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## The effects of He clusters on the mechanical properties of $Ti_3AC_2$ (A = Ge, Si): first-principles studies

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Herein, the damage to the mechanical properties of  $Ti_3AC_2$  (A = Ge, Si) was systematically investigated by first-principles calculations. It is known that the interstitial He atoms homogeneously generated in the materials would finally migrate to the A layer and form clusters of no more than 7 He atoms at a mono-vacancy in the A layer, and the cluster of 7 He atoms reduces the ideal tensile strength of  $Ti_3SiC_2$  (or  $Ti_3GeC_2$ ) to about 37.3% (or 35.5%). The strain simulations showed that the fracture would mostly occur around the A layer and enhances with increase in the cluster size, while the  $Ti_3C_2$  blocks are relatively stable during tension. Although the He damage to the mechanical properties shows the similar trend for  $Ti_3SiC_2$  and  $Ti_3GeC_2$ , the former displays better properties for applications in nuclear structural devices.

## 1. Introduction

In general, He atoms are continuously generated in nuclear structural materials from  $(n, \alpha)$  transmutation reactions and have a strong tendency to form He bubbles, leading to creep, swelling, embrittlement, or hardening of the materials.<sup>1–3</sup> This He damage has been a problem in metals used as nuclear structural materials,<sup>1,4,5</sup> recently, MAX phase materials (e.g.  $Ti_3SiC_2$  and  $Ti_3AlC_2$ ) have been considered as better candidates for nuclear structural materials<sup>6–9</sup> and some experiments have demonstrated that  $Ti_3AlC_2$  exhibits high tolerance to the He damage.<sup>10–12</sup> For example, Wang *et al.* reported that  $Ti_3AlC_2$  irradiated by 50 keV He ions with doses up to  $1 \times 10^{18} \text{ cm}^{-2}$  at room temperature displayed severe structural disorder but no evident amorphization.<sup>11</sup> Patel *et al.* demonstrated that the Al layer of  $Ti_3AlC_2$  at 500 °C irradiated by 200 keV He ions with doses of  $2 \times 10^{17} \text{ cm}^{-2}$  was disordered, whereas the  $Ti_3C_2$  layers remained intact after irradiation.<sup>12</sup> The previous theoretical studies of the MAX phase materials particularly focus on the single He atom behaviors, such as the energetically favorable interstitial sites for a single He atom to occupy and relevant effects.<sup>8,13–15</sup> It should be noted that previous experimental observations showed that the He atoms implanted in MAX phase materials usually form clusters with sizes of 0.6–1.0 nm.<sup>10,11</sup> Recently, we investigated the migration and aggregation of He atoms homogeneously generated in  $Ti_3SiC_2$  via first-principles calculations<sup>16</sup> and showed that the He atoms

would migrate to the Si layer and finally form clusters. Clearly, it is very important for the design of structural materials to study the effects of He clusters, instead of the single He atom, on the mechanical properties of  $Ti_3SiC_2$  as well as other MAX phase materials.

In the present study, we mainly focus on the mechanical properties of  $Ti_3AC_2$  (A = Ge, Si) affected by the He clusters *via* DFT calculations. First, we investigated the migration and segregation of He atoms homogeneously generated in  $Ti_3GeC_2$ . It showed that interstitial He atoms would diffuse to the Ge layer at high temperature ( $>500$  °C) and form clusters of no more than 7 He atoms by a single Ge vacancy, which is similar to the behavior of helium in  $Ti_3SiC_2$ . Then, we examined the structural changes of  $Ti_3AC_2$  in the presence of He clusters on stretching the materials and calculated the corresponding tensile stress. The results indicated that the ideal tensile strength of  $Ti_3SiC_2$  (or  $Ti_3GeC_2$ ) containing a cluster of 7 He atoms, which were formed at a vacancy in the A layer, reduces to 37.27% (or 35.47%) of the perfect ones. The structural deformation mainly takes place near the A layer, while the structure of the  $Ti_3C_2$  block changes slightly.

## 2. Computational methods

The general chemical formula of MAX phase materials is  $M_{n+1}AX_n$  with  $n = 1, 2$ , or 3, where M, A and X represent an early transition metal, the elements in group IIIA or IVA, and either carbon or nitrogen, respectively. The atoms are nano-layered arranged, as shown in Fig. 1 for  $Ti_3AC_2$ , which can be regarded as a 'zigzag' stacking of hexagonal  $Ti_3C_2$  blocks and planar A atomic sheets in the [0001] direction (z-axis) sequentially. This nano-laminated structure indicates that cleavage takes place mainly along the z-axis, which has been verified in some

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experimental observations.<sup>17–19</sup> Therefore, our examinations of the mechanical properties are restricted to the strain along the [0001] direction. Specifically, a uniaxial tensile strain  $\varepsilon$  was applied to the system along the [0001] direction step-by-step with an interval of 0.01. In each step, the system was allowed to be fully relaxed except fixing the z-axis to obtain the total energy  $E$ , which was employed to obtain ideal tensile stress:

$$\sigma = \frac{1}{V_0} \frac{\partial E}{\partial \varepsilon}, \quad (1)$$

where  $V_0$  is the original volume of the system. This procedure continues until the tension  $\sigma$  reaches a maximum value  $\sigma_M$ , which is defined as ideal tensile strength; the corresponding strain  $\varepsilon_M$  is an important parameter for design of structural materials.

