



Article DFT Calculations of the Structural, Mechanical, and Electronic Properties of TiV Alloy Under High Pressure

Fang Yu¹ and Yu Liu^{2,*}

- ¹ School of Software and Communication Engineering, Xiangnan University, Chenzhou 423000, China
- ² State Key Laboratory of Advanced Design and Manufacturing for Vehicle Body, Hunan University,
- Changsha 410082, China* Correspondence: lyu1006@hnu.edu.cn

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Abstract: A calculation program based on the density functional theory (DFT) is applied to study the structural, mechanical, and electronic properties of TiV alloys with symmetric structure under high pressure. We calculate the dimensionless ratio, elastic constants, shear modulus, Young's modulus, bulk modulus, ductile-brittle transition, material anisotropy, and Poisson's ratio as functions of applied pressure. Results suggest that the critical pressure of structural phase transition is 42.05 GPa for the TiV alloy, and structural phase transition occurs when the applied pressure exceeds 42.05 GPa. High pressure can improve resistance to volume change, as well as the ductility and atomic bonding, but the strongest resistances to elastic and shear deformation occur at P = 5 GPa for TiV alloy. Furthermore, the results of the density of states (DOS) indicate that the TiV alloy presents metallicity. High pressure disrupts the structural stability of the TiV alloy with symmetry, thereby inducing structural phase transition.

Keywords: TiV alloy; Symmetric structure; DFT calculation; mechanical property; elastic constant; electronic structure; applied pressure

1. Introduction

TiV alloys with high gravimetric and volumetric hydrogen storage capacities have been widely regarded as important hydrogen storage materials [1–4]. Iba and Akiba [5] reported TiV–Mn alloys with multiphase nanostructures of body-centered cubic (BCC) and C14-type Laves phases, which had a large hydrogen capacity and excellent desorbing properties. Then, they revealed that the improved hydrogen sorption properties were attributed to the generation of multiphase nanostructures. Yu et al. [6] studied the hydrogen storage performance of a single BCC phase Ti-40V-10Cr-10Mn alloy, and results indicated that the largest hydrogen absorption capacity of the Ti-V-Cr-Mn alloy can reach 4.2 wt%, exceeding that of other hydrogen storage alloys, such as rare-earth (RE)-, Ti-, and Zr-based alloys. Nomura and Akiba [7] also investigated 26 types of alloys composed of Ti(33–47 mol%)-V(42–67 mol%)-Fe(0–14 mol%), and then found that the most suitable proportion for hydrogen absorption was Ti_{43.5}V_{49.0}Fe_{7.5}, and the hydrogen capacity reached up to 3.90 wt% (H/M = 1.90) at 253 K. Meanwhile, Seo et al. [8] reported that the $V_{0.68}Ti_{0.20}Fe_{0.12}$ alloy showed the largest hydrogen capacity of 3.6 wt%, and heat treatment can effectively improve hydrogen capacity, such as that in the $V_{0.375}Ti_{0.20}Cr_{0.30}Mn_{0.075}$ alloy with a hydrogen capacity of 2.2 wt%. Therefore, as the new hydrogen storage materials, TiV-based alloys have been greatly investigated [4,9–11]. However, the structural, mechanical, and electronic properties of TiV alloys remain unrevealed under high pressure due to the complexity of calculations, thereby limiting the applications of TiV alloys under high pressure.

Thus, this work uses first-principle calculations to study the structural, mechanical, and electronic properties of the TiV alloy with symmetry systematically within the frame of the density functional theory (DFT) and computes in detail the some variables with respect to the different pressures, such as the dimensionless ratio, elastic constants, elastic modulus, ductile–brittle transition, anisotropy factors, and Poisson's ratio, along with electronic properties. Moreover, the calculated results agree well with other experimental data and theoretical results. Therefore, the results can provide valuable guidance for the development and application of TiV alloys in the area of hydrogen storage materials.

2. Methodology

In the present work, all DFT calculations were performed by the Cambridge Serial Total Energy Package Program [12–14], which aims to obtain the electronic and energy properties of each structure in TiV alloys. The exchange–correlation function was decided by the generalized gradient approximation of Perdew–Burke–Ernzerhof [15]. The electronic states of Ti ($4s^23p^63d^2$) and V ($4s^23p^63d^3$) are the valence electrons, and the Vanderbilt-type ultrasoft pseudopotentials were applied to address the ion–electron interactions [16]. On the basis of a precise convergence test, the plane–wave cutoff energy was optimized as 400 eV, and the Brillouin-zone *k*-point grid [17] was selected as $13 \times 13 \times 13$ in the electronic calculations of the TiV alloy. The space group of the TiV alloy belongs to *Im-3m*, and the symmetric crystal structure of the TiV alloy is shown in Figure 1, and the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [18] was applied in the process of structural geometry optimization with respect to the applied pressures ranging from –10 to 50 GPa. The energy convergence criterion was set at 1.0×10^{-6} eV/atom in self-consistent calculations, and the Hellmann–Feynman force of each atom was lower than 0.01 eV/Å.



