Structure, elastic and bonding properties of hcp Zr$_x$Ti$_{1-x}$ binary alloy from first-principles calculations

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Abstract

First principles calculations were performed to study the structural, elastic, and bonding properties of hcp Zr$_x$Ti$_{1-x}$ binary alloy. The special quasi-random structure (SQS) method is employed to mimic the random hcp Zr$_x$Ti$_{1-x}$ alloy. It is found that Bulk modulus, B, Young's modulus, E, and shear modulus, G, exhibit decreasing trends as increasing the amount of Zr. A ductile behavior Zr$_x$Ti$_{1-x}$ is predicted in the whole composition range. In terms of Mulliken charge analyze, it is found that the element Ti behave much more electronegative than Zr in hcp Zr$_x$Ti$_{1-x}$ alloy, and the amount of charge transfer between them is approximately linear to the number of Ti(Zr) surrounding Zr(Ti).

Keywords: First principles, Elastic, Special quasi-random structures, Zirconium,
1. Introduction

Group IV transition metals including titanium (Ti), zirconium (Zr), and hafnium (Hf) and their alloys have attracted enormous research and technological interests due to their excellent properties such as high strength-to-weight, high rigidity-to-weight ratio, low thermal neutron absorption cross section and good corrosion resistance [1]. Their narrow d-band characterized as in the midst of a broad sp-band is the origin of scientific interest. And the pressure-induced electrons transfer from sp-band to d-band is the driving force behind the structural and electronic transitions. As a member of the group IV alloys, Zr-Ti alloys have wide applications in aerospace, medical, nuclear industries.

At ambient condition, pure zirconium and titanium both crystallizes in hexagonal close-packed (hcp) structure (α phase). For zirconium, experiments [2, 3] found that it undergoes a crystallographic phase transition from hcp(α phase) to another hexagonal structure (ω phase) at pressure of 2-7 GPa, and it will transform to the body-centered-cubic structure (β phase) at the pressure of 30-35 GPa. However, for Ti, the experimental phase transition order at room temperature is alpha omega gamma delta, its beta phase has not been found until 216 GPa [4]. For the ZrTi system, experimentally, it is characterized by full solubility of its components [5, 6]. As in pure zirconium and titanium, three phases (α, β and ω) are observed in the ZrTi system. At ambient condition, they crystallize in hexagonal close-packed (hcp) structure (α phase), and transforms to body-centered cubic (bcc) β phase under high temperature and a three atoms hexagonal structure (ω phase) under pressure. The aim of the present paper is to use first-principles calculations
to theoretically investigate the compositional dependence of the structural, elastic and bond properties of the Zr$_x$Ti$_{1-x}$ binary alloy system.

2. Methods

In present work, the first-principles DFT calculations are performed using the projector augmented wave (PAW) \cite{7} as implemented in the Vienna ab initio simulation package (VASP) \cite{8}. To describe the exchange-correlation potential, the Perdew-Burke-Ernzerhof (PBE) \cite{9} form of the generalized gradient approximation (GGA) is employed. The Zr 4d$^2$5s$^2$5p$^0$ and the Ti 4d$^2$5s$^2$5p$^0$ orbitals are treated as valance electrons. To get accurate results, the plane wave cut-off energy is chosen as 400 eV. The Brillouin-zone integrations are performed using $\gamma$-centered grids of kpoints of 25 $\times$ 25 $\times$ 25 for $\alpha$-Zr, 25 $\times$ 25 $\times$ 25 for $\alpha$-Ti, 15$\times$ 15 $\times$ 15 for Zr$_x$Ti$_{1-x}$ in terms of Monkhorst-Pack scheme \cite{10}. The geometries are optimized until the Hellmann-Feynman forces are less than 0.01 eV/Å, and the total energy is relaxed until the difference value becoming smaller than 10-5 eV.

Using the wavefunction obtained from the DFT calculation, the QUAMBO method \cite{11,12,13,14} was implemented to exactly down-fold the occupied states to a representation of a minimal-basis set without losing any electronic structure information. The constructed orbitals are atomiclike and highly localized, and they are adapted to perform the chemical bonding analysis to the interaction mechanism of Ti and Zr.