The cleavage of  $\text{Ti}_3\text{AC}_2$  could take place around the A/Ti<sub>II</sub>, Ti<sub>II</sub>/C, or C/Ti<sub>I</sub> interface, and we calculated the cleavage energy defined as:

$$E_{\text{cl}}(d) = (E_{\text{sep}} - E_{\text{whole}})/2S, \quad (2)$$

where  $E_{\text{whole}}$  is the total energy of a piece of  $\text{Ti}_3\text{AC}_2$  with or without the presence of He clusters, and  $E_{\text{sep}}$  is the total energy of two departed parts, separated by  $d$  and cleaved from the materials between the A/Ti<sub>II</sub>, Ti<sub>II</sub>/C, or C/Ti<sub>I</sub> interlayer, and  $S$  is the area of the interfaces.

To describe the behavior of He in  $\text{Ti}_3\text{AC}_2$ , the solution energy is defined as follows:

$$E_{\text{He}}^S = E(\text{per} + \text{He}) - E(\text{per}) - E(\text{He}_{\text{iso}}), \quad (3)$$

where  $E(\text{per} + \text{He})$  and  $E(\text{per})$  are the total energies of  $\text{Ti}_3\text{AC}_2$  with and without an interstitial He atom, respectively, and

$E(\text{He}_{\text{iso}})$  the energy of an isolated He atom. The formation energy of a vacancy of species X (X can be Ti, A or C) in  $\text{Ti}_3\text{AC}_2$  is defined as:

$$E_{\text{V}_X}^f = E(\text{V}_X) - E(\text{per}) + \mu_X, \quad (4)$$

where  $E(\text{V}_X)$  is the total energy of the system containing defect X, and  $\mu_X$  denotes the corresponding chemical potential of the element.

A vacancy in  $\text{Ti}_3\text{AC}_2$  could trap more than one He atom. In order to estimate the number of He atoms that could be adsorbed by a mono-vacancy, we define trapping energy by the following equation:<sup>20,21</sup>

$$E_{\text{trap}} = E(\text{per} + n\text{He}, \text{V}) - E(\text{per} + (n-1)\text{He}, \text{V}) - E_{\text{He}}^S, \quad (5)$$

where  $E(\text{per} + n\text{He}, \text{V})$  is the energy of  $\text{Ti}_3\text{AC}_2$  with  $n$ He atoms and a single vacancy, and  $E_{\text{He}}^S$  is the lowest solution energy determined by eqn (3). The maximum number of He atoms trapped by a single vacancy is determined when  $E_{\text{trap}} > 0$ .

The first-principles calculations were performed using density functional theory (DFT) and the pseudopotential plane-wave method implemented in the VASP codes, where a gradient-corrected form of the exchange correlation functional generalized gradient approximation (GGA-PW91) was employed.<sup>22,23</sup> The cutoff energy of the plane-wave basis was set at 500 eV, and a  $3 \times 3 \times 1$  supercell containing 108 atoms was adopted to perform the calculations, where  $5 \times 5 \times 2$  Monkhorst–Pack  $k$ -point sampling for the Brillouin zone was chosen.<sup>24</sup> The lattice constants and internal freedom of the unit cell were fully optimized when atomic forces were less than 0.01 eV Å<sup>-1</sup>. The climbing image NEB method was employed to obtain the minimum energy path of the He atom.<sup>25</sup> Five images between the initial and final configurations were constructed by linear interpolation. The forces on all atoms in each image of the CI-NEB chain were converged to 0.05 eV Å<sup>-1</sup>. The tensile simulations were performed on a  $2 \times 2 \times 1$  supercell, where  $9 \times 9 \times 4$   $k$ -points were generated, and the convergence of the total energy was  $5.0 \times 10^{-5}$  eV per atom.

### 3. Results and discussions

The migration and clustering of He atoms in  $\text{Ti}_3\text{SiC}_2$  have been investigated in our recent study.<sup>16</sup> It is shown that the He atoms that are homogeneously generated will quickly migrate into the Si layer at high temperature ( $>500$  °C) and form clusters of no more than 7 He atoms at a mono-vacancy. The same procedures were performed to examine the behaviours of He atoms homogeneously generated in  $\text{Ti}_3\text{GeC}_2$ .