Figure 1. Symmetric Crystal structure of the TiV alloy.

3. Results and Discussion

3.1. Structural Properties and Stability

Prior to studying the various properties of the TiV alloy, the most stable crystal structure of the TiV alloy was first obtained, and the E - V data of total energy E with respect to volume V were calculated, and then they were accurately fitted by the Birch–Murnaghan equation of state [19], as shown in Figure 2, where the variation ranges of volume V are from 0.9 V_0 to 1.1 V_0 . During the geometry optimization of TiV alloys, the full optimization for a unit cell was implemented to obtain the total energy of the stable state. Figure 2 shows that for volume $V = V_0$ ($V_0 = 29.971 \text{ Å}^3$), the total energy reached the minimum value ($E_t = -16.457 \text{ eV}$), and the lattice constant was accordingly $a_0 = 3.107 \text{ Å}$, indicating the structural parameters of the TiV alloy under the most stable structure, where V_0 is the primitive cell volume, and a_0 is the equilibrium lattice constant at pressure P = 0 and temperature T = 0, respectively. The present results agree well with other approaches [10,20–25] and are comparatively listed in Table 1.



Figure 2. The E - V curve of total energy E with respect to cell volume V of the TiV alloy.

Table 1. Comparisons of the calculated lattice constant to the ones of others for TiV allo	эy.
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TiV Alloy	This Work	Others
Lattice constant <i>a</i> (Å)	3.107	3.156 [10], 3.163 [20], 3.165 [21] 3.120 [22], 3.159 [23], 3.140 [24] 3.280 [25]

To investigate the dependencies of the lattice constant and unit cell volume on the applied pressure, a series of structural optimizations were conducted to obtain the corresponding lattice constant under various applied pressures. Then, the dimensionless ratios a/a_0 and V/V_0 with respect to the different applied pressures, which are depicted in Figure 3, decreased monotonously with an increment of applied pressure, and the compression ratio of the volume was much larger compared with the lattice constant at the same applied pressure, thereby indicating that high pressure greatly reduces interatomic distance and leads to strong electron interactions.



Figure 3. Dependencies of dimensionless ratios a/a_0 and V/V_0 on the applied pressure for the TiV alloy.

In Figure 3, we fit the dependencies of dimensionless ratios a/a_0 and V/V_0 as a function of the applied pressure by using quadratic polynomial, and they are expressed as follows:

$$a/a_0 = 1.001 - 2.240 \times 10^{-3}P + 1.501 \times 10^{-5}P^2 \tag{1}$$

$$V/V_0 = 1.005 - 6.690 \times 10^{-3}P + 5.087 \times 10^{-5}P^2$$
⁽²⁾

In the anisotropic material, the elastic constants, which denote the ability to resist applied stress, are considered important physical quantities in measuring the structural stability of a material. For cubic crystals, the elastic constants include three coefficients, namely, C_{11} , C_{12} , and C_{44} . In accordance with the stability criterion [26,27], three elastic constants of cubic crystals fit with the following expressions:

$$(C_{11} - C_{12}) > 0, C_{11} > 0, C_{44} > 0, (C_{11} + 2C_{12}) > 0$$
 (3)

At P = 0 and T = 0, Table 2 lists the calculated elastic constants, bulk modulus *B*, Young's modulus *E*, and shear modulus *G*, as well as Poisson's ratio σ . Table 2 shows that the calculated results are consistent with the work of Ikehata et al. [25].

TiV Alloy	This Work	Ikehata et al. [25]
C ₁₁ (GPa)	178.16	169.6
C ₁₂ (GPa)	126.92	122.3
C ₄₄ (GPa)	21.52	33.6
C ₄₄ (GPa)	144.00	138.07
Young's modulus E (GPa)	65.71	81.81
Shear modulus G (GPa)	23.07	29.19
Poisson's ratio σ	0.42	0.40

Table 2. Comparisons of the calculated results with the work of Ikehata et al. [25] at P = 0 and T = 0.

