Physical properties of Ti$_3$SiC$_2$/Zr heterojunction under hydrostatic pressure

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Abstract. The geometric structure, elastic constants and electronic properties of Ti$_3$SiC$_2$/Zr heterojunctions under high hydrostatic pressure (0-10GPa) were investigated by first-principles calculations. It’s found that the increase of hydrostatic pressure loaded on the Ti$_3$SiC$_2$/Zr heterojunctions induces the monotonically decrease of their lattice parameters. Under hydrostatic pressure below 10GPa, the Ti$_3$SiC$_2$/Zr heterojunction is stable and its elastic properties change linearly with pressure. Ti$_3$SiC$_2$/Zr heterojunction under hydrostatic pressure is found to be ductile material, and its anisotropy is weak. Finally, Ti$_3$SiC$_2$/Zr heterojunction under hydrostatic pressure retains metallic properties, and hydrostatic pressure slightly changes the band structure of Ti$_3$SiC$_2$/Zr heterojunction.

1. Introduction
Recently, MAX phase compounds have attracted much attention, due to their unique properties: high-temperature stability, good thermal and electrical conductivity, high thermal shock resistance, strong damage tolerance and particular microscale ductility[1,2]. For n=2, Ti$_3$SiC$_2$ is identified as a typical MAX material, which is widely used in high temperature and chemical anticorrosive conditions, such as in the fields of nuclear power and aviation [3-5]. In the past, theoretical studies on Ti$_3$SiC$_2$ have been carried out, calculating the electronic structure, elastic and optical properties etc. Owing to their outstanding properties, such as low neutron absorption cross section etc, zirconium-based alloys are the best water-cooled reactor nuclear materials [6,7]. In recent years, as good radiation and corrosion resistant material, Ti$_3$AC$_2$ (A=Si, Al) are usually the best choice of coating material for zirconium-based alloy to prevent hydrogen embrittlement [8-10]. Recently, we designed and studied the physical properties of Ti$_3$SiC$_2$/Zr heterojunctions, which focuses on the elastic and thermal properties of Zr metal and Ti$_3$SiC$_2$. It’s reported that the mechanical and thermal properties of Zr metal and Ti$_3$SiC$_2$ matches well [11].

As is well known that in nuclear condition, materials always encounter high pressure, i.e. 10 GPa in pressurized water reactor. However, the effect of high pressure on the geometric and elastic constants of Ti$_3$SiC$_2$/Zr heterojunction has not been investigated in detail. In this article, we have investigated the geometrie structure, electronic and elastic properties of Ti$_3$SiC$_2$/Zr heterojunction by ab initio calculations using Generalized Gradient Approximation (GGA) method, and studied the effect of pressure on the geometric, electronic and elastic properties. Our present work indicates that Ti$_3$SiC$_2$/Zr heterojunction under 10GPa has
good stability and suitable elastic properties, which means that Ti$_3$SiC$_2$ is good coating material of Zr metal under high hydrostatic pressure.

![Perspective spatial model of Ti$_3$SiC$_2$/Zr heterojunction.](image)

**Figure 1.** Perspective spatial model of Ti$_3$SiC$_2$/Zr heterojunction.

2. **Calculation details**

First-principles calculations were completed by the Materials Studio software[12]. The ultrasoft pseudopotential was adopted to simulate the interaction between ions and electrons. The GGA method [13] is used to deal with the exchange correlation between atoms. Ti$_3$SiC$_2$ supercell and Zr metal supercell are assembled in the (001) direction, and the mismatch of lattice parameters $a$ and $b$ in Ti$_3$SiC$_2$/Zr are both below 4.8%, as is shown in figure 1. We fully optimized the Ti$_3$SiC$_2$/Zr heterojunction structures, under which the external pressure changes from 0 to 10 GPa. In this work, the energy deviation is less than 5.0×10^{-6}eV/atom, and convergence is assumed when the forces on atom is less than 0.01eV/Å. The plane-wave cutoff energy of 400 eV is employed. And the self-consistent field (SCF) tolerance is set to be 5.0×10^{-7}eV/atom. The calculations are carried out using a (10,10,2) Monkhorst-Pack grid[14].

3. **Results and discussion**

3.1 **Geometric structure**

Ti$_3$SiC$_2$ and Zr metal both have hexagonal structure, whose space group are P63/mmc. However, after fully relaxation, the symmetry of Ti$_3$SiC$_2$/Zr heterojunction supercells become lower, and the symmetry belongs to P-3M1. The lattice constants of optimized Ti$_3$SiC$_2$/Zr heterojunction under different pressure are listed in table 1. It’s found from table 1 that the structural parameters and total energy of Ti$_3$SiC$_2$/Zr heterojunction all change monotonically with pressure. With the increase of pressure from 0 to 10 GPa, the lattice parameters ($a$, $c$, $d$ and $V$) all decrease linearly with pressure. In figure 2, we show the pressure dependence of $a/a_0$ and $c/c_0$ as well as $V/V_0$ (where $a_0$, $c_0$ and $V_0$ are the lattice parameters under zero pressure). We notice in figure 2 that the changes of the $a/a_0$ and $c/c_0$ as well as the $V/V_0$ are approximately linear when the pressure rises from 0 to 10 GPa. These changes are in consistent with each other. It can be seen from table 1 that the total energy of the Ti$_3$SiC$_2$/Zr heterojunction increases with pressure, while the volume decreases with pressure. Moreover, the bonds in the Ti$_3$SiC$_2$/Zr heterojunction become closer, which indicating that the interactions between the atoms become stronger. Under higher and higher pressure, the contractions of inter-atomic distances results in bigger and bigger change of electronic structure of the Ti$_3$SiC$_2$/Zr material.