According to eqn (3), the solution energy of He in  $I_{\text{tetra}1}$ ,  $I_{\text{tetra}2}$ ,  $I_{\text{oct}}$ , and  $I_{\text{hex}1}$  sites labelled by 1 (or 2), 3, 4 (or 5), and 6 in Fig. 2a are 5.07, 4.25, 3.16, and 3.59 eV, respectively, which are very close to the ones for  $\text{Ti}_3\text{SiC}_2$ .<sup>16</sup> The interlayer migration paths (Fig. 2a) and the corresponding energy barriers (Fig. 2b) are also similar to the ones of  $\text{Ti}_3\text{SiC}_2$ , indicating that a He atom generated in  $\text{Ti}_3\text{GeC}_2$  (or  $\text{Ti}_3\text{SiC}_2$ ) at  $I_{\text{tetra}1}$  has to overcome an energy barrier of 1.045 eV (or 1.05 eV) jumping into the  $I_{\text{oct}}$  site near the Ge (or Si) layer. According to Arrhenius law, the period

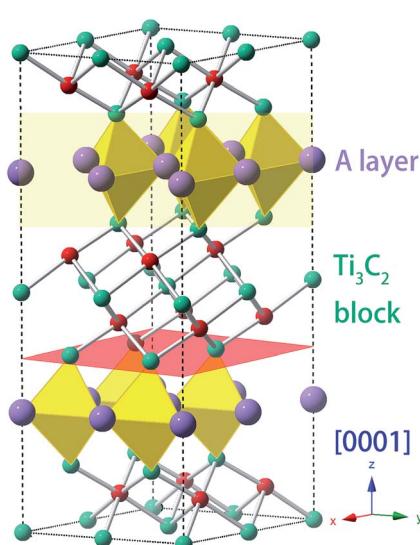


Fig. 1 Layered crystal structure of  $\text{Ti}_3\text{AC}_2$  is divided into planar A atomic sheets and  $\text{Ti}_3\text{C}_2$  blocks stacking in sequence along the z-axis in the [0001] direction. There are three total possible combination types of upper and lower surfaces, A/Ti<sub>II</sub>, Ti<sub>II</sub>/C, and C/Ti<sub>I</sub> in  $\text{Ti}_3\text{AC}_2$  phases. The green, red, and purple balls represent Ti, C, and A atoms, respectively.



