The repulsive interaction can baffle the formation of configurations and result in higher formation energies. For configurations with the same number of substitutional niobium atoms, the stronger the repulsive interaction, the higher the formation energy, and vice versa.

3. During the diffusion process of the interstitial atoms, the saddle points are not precisely located at the tetrahedral sites. Both the number and the distribution of substitutional atoms have significant influences on the diffusion activation energy.
energies. In some special cases, the diffusion process may be irreversible.

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