| $P$ (GPa) | $a$ (Å) | $c$ (Å) | $d$ (Å) | $V$ (Å$^3$) | $E$ (eV) |
|-----------|---------|---------|---------|-----------|---------|
| 0.0       | 3.13    | 51.93   | 2.67    | 440.58    | -27439.4|
| 2.5       | 3.11    | 51.42   | 2.61    | 430.70    | -27432.9|
| 5.0       | 3.09    | 51.19   | 2.59    | 423.27    | -27425.9|

Table 1. Lattice parameters and total energy of system under pressure.
Figure 2. The V/V₀, a/a₀, c/c₀ for Ti₃SiC₂/Zr heterojunction under different pressure.

3.2 Elastic constants

Elastic properties reflect material's ability to deform and recover under different forces. Under certain force range, objects all have elasticity. Ti₃SiC₂/Zr and Zr metal have six elastic constants which is Cᵢⱼ (i,j=1,2,3,4,5,6). The elastic constants of Ti₃SiC₂/Zr are calculated in detail, which are shown in table 2. The elastic constants of Ti₃SiC₂/Zr in table 2 are taken into the inequality in reference [11]. It is found that the elastic constants of Ti₃SiC₂/Zr all satisfy the inequality when the external pressure is changed from 0 to 10GPa, which means the Ti₃SiC₂/Zr heterojunction has good stability under the given pressure. In addition, the ratios of elastic parameters of Ti₃SiC₂/Zr are C₁₁/C₃₃, C₁₂/C₁₃ and C₄₄/C₆₆. All ratios deviate from 1, which means that Ti₃SiC₂/Zr heterojunctions under different pressure belong not to pseudocube crystal.

Table 2. Constants Cᵢⱼ, B (GPa), G (GPa) and ν of material under pressure p (GPa).

| p    | C₁₁ | C₁₂ | C₁₃ | C₃₃ | C₄₄ | C₆₆ | B   | G   | G/B | ν   |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.0  | 212.4 | 60.36 | 78.90 | 192.82 | 44.19 | 77.06 | 117.13 | 59.83 | 0.51 | 0.281 |
| 2.5  | 225.26 | 73.79 | 83.49 | 217.54 | 52.36 | 76.29 | 127.45 | 68.09 | 0.53 | 0.273 |
| 5.0  | 232.22 | 74.33 | 95.22 | 219.54 | 42.73 | 80.08 | 134.68 | 53.64 | 0.39 | 0.324 |
| 7.5  | 247.10 | 77.43 | 102.79 | 235.36 | 46.57 | 86.13 | 143.82 | 62.18 | 0.43 | 0.311 |
| 10.0 | 257.47 | 84.31 | 111.00 | 247.84 | 59.59 | 86.39 | 152.43 | 70.44 | 0.46 | 0.300 |

In figure 3, the variations of elastic coefficients of Ti₃SiC₂/Zr heterojunction with pressure are plotted respectively. It's found that most elastic coefficients except for C₄₄ increase monotonically with pressure from 0 to 10 GPa.
Figure 3. The elastic coefficients of Ti$_3$SiC$_2$/Zr heterojunction under pressure. According to reference [11], we get the expressions of $B_V$ and $G_V$, which are shown below:

$$B_V = (2C_{11} + C_{33} + 2C_{12} + 4C_{13})/9$$

$$G_V = (2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44} + 3C_{66})/15$$

(1)

Further using the Reuss approximation, we get the expressions of $B_R$ and $G_R$ [17], which are as follows:

$$B_R = [(C_{11} + C_{12})C_{33} - 2C_{13}^2]/(C_{11} + C_{12} + 2C_{33} - 4C_{13})$$

$$G_R = 15/(8s_{11} + 4s_{33} - 4s_{12} - 8s_{13} + 6s_{44} + 3s_{66})$$

(2)

Further, we get the expressions of $B$ and $G$, which are given in below:

$$B = (B_V + B_R)/2, \quad G = (G_V + G_R)/2$$

(3)