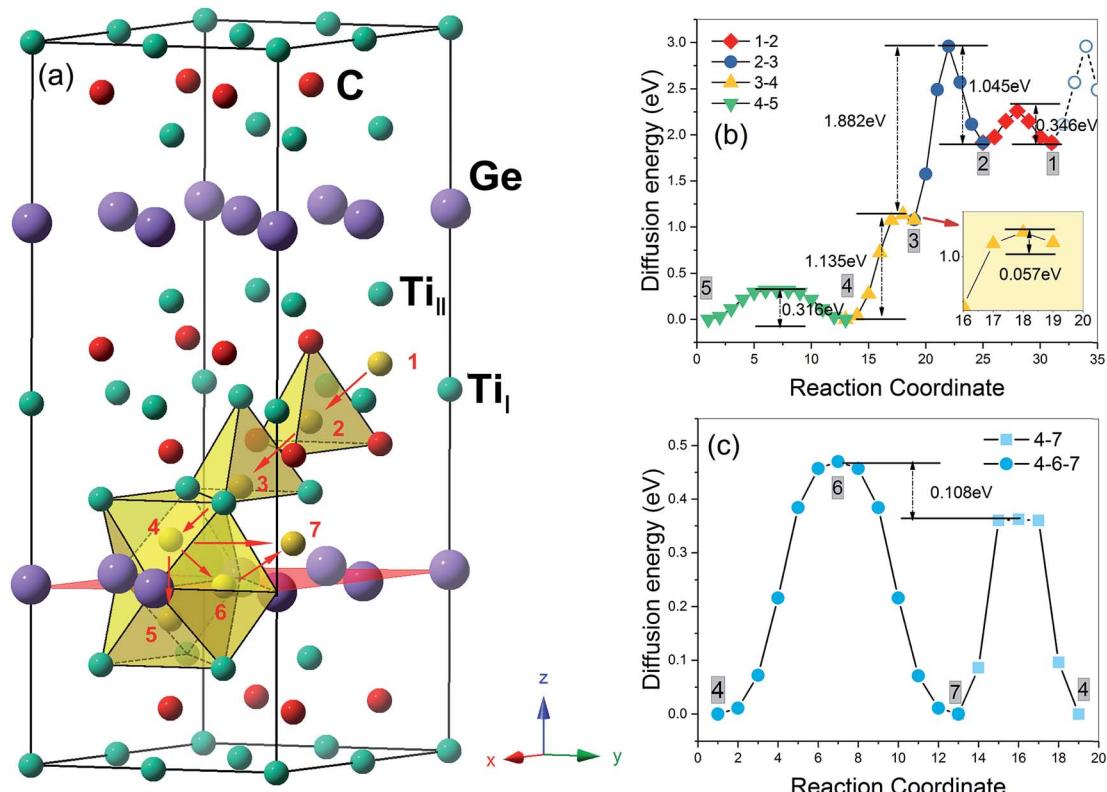


Fig. 2 Possible interstitial sites for a He atom to stay in  $\text{Ti}_3\text{GeC}_2$  labelled by 1 (or 2), 3, 4 (or 5), 6 for  $\text{I}_{\text{tetra}1}$ ,  $\text{I}_{\text{tetra}2}$ ,  $\text{I}_{\text{oct}}$ ,  $\text{I}_{\text{hex}1}$ , respectively (a); the diffusion barriers for a He atom migrating along the z-axis:  $\text{I}_{\text{tetra}1}-\text{I}_{\text{tetra}1}$  (1-2),  $\text{I}_{\text{tetra}1}-\text{I}_{\text{tetra}2}$  (2-3),  $\text{I}_{\text{tetra}2}-\text{I}_{\text{oct}}$  (3-4),  $\text{I}_{\text{oct}}-\text{I}_{\text{oct}}$  (4-5) (b); and the diffusion barriers between  $\text{I}_{\text{oct}}-\text{I}_{\text{oct}}$  (4-7) and  $\text{I}_{\text{oct}}-\text{I}_{\text{hex}1}-\text{I}_{\text{oct}}$  (4-6-7) along the Ge layer (c). The yellow balls represent He atoms.

for the He atoms staying at  $\text{I}_{\text{tetra}1}$  is about 10 hours for room temperature ( $\sim 300$  K) and reduces to  $\sim 10^{-6}$  s for the temperature of 800 K. The He atoms generated at the  $\text{I}_{\text{tetra}2}$  site will quickly diffuse into the  $\text{I}_{\text{oct}}$  site near the Ge (or Si) layer due to the small diffusion barrier. Accordingly, all the interstitial He atoms generated homogeneously in  $\text{Ti}_3\text{AC}_2$  at temperatures

above 500 °C will diffuse quickly into the A layer instead of staying in the other layers. For the diffusion of an He atom in the A layer, there exist two possible paths,  $\text{I}_{\text{oct}}-\text{I}_{\text{oct}}$  (4-7) and  $\text{I}_{\text{oct}}-\text{I}_{\text{hex}1}-\text{I}_{\text{oct}}$  (4-6-7), and the diffusion barrier of 0.36 eV along  $\text{I}_{\text{oct}}-\text{I}_{\text{oct}}$  is lower than  $\text{I}_{\text{oct}}-\text{I}_{\text{hex}1}-\text{I}_{\text{oct}}$  by 0.106 eV (Fig. 2c). However, it is significantly larger than the value (0.05 eV) in  $\text{Ti}_3\text{SiC}_2$ , indicating that the mobility of He atoms in  $\text{Ti}_3\text{GeC}_2$  along the A layer is much lower than that of  $\text{Ti}_3\text{SiC}_2$ .

It should be pointed out that vacancies could be introduced in any layer of MAX phase materials by long-term nuclear irradiation and can trap the interstitial He atoms to form He clusters. For each cluster size, we attempted various possible patterns of He clusters to choose the most energy favorable one. According to eqn (4), the formation energies of a mono-vacancy ( $\text{V}$ ) in the A, C,  $\text{Ti}_1$ ,  $\text{Ti}_{\text{II}}$  layer of  $\text{Ti}_3\text{GeC}_2$  (or  $\text{Ti}_3\text{SiC}_2$ ) are 1.98 (or 1.95), 2.33 (or 2.16), 6.85 (or 7.18), and 4.58 (or 4.99) eV, respectively, showing that vacancy most easily forms in the A layer. According to eqn (5), the calculated trapping energy as the function of number of the He atoms trapped in a mono-vacancy in the Ge layer (Fig. 3) shows that the vacancy can trap no more than 7 He atoms, which is the same as that in the Si layer of  $\text{Ti}_3\text{SiC}_2$ . The lattice constant changes of  $\text{Ti}_3\text{GeC}_2$  induced by  $\text{V}-n\text{He}$  clusters ( $n = 0, 1 \dots 7$ ) are similar to the changes of  $\text{Ti}_3\text{SiC}_2$ . For the vacancy trapping fewer than 4 He atoms, the z-axis contracts, while the x-axis expands by about 0.5%, and with the

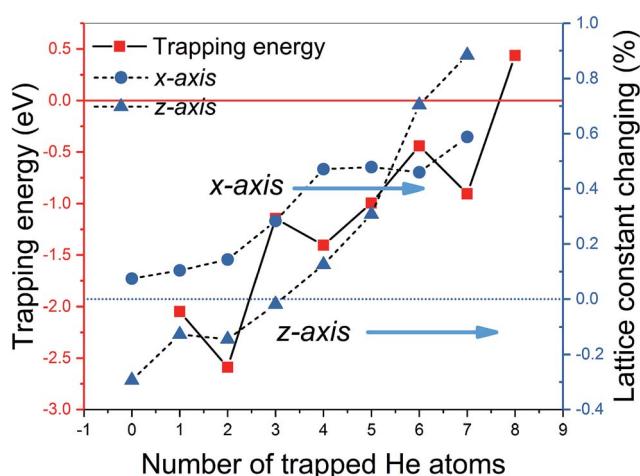


Fig. 3 The trapping energy (left y-axis) defined by eqn (5) and the corresponding lattice constant changing (right y-axis) with the number of He atoms trapped by a Ge mono-vacancy.

