

First-Principles Investigation of β -Titanium Doping with Trace Transition Metal Elements

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Abstract. The lattice parameters, formation enthalpy, and electronic structures of β -Ti doping with trace transition metal element X (X=Cr, In, Mo, Nb, Pd, Rh, Ru, Sc, Tc, and Y) were systematically calculated by first-principles simulations to explore the effect of these metal elements on the stability of β -Ti at 0 K. Based on our calculations, a satisfactory linear function is found between atomic radius of dopant X and corresponding volume difference. The formation enthalpy results show that the addition of trace transition metal X plays a positive role in the thermodynamical stability of β -Ti at 0 K. This intriguing behavior is well explained by the density of state (DOS).

1. Introduction

Due to titanium and its alloys possessing good strength-to-weight ratio, high heat resistance, and outstanding biocompatibility, they are widely used in numerous engineering fields, especially biomedicine applications.^{1,2} However, on the one hand, traditional α type and $\alpha+\beta$ type titanium alloys have a higher elastic modulus, which can result in stress shielding effect; On the other hand, they also contain elements such as Al and V, which may take poisonous effect on biological cells.³ Therefore, development of non-toxic and low-modulus β -Ti alloy has become a hot and attractive research topic in recent years.

Many traditional experiments have been done and showed that the stability of β -Ti alloy is closely related to the type and content of alloying element.³⁻⁶ So, in order to improve properties of β -Ti alloy, a better understanding of the influence mechanism of alloying element on β -Ti alloy is crucial. However, the influence mechanism is difficult to be obtained by the traditional experiments. Thus, some scholars attempt to investigate the influence mechanism by theoretical calculations.²

In this work, first-principles simulations are performed to systematically investigate the β -Ti doping with trace transition metal elements X (X=Cr, In, Mo, Nb, Pd, Rh, Ru, Sc, Tc, and Y) with a chemical formula of $\text{Ti}_{0.98}\text{X}_{0.02}$. The equilibrium volume and formation enthalpy are firstly calculated to study the effect of dopant X on the structure and thermodynamic properties of β -Ti. Secondly, the total density of states (TDOS) and the partial density of states (PDOS) of $\text{Ti}_{0.98}\text{X}_{0.02}$ systems are investigated to explore the structural stability mechanism from the electronic level.

2. First-Principles Methods

Vienna Ab-Initio Simulation Package (VASP) is used to conduct all first-principles calculations.⁷



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The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional is used to calculate the exchange-correction energy of electron.⁸ The ion-electron interaction is described by the projector augmented wave (PAW) approach. For consistency, the electronic wave functions are expanded in a plane-wave basis with a cutoff energy of 500 eV for all calculations, which is roughly 1.3 times higher than the default value. The pseudopotentials describe the valence states of metal elements are as follows: Ti($3p^6 3d^2 4s^2$), Cr($3d^5 4s^1$), In($5s^2 5p^1$), Mo($4s^2 4p^6 4d^5 5s^1$), Nb($4s^2 4p^6 4d^4 5s^1$), Pd($4d^8 5p^2$), Rh($4d^7 5s^2$), Ru($4s^2 4p^6 4d^6 5s^2$), Sc($3d^1 4s^2$), Tc($4s^2 4p^6 4d^5 5s^2$), Y($4s^2 4p^6 4d^1 5s^2$), respectively. The Methfessel-Paxton method with smearing width of 0.05 is applied to relax structure and atom positions of $Ti_{0.98}X_{0.02}$ system, while tetrahedron method with Blöchl correction is used to get accurate energy and stress during the static calculations. To ensure a good precision in the calculation, the energy convergence criterion of the electronic self-consistency is set to 10^{-6} eV per atom, and the force convergence criterion is 10^{-2} eV/Å per atom. Spin-orbit coupling is included in all simulations, as implemented within the PAW method in the VASP code.

To research the effect of transition metal element on physical and chemical properties of β -Ti, we construct the a series of supercells (containing 27 Ti unit cells) with one of the titanium atoms substituted by a metal element X atom (X=Cr, In, Mo, Nb, Pd, Rh, Ru, Sc, Tc, and Y), shown in figure 1. The Brillouin zone is sampled by a $3 \times 3 \times 3$ Monkhorst-Pack **k**-point grid for $Ti_{0.98}X_{0.02}$ systems and by a $15 \times 15 \times 15$ Monkhorst-Pack **k**-point grid for pure Ti and X cell, respectively.