The concept of SQS was first proposed by Zunger et al. \cite{15} to mimic disordered (random) solution. There exists a one-to-one correspondence between a given structure and a set of correlation functions, which is the key
for SQS methods. In a substitutional binary alloy case, the correlation function $\prod_{k,l}$ for a figure (cluster) $f(k, l)$ with $k$ vertices and separated by an $l$th neighbor distance is defined as follows:

$$\prod_{k,l} = \frac{1}{N_{k,l}} \sum_{k,l} \sigma_1 \sigma_2 \cdots \sigma_k$$  \hspace{1cm} (1)

where $\sigma_k$ is a spinlike variable which takes the value of +1 or -1 depending on whether the atomic site is occupied by an $A$ or $B$ atom. Specially, for a random alloy of $A_{1-x}B_x$, Eq. (1) is simply by $(2x - 1)^k$. The optimum SQS for a given number of atoms is the one that best matches with the correlation function of the random alloy. In the present work, SQS models were generated using the Monte Carlo algorithm implemented by Walle et al.[16]. Their pair correction functions $\Pi_{2,l}$ (l up to the 11th nearest neighbor) are shown in Table 1. For Zr$_4$Ti$_{12}$, the $\Pi_{2,l}$ match the random ones well until $l$=6; and $l$=8 for Zr$_8$Ti$_8$. An example (Zr$_4$Ti$_{12}$) of SQSs generated in present work is given in Fig. 1.

In principle, the point group symmetry of the original alloy is broken by the SQS method. As a result, there will be 21 elastic constant elements for a SQS model [17]. Traditional, the energy-strain approach [18] and the stress-strain approach [19] are two ways of calculating single crystal elastic constants from first-principles calculations. In order to obtain 21 elastic constant with the energy-strain approach, we need to impose 21 independent deformation on the original structure. Extremely computing power is required. In order to calculate single crystal elastic constants from first-principles calculations, the stress-strain approach was adopted in the present work. A set of small strains $\varepsilon = (\varepsilon_1\varepsilon_2\varepsilon_3\varepsilon_4\varepsilon_5\varepsilon_6)$ (where $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ are the normal strains, $\varepsilon_4$, $\varepsilon_5$, and $\varepsilon_6$ are the shear strains in Voigt’s notation) is imposed on a crystal,
the deformed structure lattice vectors \( \overline{R} \) are obtained by transforming the original one \( R \) as follows:

\[
\overline{R} = R \begin{pmatrix}
1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\
\varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\
\varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3
\end{pmatrix}
\] (1)

As a result, a set of stress \( t = (t_1 t_2 t_3 t_4 t_5 t_6) \) is determined by first-principles calculations in this work. In present work, we apply the following six linearly independent sets of strains \[20\]

\[
\begin{pmatrix}
x 0 0 0 0 0 \\
0 x 0 0 0 0 \\
0 0 x 0 0 0 \\
0 0 x 0 0 0 \\
0 0 0 0 x 0 \\
0 0 0 0 0 x
\end{pmatrix}
\] (2)

with \( x = \pm 0.007 \). Using a 6 \( \times \) 6 elastic constants matrix, \( C \), with components of \( C_{ij} \) in Voigt’s notation, the generalized Hooke’s law is expressed as \( t = \varepsilon C \). Consequently, the stiffness constants matrix is obtained from

\[
C = \varepsilon^{-1} t,
\]

where “\( -1 \)” represents the pseudo-inverse, which can be solved by the singular value decomposition method. Finally, we get the macroscopic hcp elastic constant, \( C_{11}, C_{12}, C_{13}, C_{33}, C_{44} \), by averaging \[21\]
\[ \bar{C}_{11} = 3(C_{11} + C_{22})/8 + C_{12}/4 + C_{66}/2 \]
\[ \bar{C}_{12} = (C_{11} + C_{22})/8 + 3C_{12}/4 - C_{66}/2 \]
\[ \bar{C}_{13} = (C_{13} + C_{23})/2 \]
\[ \bar{C}_{33} = C_{33} \]
\[ \bar{C}_{44} = (C_{44} + C_{55})/2 \]

3. Results and discussion

3.1. Elastic properties

Elastic constants are very important because they can measure the resistance and mechanical properties of a solid to external stress or pressure. All independent elastic constants of Zr\textsubscript{x}Ti\textsubscript{1-x} (x=0,0.25,0.5,0.75,1) are calculated using strain-stress method in present work, and the results are summarized in Table 2. Small deviations from a perfect hcp structure are observed in the elastic tensors of the SQS models. These elastic constants decrease as Zr content increases except \(C_{12}, C_{13}, C_{23}\). According to Eq.(3), the averaged \(C_{11}, C_{12}, C_{13}, C_{33}, C_{44}\) are obtained for hcp crystals. The obtained constants of all composition meet the requirement of the Born stability criteria\cite{22} for hcp system

\[ C_{11} > 0, C_{44} > 0, C_{11} > |C_{12}|, (C_{11} + 2C_{12})C_{33} > 2C_{13}^2. \]

, The polycrystalline bulk modulus B, shear modulus G are deduced from the Voigt-Reuss-Hill(VRH) approach \cite{23}. Young’s modulus and Poisson’s (\(v\)) ratio are calculated by the following formulas:

\[ E = 9BG/(3B + G), v = (3B - 2G)/[2(3B + G)] \]
The results and B/G are listed in Table 3. The bulk moduli for all the composition show a excellent agreement with those obtained by fitting to a Birch-Murnaghan equation of state (list in Table 1), which is a proof of consistency and reliability of our calculations. Additionally, the deduced bulk moduli B change smoothly and decrease with increasing the amount of Zr, while the Young’s modulus E and shear modulus G show the same trend until x=0.75.