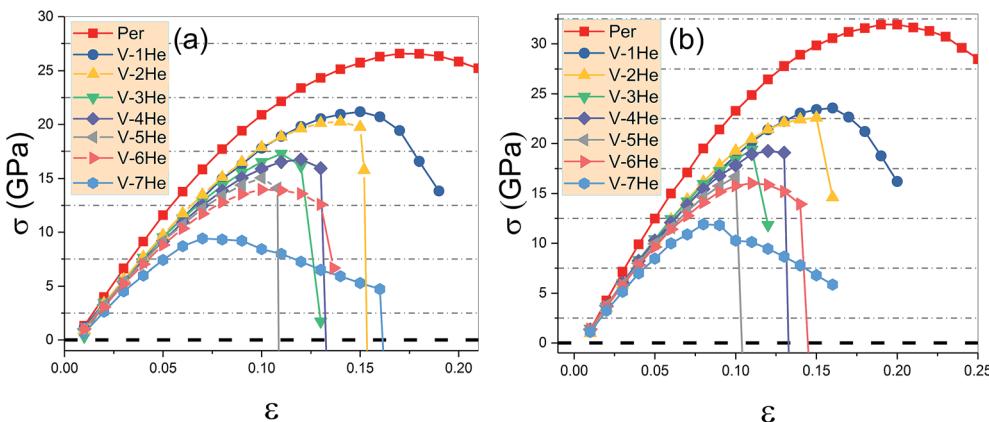


Fig. 4 The ideal tensile stress as the function of strain  $\epsilon$  in the [0001] direction in the presence of V- $n$ He ( $n = 0, 1 \dots 7$ ) for  $\text{Ti}_3\text{GeC}_2$  (a) and  $\text{Ti}_3\text{SiC}_2$  (b).

Table 1 The ideal tensile strength  $\sigma_M$  of  $\text{Ti}_3\text{AC}_2$  ( $\text{A} = \text{Ge, Si}$ ) with V- $n$ He clusters ( $n = 0, 1 \dots 7$ )

|                           | $\sigma_M$ (GPa) |       |       |       |       |       |       |       |
|---------------------------|------------------|-------|-------|-------|-------|-------|-------|-------|
|                           | Per              | 1He   | 2He   | 3He   | 4He   | 5He   | 6He   | 7He   |
| $\text{Ti}_3\text{GeC}_2$ | 26.56            | 21.19 | 20.86 | 17.27 | 16.75 | 15.05 | 13.96 | 9.42  |
| $\text{Ti}_3\text{SiC}_2$ | 31.93            | 23.57 | 22.59 | 19.38 | 19.24 | 16.70 | 16.04 | 11.90 |

increase in the He atoms, both the  $x$ - and  $z$ -axes expand by 0.6% and 0.9%, respectively.

As shown in Fig. 4, the ideal tensile strengths  $\sigma_M$  of perfect  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  are 31.93 GPa and 26.56 GPa, respectively, and the corresponding strains  $\epsilon_M$  are 0.19 and 0.17, suggesting that  $\text{Ti}_3\text{SiC}_2$  has better mechanical properties than  $\text{Ti}_3\text{GeC}_2$ . With presence of the He cluster formed by a mono-vacancy in the A layer, the mechanical strength is significantly degraded as the size of the cluster increases as summarized in Table 1. For example, in the presence of a V-1He cluster, the  $\sigma_M$  of  $\text{Ti}_3\text{SiC}_2$  (or  $\text{Ti}_3\text{GeC}_2$ ) reduces to 23.57 GPa (or 21.19 GPa), which is about 73.8% (or 79.8%) of the values for the perfect materials; meanwhile, the corresponding  $\epsilon_M$  decreases to 0.16 (or 0.15), and in the presence of a V-7He cluster, the  $\sigma_M$  and  $\epsilon_M$  of  $\text{Ti}_3\text{SiC}_2$  (or  $\text{Ti}_3\text{GeC}_2$ ) reduce to 11.90 GPa (or 9.42 GPa) and 0.08 (or 0.07), which are about 37.3% (or 35.5%) and 42.1% (41.2%) of the perfect ones. Clearly, the presence of V- $n$ He clusters ( $n = 1, 2 \dots 7$ ) strengthens the embrittlement.<sup>26-28</sup>

In the presence of He clusters trapped by a mono-vacancy in the A layer, the distances of A/Ti<sub>II</sub>, Ti<sub>II</sub>/C, and C/Ti<sub>I</sub> interlayers denoted by  $d_1$ ,  $d_2$  and  $d_3$  under strain in the [0001] direction were examined. As shown in Fig. 5, the V- $n$ He clusters ( $n = 1, 2 \dots 7$ ) result in swelling of the A/Ti<sub>II</sub> interlayer and contracting of the Ti<sub>II</sub>/C interlayer, while the C/Ti<sub>I</sub> interlayer remains nearly unchanged; the swelling is about ten times higher than the contracting (Fig. 5a1 and b1). For the materials without strain,  $d_1$  of  $\text{Ti}_3\text{SiC}_2$  (or  $\text{Ti}_3\text{GeC}_2$ ) increases from 2.03 to 2.41 Å (or 2.10 to 2.45 Å) as the He atoms increase from 1 to 7; meanwhile,  $d_2$  of  $\text{Ti}_3\text{SiC}_2$  (or  $\text{Ti}_3\text{GeC}_2$ ) decreases from 1.11 to 1.05 Å (or 1.09 to 1.03 Å). With the increase of the strain, the change in  $d_1$  is

