First-principles study of $\beta$-titanium alloy TiX (X=Al, Ni, Fe) for key parts of automobile engines

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Abstract: As we all know, titanium alloys have excellent comprehensive mechanical properties, such as high ductility, rigidity, and density, which are superior to aluminium alloys. However, due to their high price, titanium alloys have not been able to be used in automobile engine bodies, but on small engine components, such as titanium alloys have been well used in connecting rods, valves, engine exhaust systems and fasteners. This article uses a new alloy design concept to design a new beta titanium alloy, hoping that it may be applied to small parts of automobile engines. Based on the density functional theory, the first-principles calculation method was used to study the structure and stability, formation heat, binding energy and elastic properties of TiX (X = Al, Ni, Fe) $\beta$ titanium alloy. The results show that these types of $\beta$ titanium are structurally and mechanically stable. By using Voigt-Reuss-Hill (VRH), the theoretical elastic constants $C_{ij}$, bulk elastic modulus B, shear modulus G, Young's modulus E, Poisson's ratio $\nu$ of these $\beta$ titanium alloys are further obtained. The ductility and plastic toughness of these kinds of $\beta$ titanium alloys are analysed, and the $\beta$ titanium alloy system with excellent comprehensive performance is determined, which also provides a basis for the next element selection of the $\beta$ titanium alloy system for automobile engines.

1. Introduction
The lightweight of automobile is an important subject of contemporary automobile’s development. Its basic requirements are (1) the price of automobile should be reduced or maintained at a reasonable level to keep commercial competitiveness. That is to say, the lightweight technology of automobile must take into account the quality, performance and price; (2) While reducing the weight, fuel consumption and emission, we also strive for its high output power, high response, low noise, low vibration, good handling, high reliability and high comfort; (3) Under the premise of ensuring the quality and functions of the car, it is necessary to minimize the quality of various parts, reduce fuel consumption, and emission pollution. Although traditional aluminum alloy, magnesium alloy, and titanium alloy material technologies have significantly improved the performance and service life of automotive materials [1-3], reducing costs and improving the overall performance of automotive materials are still of great importance for researchers. With the improvement of human living standards, automobiles have become an indispensable means of transportation, so it is necessary to develop new low-cost, lightweight materials.

With the advancement of titanium alloy manufacturing technology (light weight, corrosion resistance, high strength, good toughness) [4-7], titanium alloy is expected to play an essential role in the development of new automotive engine materials with its unique advantages. The research of U.S. industry predicts that in the future[8], titanium and titanium alloys will provide automotive materials
with the most comprehensive performance, and will expand their applications in automotive engines, automotive chassis components, fasteners, etc. β-titanium alloys can make automotive titanium alloy materials have advanced properties through different selection and design, which is a more promising direction for the development of automotive materials. Calculation model design and simulation test can partially replace expensive, time-consuming and laborious experiments, and make β-titanium alloy materials for automobiles have a broader application prospect [9,10].

2. Calculation method
The calculation is carried out under the CASTEP calculation program in the Materials Studio software package in this article. CASTEP is an ab initio quantum mechanics calculation program based on density functional theory and plane wave pseudopotential method. In the calculation, the generalized gradient approximation (GGA) PBE is used to deal with the exchange correlation energy between electrons, and the electron wave function is expanded by the plane wave basis vector set, moreover, ultrasoft pseudopotential is applied to describe the interaction potential between the real ion and the valence electron [11]. The basic parameters are set to plane wave cut-off energy Ecut=300eV, what’s more, the total energy and charge density in the Brillouin zone are calculated by using the Monkhorst-Pack scheme. The selection of k-points is 4×4×4 and the self-consistent convergence accuracy is 2×10⁻⁶eV/atom.

3. Results and discussion

3.1. Structure and stability
Applying density functional theory and first-principles calculations, the crystal structure parameters, formation heat, binding energy, single crystal elastic constant Cij, elastic flexibility Sij, and polycrystalline elastic properties of TiX (X=Al, Ni, Fe) are simulated. The Cambridge Sequential Total Energy Package (CASTEP) program package that is based on the density functional theory-based total energy plane wave pseudopotential method in the Materials studio8.0 software calculates the body-core structure of TiX (X=Al, Ni, Fe) Lattice constants and related elastic properties. Figure 1 shows a TiX (X=Al, Ni, Fe) alloy with a body-centered structure of 2a×2a×1a. The calculated lattice parameters of the TiX alloy are a=5.7328Å, b=2.8664Å and c=2.8664Å.