Empirical, there are two common ways to judge a material ductile or brittle. According Pugh’s suggestion, a higher ratio ( > 1.75) of bulk to shear moduli, B/G, indicates ductile behavior [24]. Another is the Poisson’s ration, the transsion from brittleness to ductility occurs when $\nu \approx 1/3$ [25]. Poisson’s ratio, $\nu$, and the B/G ratio as a function of Zr content, x, are listed in Table 3. Both criterion confirms the ductile behavior of Zr$_x$Ti$_{1-x}$ over the whole composition range. The value of B/G and $\nu$ for ZrTi alloy are higher than the one for pure metal, indicating the ductility of Zr is enhanced when alloying with Ti.

3.2. Mulliken charge

In order to understand the bond property between atoms, the atomic Mulliken charge of Zr-Ti binary alloy are investigated, and the results are given in Table 4, which clearly indicates that Ti atoms gain electrons while Zr atoms loss electrons. To investigate the origin of charge transfer, we further investigate the relationship between charge transfer and the amount of other element atom of its nearest neighbors by fitting the data using a line relationship. The results are showed in Fig. 2. Obviously, they are line-like. So we conclude that the charge transfer is mainly determined by the number
of other element atom in its nearest neighbors.

4. Conclusion

The structural, elastic and bond properties of the $\text{Zr}_x\text{Ti}_{1-x}$ alloy have been studied using first-principles calculations. The SQS method are adopted to mimic the ZrTi random system. It can be found that hcp structured $\text{Zr}_x\text{Ti}_{1-x}$ is a ductile material over the whole composition. The bulk Bulk modulus, $B$, Young’s modulus, $E$, and shear modulus, $G$ all have a decreasing trend with increasing the content of Zr. The effect of alloy will enhanced the ductility of pure metal Zr or Ti. From mulliken charge analysis, we could conclude that the amount of charge transfer is determined by the number of other element in its nearest neighbors, and there is a line-like relationship between them.
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Figure 1: The SQS structure of Zr$_x$Ti$_{1-x}$ with x = 0.5 represented by VESTA$^{[26]}$. Zr: green spheres; Ti: blue spheres

Table 1: Pair correction functions $\Pi_{2,l}$ (l up to the 11th nearest neighbor) for the random structures and SQS structures

| Structure          | $\Pi_{2,1}$ | $\Pi_{2,2}$ | $\Pi_{2,3}$ | $\Pi_{2,4}$ | $\Pi_{2,5}$ | $\Pi_{2,6}$ | $\Pi_{2,7}$ | $\Pi_{2,8}$ | $\Pi_{2,9}$ | $\Pi_{2,10}$ | $\Pi_{2,11}$ |
|--------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Random(Zr$_{0.5}$Ti$_{0.5}$) | 0           | 0           | 0           | 0           | 0           | 0           | 0           | 0           | 0           | 0           | 0           |
| SQS(Zr$_{8}$Ti$_{8}$)     | 0           | 0           | 0           | 0           | 0           | 0           | 0           | -0.333333   | 0           | 0           | 0           |
| Random(Zr$_{0.25}$Ti$_{0.75}$) | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        |
| SQS(Zr$_{4}$Ti$_{12}$)    | 0.25        | 0.25        | 0.25        | 0.25        | 0.25        | 0.333333    | 0.458333    | 0.166667    | 0.25        | 0.166667    | 0.25        |
Figure 2: The charge transfer of ZrTi binary alloy with the mulliken charge method
Table 2: The elastic constants (in GPa) calculated by stress-strain approach