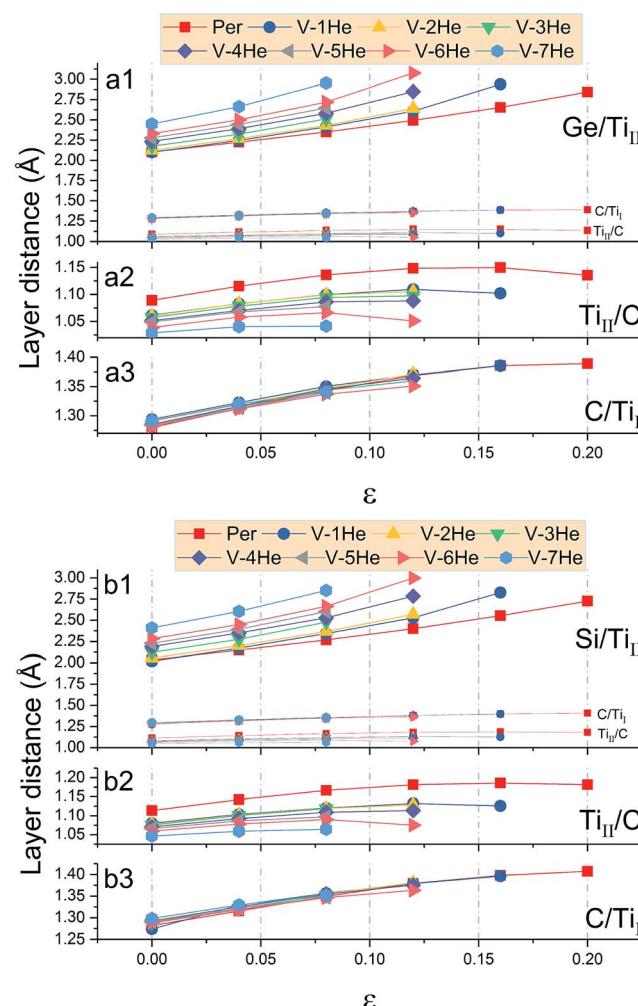


Fig. 5 The distances between A/Ti<sub>II</sub>, Ti<sub>II</sub>/C, and C/Ti<sub>I</sub> interlayers as the function of strain  $\epsilon$  for  $\text{Ti}_3\text{GeC}_2$  (a1) and  $\text{Ti}_3\text{SiC}_2$  (b1) with the presence of V- $n$ He clusters ( $n = 0, 1 \dots 7$ ) existing in the A layer. For clarity, the distances of Ti<sub>II</sub>/C and C/Ti<sub>I</sub> interlayers are magnified in (a2, a3) and (b2, b3), respectively.

**Table 2** The maximum strain  $\varepsilon_M$  of  $\text{Ti}_3\text{AC}_2$  ( $\text{A} = \text{Ge, Si}$ ) with  $\text{V}-n\text{He}$  clusters ( $n = 1, 2 \dots 7$ ) and the corresponding strain of each  $\text{A}/\text{Ti}_{\text{II}}$ ,  $\text{Ti}_{\text{II}}/\text{C}$ , and  $\text{C}/\text{Ti}_{\text{I}}$  interlayer