The body modulus and shear modulus calculated according to relations (1-3) are shown in table 2. From the data in table 2, the $G/B$ values for the Ti$_3$SiC$_2$/Zr heterojunction under 0, 2.5, 5.0, 7.5 and 10.0GPa are 0.51, 0.53, 0.39, 0.43 and 0.46 respectively. Thus, the Ti$_3$SiC$_2$/Zr heterojunction materials under pressure (0-10GPa) are ductile materials, for all $G/B < 0.57$. Based on the above results, $\nu$, $A$, and $Y$ can also be calculated, their expressions are as follows:

$$\nu = (B - 2/3G)/(2B + 2/3G), \quad A = 2C_{44}/(C_{11} - C_{12}), \quad Y = 9GB/(G + 3B)$$

(5)

Our calculation results of $\nu$, $A$, and $Y$ according to equations (5) are listed in table 3. The value of $\nu$ for Ti$_3$SiC$_2$/Zr under pressure are close to 0.33, which are the normal value for a metallic material, which means that the bonding between the atoms in the Ti$_3$SiC$_2$/Zr heterojunctions are dominated by ionic bonds. The anisotropic factors for Ti$_3$SiC$_2$/Zr decrease with pressure, and they are all less than 1, therefore, it can be concluded that the anisotropy of all these materials are weak. The anisotropic factors for Ti$_3$SiC$_2$ and Zr are 1.36 and 1.06, respectively, which are larger than the value of $\nu$ for Ti$_3$SiC$_2$/Zr. Therefore, it’s found that after assembling of Ti$_3$SiC$_2$ and Zr into Ti$_3$SiC$_2$/Zr heterojunction, the elastic anisotropy of materials become weaker than those of pristine Ti$_3$SiC$_2$ and Zr metal. Young’s modulus for materials usually indicate their deformations under different stress. In table 3, it is shown that the value of $Y$ for Ti$_3$SiC$_2$/Zr changes non-linearly with pressure.

Table 3. Parameters $\nu$, $A$, and $Y$ (GPa) of material under various pressure (GPa).

| Pressure | $\nu$ | $A$ | $Y$ |
|----------|-------|-----|-----|
| 0.0      | 0.28  | 0.58| 153.37|
| 2.5      | 0.27  | 0.54| 173.39|
| 5.0      | 0.32  | 0.45| 142.05|
| 7.5      | 0.31  | 0.37| 163.05|
| 10.0     | 0.30  | 0.18| 183.11|
3.3 Electronic properties

In this section, we mainly calculated the band structures of Ti₃SiC₂/Zr heterojunctions under hydrostatic pressure. The band structures of Ti₃SiC₂/Zr heterojunctions under three different pressure (0, 5 and 10GPa respectively) are shown in figure 4. It can be seen from figure 4 that the Ti₃SiC₂/Zr under different pressure all exhibit conduction bands crossing the Fermi level, which indicates that all these systems have metallic properties. Obviously, the high hydrostatic pressure doesn’t change the metallic properties of Ti₃SiC₂/Zr heterojunctions, but changes their band structure (As shown in figure 4) [11].

![Figure 4](image)

**Figure 4.** Band structures of Ti₃SiC₂/Zr heterojunction under different pressure.

The total density of state (TDOS) and partial density of state (PDOS) of Ti₃SiC₂/Zr heterojunction under different hydrostatic pressure were calculated by GGA-PBE functions. For brevity, taking the case of \( p = 5 \) GPa as an example, the total density of state (TDOS) and partial density of state (PDOS) of Ti₃SiC₂/Zr heterojunction under hydrostatic pressure of 5GPa are shown in figure 5. From the figure 5, we can see that N (EF) values are all greater than zero, which means that the Ti₃SiC₂/Zr heterojunction under hydrostatic pressure are metallic. The peak near Fermi level in figure 5 is mainly attributable to the hybridization of Ti-3d and Zr-4d. The hybridization between atoms indicate that the bonds in Ti₃SiC₂/Zr heterojunction is partly covalent. These results are in agreement with our previous report [11].

![Figure 5](image)

**Figure 5.** The TDOS and PDOS of Ti₃SiC₂/Zr heterojunction under \( p = 5 \) GPa.

4. Conclusion

In this paper, a few physical properties of Ti₃SiC₂/Zr under different hydrostatic pressure were analyzed by the first-principles method. First of all, the geometric structures of Ti₃SiC₂/Zr heterojunctions under static pressure were optimized, and it’s found that the increase of hydrostatic pressure caused the monotonically decreases of their lattice parameters. And the total energy of the Ti₃SiC₂/Zr heterojunction increase with
hydrostatic pressure. Secondly, when the external hydrostatic increase from 0 to 10GPa, the Ti$_3$SiC$_2$/Zr heterojunction is stable and its most elastic coefficients change linearly with pressure. Moreover, it’s found that Ti$_3$SiC$_2$/Zr heterojunction materials under hydrostatic pressure are ductile material, and its anisotropy is weak. Finally, the energy band structure and DOS of Ti$_3$SiC$_2$/Zr heterojunction under different hydrostatic pressure were investigated. Our results show that hydrostatic pressure doesn’t change their metallic properties, but slightly changes their band structure.

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