Figure 4 demonstrates the dependencies of elastic constants C_{11} , C_{12} , and C_{44} on the applied pressure for the TiV alloy, revealing that for the pressure *P* changing from 0 GPa to 42.05 GPa, C_{11} and C_{12} increase gradually, but the elastic coefficient C_{44} decreases. Furthermore, the elastic coefficient C_{44} reduces slowly to zero with increasing applied pressure and then dramatically transforms into a negative value under the high pressure exceeding 42.05 GPa, which is unfit for the stability criterion of Equation (3). Thus, a high pressure exceeding 42.05 GPa disrupts the crystalline structure of the TiV alloy, namely, the TiV alloy is inclined to induce structural phase transition in the case of a high pressure of 42.05 GPa.



Figure 4. Dependencies of the elastic constants C_{ij} on the applied pressure for the TiV alloy.

3.2. Mechanical Properties

The mechanical properties of materials, such as high strength, good plasticity, and excellent deformation resistance, are closely related to material moduli, like shear modulus G, Young's modulus E, and bulk modulus B [28,29]. A large modulus has great resistance to material deformation.

Furthermore, we can apply Equations (4)–(6) [30] to calculate the modulus values of these materials. These modulus values depend on the calculated elastic constants, as listed in Table 2:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{4}$$

$$G = \frac{1}{2}(G_V + G_R) \tag{5}$$

$$E = \frac{9BG}{3B+G} \tag{6}$$

where $G_V = (C_{11} - C_{12} + 3C_{44})/5$ and $G_R = 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})]$, and G_V and G_R denote the Voigt and Reuss shear moduli, respectively.

Figure 5 demonstrates the dependencies of shear modulus *G*, Young's modulus *E*, and bulk modulus *B* on the applied pressure. Prior to structural phase transition, the bulk modulus *B* increased with increasing applied pressure, indicating that the high pressure leads to a strong resistance to volume change for the TiV alloy, and the maximum bulk modulus B_{max} is equal to 233.90 GPa at P = 42.05 GPa. However, shear modulus *G* and Young's modulus *E* initially increased from 0 GPa to 5 GPa and then decrease slowly with increasing applied pressure. The maximum values of Young's modulus *E* and shear modulus *G* were 68.47 and 23.98 GPa at P = 5 GPa, respectively, implying that the applied pressure at this value generates the maximum resistance to elastic and shear deformations for the TiV alloy.



Figure 5. Dependencies of shear modulus *G*, Young's modulus *E*, and bulk modulus *B* on the applied pressure for the TiV alloy.

To study the structural phase transition of materials, the present work aimed to analyze the ductile–brittle transition under different pressures. Pugh [28] raised that the modulus ratio B/G can be considered the key physical quantities in measuring the ductile/brittle properties for polycrystalline materials. Generally, 1.75 is the critical value of the ratio B/G for distinguishing ductile and brittle materials. The materials are characterized for the ductility by B/G > 1.75, and they are characterized for the brittleness by B/G < 1.75. Moreover, the ductility of materials increases with increasing B/G ratio. Otherwise, the brittleness increases. These conditions are equally suitable for investigating the ductile–brittle transition of intermetallic compounds [31]. Figure 6 exhibits the calculated results of the present work, showing that the modulus ratio B/G is approximately 6.24 under P = 0 GPa, and the B/G ratio (> 1.75) increases with an increase of applied pressure. Thus, the results from Figure 6 indicate that the TiV alloy is essentially characterized by excellent ductility, and high pressure can improve the ductility of the TiV alloy.



Figure 6. Dependencies of the modulus ratio B/G on the applied pressure for the TiV alloy.

3.3. Anisotropy

For anisotropic materials, we used elastic anisotropy to study their mechanical properties. The anisotropy factor *A* plays a key role in measuring the elastic anisotropy of materials, which are characterized by the isotropy at A = 1. Otherwise, they are characterized by the anisotropy at $A \neq 1$. Various anisotropy factors A ($A \neq 1$) correspond to the varying degrees of material anisotropy, and the material anisotropy is stronger when the anisotropy factors A are more deviated [32,33]. In the light of the work of Yoo [34], the cross-slip pinning model was presented to investigate the cross-slip pinning process of screw dislocations. The large factor A can increase the driving force of screw dislocation motion, and then promote the cross-slip pinning process of such dislocations. Here, we calculated the anisotropy factors $A_{(100)[001]}$ and $A_{(110)[001]}$ using Equations (7) and (8), respectively. They are expressed by the three elastic constants of cubic crystals, as follows [35,36]:

$$A_{(100)[001]} = \frac{2C_{44}}{C_{11} - C_{12}} \tag{7}$$

$$A_{(110)[001]} = \frac{C_{44}(C' + 2C_{12} + C_{11})}{C_{11}C' - C_{12}^2}$$
(8)

where $C' = C_{44} + (C_{11} + C_{12})/2$, $A_{(100)[001]}$ is the anisotropy factor in the (100)[001] direction, and $A_{(110)[001]}$ in the (110)[001] directions. Based on the calculations of Equations (7) and (8), Figure 7 shows the dependencies of the two anisotropy factors on the applied pressure. These factors helped investigate the mechanical properties of the TiV alloy under various pressures. Results in Figure 7 indicate that the anisotropy factors of the TiV alloy are $A_{(100)[001]} = 0.840$ and $A_{(110)[001]} = 0.875$ at P = 0 GPa, suggesting that the TiV alloy is essentially characterized by the anisotropy. As the applied pressure increases, the anisotropy factors $A_{(100)[001]}$ and $A_{(110)[001]}$ decrease rapidly, indicating that a larger applied pressure leads to a stronger anisotropy for the TiV alloy. Moreover, the cross-slip process of screw dislocations can be accelerated due to the strong anisotropy caused by the high pressure.



Figure 7. Dependencies of anisotropy factors on the applied pressure for the TiV alloy.

To investigate the plastic property of the TiV alloy under different pressures, we introduced the Poisson's ratio σ . Generally, the range of Poisson's ratio σ is between -1 and 0.5, and the material has better plasticity when Poisson's ratio σ is larger. Based on the key factors of atomic scale, Poisson's ratio σ mainly depended on the type of interatomic bonding [36]. In the work of Reed and Clark [37], Poisson's ratios $\sigma_{\min} = 0.25$ and $\sigma_{\max} = 0.5$ were identified as the minimum and maximum values in investigating central force solids, respectively. Herein, we define the $\sigma_{[001]}$ and $\sigma_{[111]}$ as the Poisson's ratios in the directions of [001] and [111], respectively, and they were obtained using Equations (9) and (10) [36,38]. Figure 8 depicts the dependencies of Poisson's ratios $\sigma_{[001]}$ and $\sigma_{[111]}$ on the applied pressure. We can obtain the values of $\sigma_{[001]} = 0.416$ and $\sigma_{[111]} = 0.429$ at P = 0 GPa. Thus, for the TiV alloy in nature, interatomic bonding is mainly characterized by the central force in the directions of [001] and [111]. As the applied pressure increases, the value of $\sigma_{[001]}$ initially decreases and then increases, but that of $\sigma_{[111]}$ gradually increases and then tends to achieve the maximum value of $\sigma_{\max} = 0.5$, thereby indicating that the high pressure enhances the central force and plasticity of the TiV alloy in the [111] uniaxial direction.

$$\sigma_{[001]} = \frac{C_{12}}{C_{11} + C_{12}} \tag{9}$$

$$\sigma_{[111]} = \frac{C_{11} + 2C_{12} - 2C_{44}}{2(C_{11} + 2C_{12} + C_{44})} \tag{10}$$



Figure 8. Dependencies of Poisson's ratios on the applied pressure for the TiV alloy.

The mechanical properties of the materials can also be evaluated by other physical quantities. The evaluation provides valuable guidance for studying material strength and deformation. Variables $G_{(100)[010]}$ and $G_{(110)[1\overline{10}]}$ are the shear moduli in the (100)[010] and $(110)[1\overline{10}]$ directions, respectively, where they are expressed by $G_{(100)[010]} = C_{44}$ and $G_{(110)[1\overline{10}]} = (C_{11} - C_{12})/2$. Similarly, variable $E_{(100)}$ is the Young's modulus in the (100) uniaxial directions, and $E_{(100)} = (C_{11} - C_{12})[1 + C_{12}/(C_{11} + C_{12})]$ [33, 39]. According to the definitions of these moduli, Figure 9 exhibits their dependencies on the applied pressure. Results show that shear modulus $G_{(110)[1\overline{10}]}$ is always greater than $G_{(100)[010]}$ under any pressure, thereby indicating that the $(110)[1\overline{10}]$ direction has stronger resistance to shear deformation compared with the (100)[010] direction. Moreover, $G_{(110)[1\overline{10}]}$ increases gradually with increasing applied pressure, thereby revealing that the high pressure enhances the resistance to shear deformation in the $(110)|\overline{110}|$ direction. However, the high pressure reduces the resistance to shear deformation in the (100)[010] direction due to the decrement of $G_{(100)[010]}$. Young's modulus $E_{(100)}$ increases gradually with increasing applied pressure. Thus, high pressure improves the resistance to elastic deformation in the (100) directions. As another physical quantity, the Cauchy pressure $C_{12} - C_{44}$ is generally used to reflect the characteristic of atomic bonding, and it can reveal the nature of the bonding from the atomic scale [40]. A positive Cauchy pressure denotes that the atomic bonding exhibits metallic properties. Thus, a homogeneous electron gas exists near the spherical atoms, and the electron distribution shows the same characteristics without regionality and directionality. However, a negative Cauchy pressure is characterized by the directional bonding, and the directional characteristic increases with increasing Cauchy pressure [33,41]. Results in Figure 9 show that the value of Cauchy pressures $C_{12} - C_{44}$ is always positive under any pressure and increases linearly with increasing applied pressure, thereby suggesting that the atomic bonding of the TiV alloy is mainly the metallic bond, and high pressure leads to a strong atomic bonding.