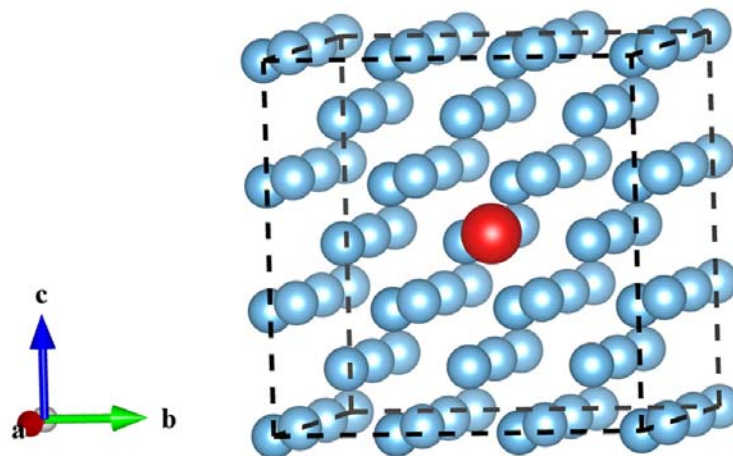


Figure 1. The atomic structure diagram of $Ti_{0.98}X_{0.02}$. The red ball represents the metal X atom and the rest blue balls represent Ti atoms.

3. Results and Discussions

3.1. Structural Optimization

The lattice parameter of pure β -Ti calculated from first-principles simulation is 3.252 Å, which is similar to experimental value of 3.283 Å with an absolute deviation of 0.9%.⁹ Hence, we have reason to consider that the zero-pressure geometry optimization method in this study is reliable. Using the same method, the equilibrium lattice parameters of $Ti_{0.98}X_{0.02}$ systems are obtained and summarized in table 1. It can be found that $Ti_{0.98}X_{0.02}$ systems are still bcc structures after β -Ti is doped with a low concentration of X. What's more, it is obvious that different metal elements have different effects on the equilibrium volume of β -Ti. This intriguing behavior can be explained from atomic radius. As shown in figure 2, the relationship between atomic radius of X and volume change can be fitted satisfactorily to a linear function with an R^2 value of 0.95,

$$y = 42.6x - 58.1 \quad (1)$$

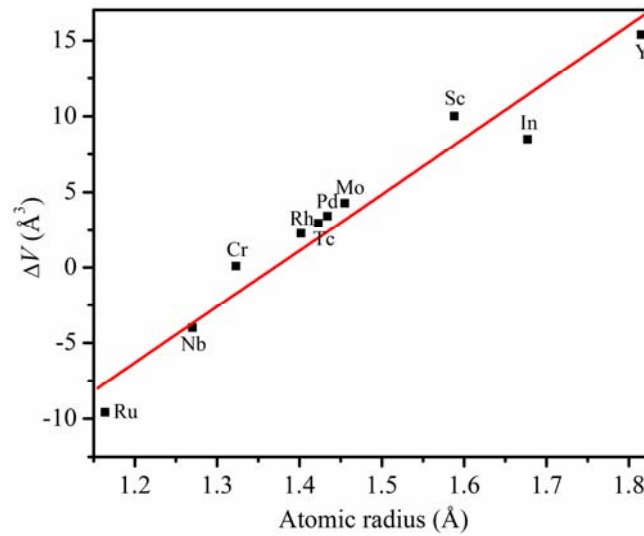


Figure 2. Effect of atomic radius of dopants X on the volume change.

Table 1. The DFT calculated lattice parameters (a , b , and c), equilibrium volume (V_0), volume change (ΔV), zero-point energy (ΔZPE), and formation enthalpy (ΔH_f) of $\text{Ti}_{0.98}\text{X}_{0.02}$ systems.

System	a (Å)	b (Å)	c (Å)	V_0 (Å ³)	ΔZPE (kJ/mol)	ΔH_f (kJ/mol)
$\text{Ti}_{0.98}\text{Cr}_{0.02}$	9.751	9.750	9.750	926.95	1.44	-8.99 -9.77 ^a
$\text{Ti}_{0.98}\text{In}_{0.02}$	9.781	9.779	9.779	935.35	1.49	-5.32
$\text{Ti}_{0.98}\text{Mo}_{0.02}$	9.736	9.736	9.736	922.88	1.43	-10.36 -10.33 ^a
$\text{Ti}_{0.98}\text{Nb}_{0.02}$	9.731	9.739	9.739	922.97	1.34	-9.30 -10.95 ^a
$\text{Ti}_{0.98}\text{Pd}_{0.02}$	9.762	9.762	9.762	930.29	1.36	-9.77
$\text{Ti}_{0.98}\text{Rh}_{0.02}$	9.756	9.759	9.759	929.14	1.24	-11.20
$\text{Ti}_{0.98}\text{Ru}_{0.02}$	9.717	9.716	9.716	917.29	2.75	-11.40
$\text{Ti}_{0.98}\text{Sc}_{0.02}$	9.783	9.786	9.786	936.88	1.85	-8.02
$\text{Ti}_{0.98}\text{Tc}_{0.02}$	9.759	9.761	9.761	929.81	2.42	-9.82
$\text{Ti}_{0.98}\text{Y}_{0.02}$	9.801	9.805	9.805	942.25	1.86	-8.56