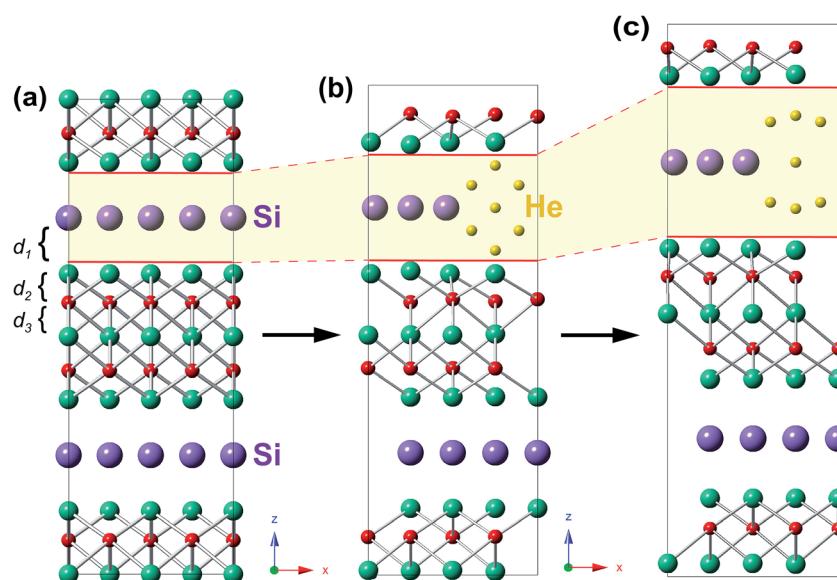
| Block   | Layer                             | Per    | 1He    | 2He    | 3He    | 4He    | 5He    | 6He    | 7He    |
|---|-----------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| <b><math>\text{Ti}_3\text{GeC}_2 (\varepsilon)</math></b> |                                   |        |        |        |        |        |        |        |        |
| $\text{Ti}_3\text{Ge}$                                    | Bulk                              | 0.17   | 0.15   | 0.14   | 0.11   | 0.12   | 0.1    | 0.1    | 0.07   |
|   | $\text{Ge}/\text{Ti}_{\text{II}}$ | 0.2832 | 0.3421 | 0.3221 | 0.2374 | 0.2757 | 0.2209 | 0.2417 | 0.1675 |
|   | $\text{Ti}_{\text{II}}/\text{C}$  | 0.0536 | 0.0434 | 0.0378 | 0.0407 | 0.0349 | 0.0260 | 0.0204 | 0.0146 |
|   | $\text{C}/\text{Ti}_{\text{I}}$   | 0.0830 | 0.0708 | 0.0700 | 0.0585 | 0.0614 | 0.0509 | 0.0494 | 0.0344 |
| <b><math>\text{Ti}_3\text{SiC}_2 (\varepsilon)</math></b> |                                   |        |        |        |        |        |        |        |        |
| $\text{Ti}_3\text{Si}$                                    | Bulk                              | 0.19   | 0.16   | 0.15   | 0.11   | 0.12   | 0.1    | 0.11   | 0.08   |
|   | $\text{Si}/\text{Ti}_{\text{II}}$ | 0.3183 | 0.3997 | 0.3531 | 0.3017 | 0.2710 | 0.2306 | 0.2678 | 0.1835 |
|   | $\text{Ti}_{\text{II}}/\text{C}$  | 0.0629 | 0.0423 | 0.0380 | 0.0418 | 0.0400 | 0.0298 | 0.0228 | 0.0169 |
|   | $\text{C}/\text{Ti}_{\text{I}}$   | 0.0977 | 0.0959 | 0.0804 | 0.0652 | 0.0647 | 0.0525 | 0.0559 | 0.0413 |

significantly faster than that in  $d_2$ . For example, in the presence of a V-7He cluster, when the strain reaches the maximum value  $\varepsilon_M$ , 0.08 for  $\text{Ti}_3\text{SiC}_2$  (or 0.07 for  $\text{Ti}_3\text{GeC}_2$ ),  $d_1$  of  $\text{Ti}_3\text{SiC}_2$  (or  $\text{Ti}_3\text{GeC}_2$ ) changes from 2.41 to 2.85 Å (or 2.45 to 2.86 Å), increasing by about 18.35% (or 16.75%), while  $d_2$  changes from 1.05 to 1.06 Å (or 1.03 to 1.04 Å), increasing by only 1.69% (or 1.46%). Under the maximum strain  $\varepsilon_M$  for  $V-n\text{He}$  clusters ( $n = 1, 2 \dots 7$ ) existing in the A layer, the strain of each interlayer is listed in Table 2. The results show that strain of the A/ $\text{Ti}_{\text{II}}$  interlayer is much larger than that of the others, and the differences become larger with the increase in cluster size. On further increasing the strain, fracture took place around the A layer. Fig. 6a and b show the structural changes of perfect  $\text{Ti}_3\text{SiC}_2$  caused by the presence of a V-7He cluster without strain. When this system was stretched to its maximum strain by 8%, the distance between the A/ $\text{Ti}_{\text{II}}$  interlayer containing a V-7He cluster increases by about 18.35%, while the distance between other A/ $\text{Ti}_{\text{II}}$  interlayers without the cluster remains nearly unchanged (Fig. 6c).

For  $\text{Ti}_3\text{GeC}_2$ , similar structural changes were also observed, showing heavy damage effects of the cluster on the bond energy.

It is notable that both the  $\text{Ti}_{\text{II}}/\text{C}$  and  $\text{C}/\text{Ti}_{\text{I}}$  interlayers are within the  $\text{Ti}_3\text{C}_2$  blocks, so the above simulation results suggest that  $\text{Ti}_3\text{C}_2$  blocks contribute more to the mechanical strength and structural stability. These results are consistent with the experimental observations that A layer is easily disordered, while the  $\text{Ti}_3\text{C}_2$  structure appeared unperturbed after irradiation.<sup>9,12</sup>

The above results suggest that the fracture of  $\text{Ti}_3\text{AC}_2$  would mostly occur between the A/ $\text{Ti}_{\text{II}}$  interlayer, which can be understood as follows. First, the MAX phases have the stacking sequence .../[M-X]/A/[M-X]/... in the [0001] direction with a characteristic 'zigzag' mode, and the bonds inside [M-X] blocks are relatively stronger than those between the A layer and [M-X] blocks.<sup>29-31</sup> Second, the presence of He clusters in the A layer severely reduces the strength of the Ti-A bonds, which can be seen from the maximum cleavage energy,  $G_c$ ,



**Fig. 6** The optimized structure of perfect  $\text{Ti}_3\text{SiC}_2$  (a) and the structure with a V-7He cluster existing in one of the Si layers without strain (b), which changes  $\text{Ti}_3\text{SiC}_2$  with the presence of a V-7He cluster to (c) when the system was stretched by 8% to its maximum strain.