Figure 9. Dependencies of material moduli on the applied pressure for the TiV alloy.

3.4. Electronic Properties

To further investigate the bonding mechanisms of the TiV alloy, we obtained the electronic structures to reveal the stability changes of the TiV alloy under different pressures. Figure 10 depicts the partial density of states (PDOS) and total DOS (TDOS) of the TiV alloy under P = 0 GPa, and the Fermi level ($E_F = 0$ eV) is marked by the red dash line. The value of TDOS at E_F was not equal to zero, indicating that the TiV alloy presents the metallicity in nature and agrees well with the results in Figure 9. In light of the PDOS of the TiV alloy, the contributions to DOS are mainly obtained from the Ti-3d and V-3d states at the E_F , and the Ti-4s and V-4s states have no contributions to DOS.



Figure 10. PDOS and TDOS for the TiV alloy under P = 0 GPa.

Simultaneously, we also investigated the influences of the applied pressure on TDOS of the TiV alloy, and Figure 11 demonstrates the dependencies of the TDOS of the TiV alloy on the applied pressure. With increasing applied pressure, the valence band energy increases but the conduction band energy decreases, thereby resulting in the decrement of the band gap between valence band and conduction band. Then, the stability of the crystal structure decreases to a certain extent. The crystal structure of the TiV alloy easily produces the structural phase transition under high pressure. Results agree well with the previous results.



Figure 11. TDOS for the TiV alloy under various pressures.

Figure 12 plots the schematic of the isosurface contours of charge density under different pressures. The figure intuitively reflects the local chemical bonding between Ti and V atoms. Figure 12 shows that the local charge density between Ti and V atoms increases gradually with the increase of applied pressure, suggesting that the electron interaction between Ti and V atoms becomes increasingly strong under high pressure. Meanwhile, the results indirectly reflect that the local chemical bonding combined with the electrons and ions, between Ti and V atoms becomes stronger with increasing the applied pressure as well. The high pressure induces strong interactions between the Ti and V atoms, leading to structural instability under high pressure. Thus, the high pressure tends to destroy the structural stability of the TiV alloy, thereby inducing structural phase transition.



Figure 12. Schematic of isosurface contours of charge density for the TiV alloy under different pressures. The isosurface levels are set as 0.0406 r_0^{-3} (r_0 : Bohr radius).

4. Conclusions

- (1) The critical pressure of the structural phase transition for the TiV alloy is 42.05 GPa, and the symmetric crystal structure of the TiV alloy produces structural phase transition when the applied pressure exceeds 42.05 GPa.
- (2) The high pressure can improve resistance to volume change, but the biggest resistances to elastic and shear deformation occur under P = 5 GPa for the TiV alloy.
- (3) The results of Pugh's *B*/*G* ratio suggest that the TiV alloy is essentially characterized by excellent ductility, and high pressure can enhance the ductility of the TiV alloy.
- (4) The $(110)[1\overline{10}]$ direction has stronger resistance to shear deformation than the (100)[010] direction, and high pressure improves resistance to elastic deformation in the $\langle 100 \rangle$ direction. Cauchy pressure reveals that the atomic bonding of the TiV alloy is mainly the metallic bond, and high pressure leads to strong atomic bonding.
- (5) DOS results indicate that the TiV alloy presents metallicity, and high pressure disrupts the structural stability of the TiV alloy, thereby inducing structural phase transition.

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