^a Zou et al., first-principles calculation with PAW-GGA-PBE.²

3.2. Thermodynamic Property of $\text{Ti}_{0.98}\text{X}_{0.02}$ System

After the $\text{Ti}_{0.98}\text{X}_{0.02}$ systems and pure transition metal (Ti, Cr, In, Mo, Nb, Pd, Rh, Ru, Sc, Tc, and Y) cells are successfully optimized, the ground state total energies of these systems are obtained by static calculations. The formation enthalpy of $\text{Ti}_{0.98}\text{X}_{0.02}$ can be obtained from these total energies. In this study, to make simulation results more reliable compared with experimental results, the zero-point energy correction is added to the formation enthalpy, defined as follows,¹⁰

$$\Delta H_f(\text{Ti}_{0.98}\text{X}_{0.02}) = E_{\text{total}}(\text{Ti}_{0.98}\text{X}_{0.02}) - 0.98E(\text{Ti}) - 0.02E(\text{X}) - \Delta ZPE \quad (2)$$

where $E_{\text{total}}(\text{Ti}_{0.98}\text{X}_{0.02})$ is the total energy per atoms of $\text{Ti}_{0.98}\text{X}_{0.02}$ system, $E(\text{Ti})$ and $E(\text{X})$ are the energy per atom of Ti and transition metal X in their ground states, ΔZPE is the zero-point energy correction originated from lattice vibration.

The formation enthalpy of $\text{Ti}_{0.98}\text{X}_{0.02}$ system is calculated and listed in table 1. Previous DFT simulating results are also introduced in table 1 for comparison to verify the accuracy of present

calculations. We can find that the formation enthalpy values of $\text{Ti}_{0.98}\text{Cr}_{0.02}$, $\text{Ti}_{0.98}\text{Mo}_{0.02}$ and $\text{Ti}_{0.98}\text{Nb}_{0.02}$ are -8.99, -10.36 and -9.30 kJ/mol, respectively. These values are in good agreement with previously reported values of -9.77 kJ/mol for $\text{Ti}_{0.95}\text{Cr}_{0.05}$, -10.33 kJ/mol for $\text{Ti}_{0.95}\text{Mo}_{0.05}$ and -10.95 kJ/mol for $\text{Ti}_{0.95}\text{Nb}_{0.05}$.² Thus, it can be concluded that the method of our formation enthalpy is reasonable.

Based on the known reports, the formation enthalpy can be used to preliminarily judge the thermodynamic stability of structure.¹¹ From the table 1, it can be found that the formation enthalpy of $\text{Ti}_{0.98}\text{X}_{0.02}$ system is slightly less than 0, about -10 kJ/mol. The negative formation enthalpy indicates that formation of $\text{Ti}_{0.98}\text{X}_{0.02}$ from pure titanium and X is exothermic, that is to say, adding a small amount of transition metal X tends to enhance the thermodynamic stability of β -Ti at 0 K. And the enhancement ability of these metallic elements X on the β -Ti is in the order of $\text{Ru} > \text{Rh} > \text{Mo} > \text{Tc} > \text{Pd} > \text{Nb} > \text{Cr} > \text{Y} > \text{Sc} > \text{In}$.

3.3. Electronic Structure of $\text{Ti}_{0.98}\text{X}_{0.02}$ System

The TDOS and PDOS of these systems are calculated to explore the strengthening mechanism of trace metallic element X on β -Ti from the electronic level. Figure 3 describes the TDOS of $\text{Ti}_{0.98}\text{X}_{0.02}$ systems and β -Ti and the corresponding site projected PDOS of Ti and transition metal X, respectively. Firstly, it is evident that the TDOS curves of $\text{Ti}_{0.98}\text{X}_{0.02}$ systems and β -Ti located in a range from -6 to 2.5 eV mainly originate from the contribution of Ti-d orbit. The results are in good agreement with Kuroda et al. proposed theory that the d electronic orbit plays an important role in mechanical properties and phase stability of β -Ti.¹² Secondly, the Fermi level marked by a vertical pink dash line is set to zero energy in figure 3. The left side of the Fermi level is the valance band and the right side of the Fermi level is the conduction band. Obviously, we find that the value at the Fermi level of β -Ti is about 60 and the values at the Fermi level of $\text{Ti}_{0.98}\text{X}_{0.02}$ systems are in the range from 15 to 30. The value at Fermi level is related to the phase stability, the lower value at Fermi level, the more structure stable. So, the greatly reduced the value at Fermi level indicates that all dopants X in this study help to strengthen the structural stability of β -Ti at 0 K. This can be attributed that the transition metal elements X can provide additional d-type electrons required to improve stability of β -Ti. From these discussions, we explain that the addition of trace transition metal X plays a positive role in the stability of β -Ti from the atomic and electronic level.