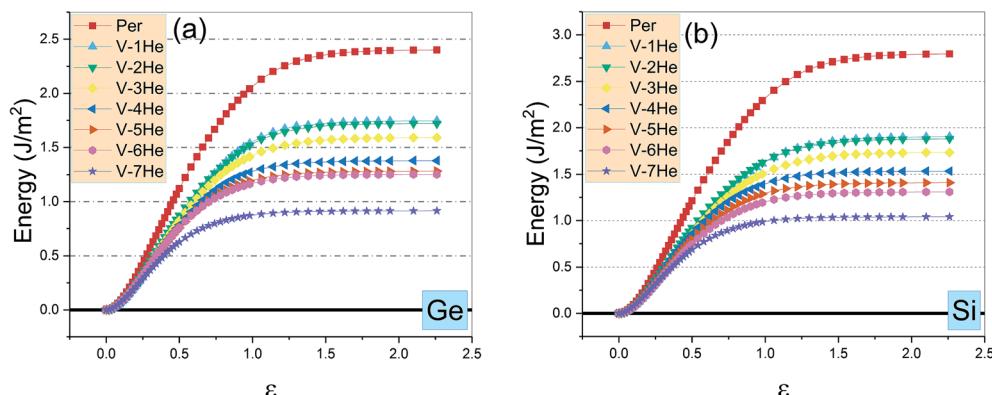


Fig. 7 The cleavage energy  $E_{\text{cl}}$  as the function of strain  $\varepsilon$  of the A/Ti<sub>II</sub> interlayer in the presence of V- $n$ He clusters ( $n = 1, 2, \dots, 7$ ) for Ti<sub>3</sub>GeC<sub>2</sub> (a) and (b) Ti<sub>3</sub>SiC<sub>2</sub>.

which is the saturated value of  $E_{\text{cl}}(d)$  when the distance  $d$  reaches infinity (cf. eqn (2)). As shown in Fig. 7, for the cleavage energy as the function of the strain  $\varepsilon$  of the A/Ti<sub>II</sub> interlayer, the calculated  $G_c$  for Ti<sub>3</sub>SiC<sub>2</sub> (or Ti<sub>3</sub>GeC<sub>2</sub>) without He clusters is 2.79 J m<sup>-2</sup> (or 2.40 J m<sup>-2</sup>), which is in good agreement with the value, 2.82 J m<sup>-2</sup>, reported in ref. 26. However, the value keeps decreasing with the increase in size of He cluster in the A layer and reduces to 37.22% (or 38.13%) of the perfect materials.

Although the He damage for Ti<sub>3</sub>GeC<sub>2</sub> is similar to that for Ti<sub>3</sub>SiC<sub>2</sub>, the latter should be a better candidate as a nuclear structural material because its ideal tensile strength  $\sigma_M$  and maximum strain  $\varepsilon_M$  are always clearly higher than that of the former in the presence (or absence) of the He clusters. In addition, the high mobility of a single He atom in the Si layer with only 0.05 eV diffusion barrier, which is significantly smaller than the value of 0.36 eV in the Ge layer, is beneficial for the He atoms to migrate quickly to the grain boundary.

## 4. Conclusion

Using DFT calculations, we systematically investigated the effects of He clusters formed in Ti<sub>3</sub>AC<sub>2</sub> (A = Ge, Si) on the mechanical properties and obtained the following conclusions. First, the interstitial He atoms homogeneously generated in Ti<sub>3</sub>AC<sub>2</sub> would immediately ( $\sim 10^{-6}$  s) migrate to the A layer at higher temperature ( $> 500$  °C) and form clusters of no more than 7 He atoms at a mono-vacancy in the A layer. Second, the cluster of V-7He atoms severely reduces the ideal tensile strength, 31.93 GPa, of Ti<sub>3</sub>SiC<sub>2</sub> (or 26.56 GPa of Ti<sub>3</sub>GeC<sub>2</sub>) to 11.90 GPa (or 9.42 GPa), and the corresponding maximum strain changes from 0.19 (or 0.17) to 0.08 (or 0.07), showing heavy damage effects on the mechanical properties. Third, the strain simulations showed that the fracture of Ti<sub>3</sub>AC<sub>2</sub> would mostly occur around the A layer with the presence (or absence) of the He clusters, whereas Ti<sub>3</sub>C<sub>2</sub> blocks are relatively stable, and the embrittlement was enhanced with the increase in He cluster size. At last, we conclude that as nuclear structural materials, Ti<sub>3</sub>SiC<sub>2</sub> should be better than Ti<sub>3</sub>GeC<sub>2</sub>.

## Conflicts of interest

There are no conflicts to declare.

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