![Figure 1. Binary TiX (X=Al, Ni, Fe) β titanium alloy with body-centered cubic structure.](image)

Binding energy is the energy released by atoms from a free state to form a compound, in other words, the work done by the outside world when the crystal is broken down into individual atoms. Therefore, the greater the absolute value of the binding energy of the crystal is, the more stable the formation of the crystal is. The heat of formation is defined as the energy released or absorbed by different types of atoms from their elementary state to produce compounds. The more negative the heat of formation is, the more stable the compound is. If it is positive, it means that the energy required to break the bond between the elemental atoms of A and B is greater than the energy released during the bond of AB, so the compound cannot exist stably. The heat of formation is to determine which configuration is easier to form, and the binding energy is to determine which configuration is more stable.
The formula for calculating binding energy and heat of formation are [12,13]:

\[ E_c = \frac{E_{\text{tot}} + nE_{\text{atom}}^A + mE_{\text{atom}}^B}{n + m}, \quad H_f = \frac{E_{\text{tot}} + nE_{\text{solid}}^A + mE_{\text{solid}}^B}{n + m} \quad (1) \]

Figure 2 shows the element formation heat and isolated atomic energy. According to figure 2, the formation heat of different elements and isolated atomic energy, the formation heat and binding energy of the required alloy system structure can be analyzed to determine the structural stability. Figure 3 illustrates the total energy, secondary solid solution forming heat and binding energy of TiX (X=Al, Ni, Fe) \( \beta \) titanium alloy system. It can be seen from figure 3 that the stability of TiAl, TiNi, and TiFe alloys is enhanced in turn.

### 3.2. Elastic property

The elastic constant of an alloy characterizes the ability of the crystal structure to resist external stress [14]. Through the analysis of the elastic constant of \( \beta \) titanium alloy, the elastic properties of \( \beta \) titanium alloy can be further predicted. In this section, basing on the established crystal structure model of the \( \beta \)-titanium alloy system with a body-centered structure, the single crystal elastic constants, polycrystalline elastic properties and the elastic anisotropy properties of the TiX (X=Al, Ni, Fe) alloy are calculated.

By applying different types of strain on the TiX (X=Al, Ni, Fe) crystal structure of the body-centered structure, the single crystal elastic constant \( C_{ij} \) of the TiX (X=Al, Ni, Fe) alloy is calculated using equation (2) as Table 1 shows:

\[
(C_{11} + C_{22} - 2C_{12}) > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0, \quad (C_{22} + C_{33} - 2C_{23}) > 0, \quad C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, \\
C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0, \quad (C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0 \quad (2)
\]

The bulk modulus \( B \) is a characterization of the material's ability to resist volume deformation during pressure application and the shear modulus \( G \) is a characterization of the material's ability to resist
reversible deformation during shear deformation, and the Young's modulus $E$ reflects to a certain extent the hardness of the material. Poisson's ratio $\nu$ is usually used to characterize the ability of a material to resist shear stress. The larger the Poisson's ratio is, the better the shape of the material is. In addition to Poisson's ratio, Pugh also gave a criterion for judging the toughness and brittleness of materials [15], that is, the ratio of the bulk modulus to the shear modulus $B/G$.

$$B = \frac{B_V + B_R}{2}, \quad G = \frac{G_V + G_R}{2}, \quad E = \frac{9BG}{3B+G}, \quad \nu = \frac{3B-E}{6B} \tag{3}$$

The subscripts $V$ and $R$ represent the calculation results of Voigt and Reuss approximate models, respectively, and the expression is shown in equation (4). In the formula, $C_{ij}$ and $S_{ij}$ are the elastic constant and elasticity of the material single crystal, respectively, and $S_{ij}$ is the inverse matrix of $C_{ij}$.