| $Zr_xTi_{1-x}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{22}$ | $C_{23}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{14}$ | $C_{24}$ | $C_{34}$ | $C_{46}$ | $C_{56}$ | $C_{66}$ | $C_{16}$ | $C_{26}$ | $C_{36}$ | $C_{46}$ | $C_{56}$ | $C_{66}$ |
|-----------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 0.00            | 176.7   | 177.7   | 188.3   | 89.5    | 82.0    | 84.0    | 40.6    | 40.3    | 52.6    | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     |
| 0.25            | 163.2   | 153.1   | 147.5   | 76.1    | 89.6    | 87.2    | 40.7    | 32.3    | 42.3    | 2.8     | -1.3    | 5.2     | -7.0    | -3.2    | 0.7     | 5.5     | 6.1     | 3.0     | -2.3    | 2.2     | 1.8     | -6.1    | 1.3     | 1.5     | 4.9     | -1.0    | 1.1     | -2.9    |
| 0.50            | 148.7   | 135.6   | 134.6   | 83.8    | 79.2    | 88.6    | 31.5    | 36.1    | 28.8    | -2.7    | 7.0     | 0.7     | -0.9    | 0.8     | -6.1    | 1.3     | 4.9     | -1.0    | 1.1     | -2.9    | -10.8   | 1.5     | 4.9     | -1.0    | 1.1     | -2.9    | -10.8   |
| 0.75            | 145.8   | 129.4   | 129.5   | 75.4    | 84.4    | 82.7    | 28.9    | 33.8    | 3.1     | 3.9     | 8.4     | -2.8    | -0.7    | 1.6     | 4.1     | 0.8     | -0.9    | 0.8     | 4.2     | 0.2     | -10.8   | 1.5     | 4.9     | -1.0    | 1.1     | -2.9    | -10.8   |
| 1.00            | 153.1   | 153.0   | 153.1   | 63.6    | 70.5    | 70.1    | 26.2    | 26.2    | 45.2    | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     | 0.0     |

Table 3: The elastic constants $C_{ij}$ (GPa), shear modulus $G$ (GPa), bulk modulus $B$ (GPa), Young’s modulus $E$ (GPa), Poission ratio $\nu$ at various composition for ZrTi alloy

| $Zr_xTi_{1-x}$ | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{13}$ (GPa) | $C_{22}$ (GPa) | $C_{23}$ (GPa) | $C_{33}$ (GPa) | $C_{44}$ (GPa) | $C_{44}$ (GPa) | $B$ (GPa) | $G$ (GPa) | $E$ (GPa) | $\nu$ |
|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|-----------|-----------|-----------|------|
| 0.00            | 181.6         | 85.1          | 83.5          | 188.3         | 40.5          | 117.3         | 45.6          | 117.3         | 45.6      | 2.6       | 121.0     | 0.33  |
| 0.25            | 158.8         | 75.5          | 88.4          | 147.5         | 36.5          | 107.7         | 36.8          | 107.7         | 36.8      | 2.9       | 99.1      | 0.35  |
| 0.50            | 142.0         | 84.0          | 83.9          | 134.6         | 33.8          | 102.4         | 30.3          | 102.4         | 30.3      | 3.4       | 82.7      | 0.37  |
| 0.75            | 138.9         | 74.0          | 83.6          | 129.5         | 26.3          | 98.9          | 27.8          | 98.9          | 27.8      | 3.5       | 76.3      | 0.37  |
| 1.00            | 153.3         | 63.4          | 70.6          | 163.1         | 26.2          | 97.5          | 36.0          | 97.5          | 36.0      | 2.7       | 96.0      | 0.34  |
Table 4: Charge transfer according to Mulliken charge

|       | Zr0.25Ti0.75 | Charge Transfer | Zr0.5Ti0.5 | Charge Transfer | Zr0.75Ti0.25 | Charge Transfer |
|-------|--------------|----------------|------------|----------------|--------------|----------------|
| Zr1   | -0.2000      | Zr1            | -0.1509    | Zr1            | -0.1382      |
| Zr2   | -0.4074      | Zr2            | -0.1653    | Zr2            | -0.0311      |
| Zr3   | -0.2229      | Zr3            | -0.2061    | Zr3            | -0.1335      |
| Zr4   | -0.5269      | Zr4            | -0.0621    | Zr4            | -0.2778      |
| Ti5   | 0.0943       | Zr5            | -0.1748    | Zr5            | 0.0042       |
| Ti6   | 0.0147       | Zr6            | -0.3780    | Zr6            | -0.0871      |
| Ti7   | 0.1865       | Zr7            | -0.2211    | Zr7            | -0.1850      |
| Ti8   | 0.2337       | Zr8            | -0.3854    | Zr8            | -0.0124      |
| Ti9   | -0.0051      | Ti9            | 0.1597     | Zr9            | -0.2204      |
| Ti10  | 0.0903       | Ti10           | 0.0870     | Zr10           | -0.2293      |
| Ti11  | 0.1793       | Ti11           | 0.1600     | Zr11           | -0.0562      |
| Ti12  | -0.0097      | Ti12           | 0.2633     | Zr12           | -0.0640      |
| Ti13  | 0.2233       | Ti13           | 0.4042     | Ti13           | 0.3147       |
| Ti14  | 0.2843       | Ti14           | 0.1512     | Ti14           | 0.3467       |
| Ti15  | 0.0080       | Ti15           | 0.3217     | Ti15           | 0.3187       |
| Ti16  | 0.0577       | Ti16           | 0.1969     | Ti16           | 0.4507       |