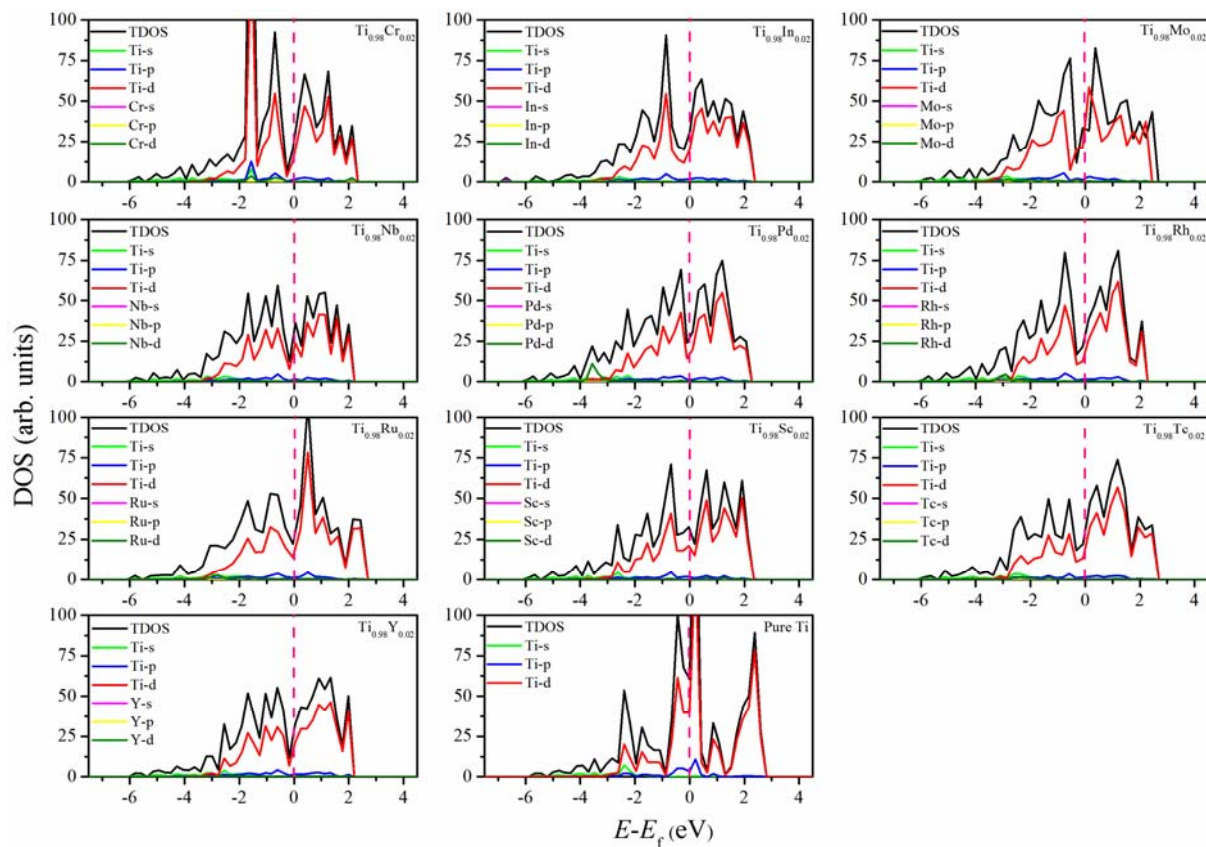


Figure 3. The calculated TDOS and PDOS of $\text{Ti}_{0.98}\text{X}_{0.02}$ systems and $\beta\text{-Ti}$. A vertical dotted line denotes the Fermi energy.

4. Conclusions

To improve our fundamental understanding of the effect of trace metallic elements on $\beta\text{-Ti}$, first-principles simulations are proposed to systematically investigate the lattice constant, formation enthalpy, electronic structure of $\text{Ti}_{0.98}\text{X}_{0.02}$ systems ($\text{X}=\text{Cr}, \text{In}, \text{Mo}, \text{Nb}, \text{Pd}, \text{Rh}, \text{Ru}, \text{Sc}, \text{Tc}$, and Y). We disclose a favorable linear function between the atomic radius and corresponding volumetric change. Furthermore, the negative formation enthalpy suggests that adding trace transition metal has a tendency to improve thermodynamic stability of $\beta\text{-Ti}$ in the ground state, which is well explained by the displacement of TDOS at the Fermi level.

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