$$B_V = \frac{1}{9} (C_{11} + C_{22} + C_{33} + \frac{2}{9} (C_{12} + C_{13} + C_{23}))$$

$$B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})}$$

$$G_V = \frac{1}{15} (C_{11} + C_{22} + C_{33} - C_{12} + C_{13} + C_{23}) + \frac{1}{5} (C_{12} + C_{13} + C_{23})$$

$$G_R = \frac{1}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})} \tag{4}$$

Table 1. Theoretical elastic constant $C_{ij}$ of binary $\beta$ titanium alloy single crystal.

| Alloys | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{22}$ | $C_{23}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| TiAl   | 174.30  | 89.67   | 100.51  | 174.30  | 100.51  | 152.30  | 75.81   | 75.81   | 64.99   |
| TiNi   | 206.45  | 74.08   | 101.62  | 206.45  | 101.62  | 158.39  | 79.51   | 79.51   | 59.61   |
| TiFe   | 113.40  | 32.54   | 60.31   | 113.40  | 60.31   | 116.88  | 43.08   | 43.08   | 25.06   |

Table 2. Elastic properties of binary $\beta$ titanium alloy.

| Alloys | $B_V$  | $B_R$  | $B_H$  | $G_V$  | $G_R$  | $G_H$  | $E$    | $\nu$  | $B/G$  |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| TiAl   | 100.36 | 100.17 | 100.27 | 51.50  | 171.00 | 111.25 | 243.64 | 0.10   | 0.90   |
| TiNi   | 125.10 | 124.61 | 124.86 | 63.33  | 56.43  | 59.88  | 154.88 | 0.29   | 2.09   |
| TiFe   | 72.22  | 70.65  | 71.44  | 34.94  | 32.18  | 33.56  | 87.05  | 0.30   | 2.13   |

It can be concluded from Table 2 that TiAl and TiNi alloys have relatively strong resistance to volume deformation and reversible deformation; TiNi and TiFe alloys have better plastic toughness.

The elastic anisotropy of materials is not only related to the material-induced microcracks but also plays an important role in engineering applications. The most commonly used method to characterize structural elastic anisotropy is the percentage of elastic anisotropy in compression and shear, $AB$ and $AG$. The expressions are demonstrated in equation (5),

$$A_{B/V} = \frac{B_V - B_R}{B_V + B_R}, \quad A_{G/V} = \frac{G_V - G_R}{G_V + G_R} \tag{5}$$

When the value of $AB$ and $AG$ is 100%, the material is completely anisotropic; 0 indicates that the material is completely isotropic. It can be shown from the shear ratio in Table 3 that the three materials are approximately isotropic. What is more, from the compression ratio, it can be concluded that TiAl is approximately anisotropic, and TiNi and TiFe are approximately isotropic.
Table 3. Titanium alloy system shear ratio and compression ratio.

| Alloys | \( A_\text{H}(\%) \) | \( A_\text{C}(\%) \) |
|--------|----------------|----------------|
| TiAl   | 0.095          | -53.708        |
| TiNi   | 0.196          | 5.762          |
| TiFe   | 1.099          | 4.112          |

4. Conclusion

The overall performance of titanium alloy small parts for automobile engines depends on the chemical composition and organizational structure of the material. This paper applies first-principles calculation methods to predict the structural stability, heat of formation, binding energy and elastic properties of TiX (X=Al, Ni, Fe) alloys, and the following conclusions are obtained:

(1) By calculating the formation heat and binding energy of TiX (X=Al, Ni, Fe) \( \beta \)-titanium alloys, the results demonstrate that these types of \( \beta \)-titanium alloys all satisfy the thermodynamic stability.

(2) The calculation of the elastic properties of TiX (X=Al, Ni, Fe) \( \beta \)-titanium alloys shows that these \( \beta \)-titanium alloys all satisfy the mechanical stability, moreover, TiAl alloys have strong resistance to volume deformation and reversible deformation. TiNi alloy and TiFe alloy have strong ductility.

(3) In-depth study of the influence of alloying elements on the elastic properties of titanium alloys provides a theoretical basis for the design and development of \( \beta \)-titanium alloys for new automobile engines.

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