First-principles study on the helium migration energies in $B_{12}X_2$ ($X=O, Si, P, As$) crystals for neutron absorber use

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**ABSTRACT**

Boron-carbide-based materials ($B_{12}X_2$) with two-atom instead of three-atom chains have better ductility, which indicates that they may be better alternatives to nuclear absorber materials than $B_4C$. In this study, we investigated the migration energy of neutron-induced helium interstitials using density functional theory calculations. As a result, we discovered that the migration energy of helium in $B_{12}Si_2$ and $B_{12}O_2$ is lower than that in $B_4C$, which suggests that these materials might be better in inhibiting the introduction of helium gas and subsequent volume expansion during the neutron irradiation. Moreover, we found that $B_{12}P_2$ and $B_{12}As_2$ have isotropic helium migration barriers, while $B_4C, B_{12}Si_2$, and $B_{12}O_2$ exhibited a strong anisotropy in the helium migrations.

**1. Introduction**

Boron carbide ($B_4C$) is the leading candidate for a neutron absorber for next-generation fast reactors, which are entrusted with the important task of providing sustainable nuclear energy [1,2]. However, due to the helium gas produced from the $^{10}B(n, a)^7Li$ reaction, the volume swelling of the $B_4C$ pellets during use has been a critical safety issue for the long-term use of the control rods [3–5]. Moreover, the brittleness of $B_4C$ makes the pellets very easy to break into small fragments under the internal stress induced by the heat gradient and helium gas production. These small fragments may enter the reserved narrow gaps between the absorber pellets and cladding tube, which would directly result in an early swelling-induced cladding failure. Considering the fact that the service life of the $B_4C$ control rods currently employed in the Japanese experimental fast reactor JOYO is far below the expected value [4,5], it is essential to develop a more reliable neutron absorber material that can withstand prolonged use in fast reactors.

Recently, with the use of theoretical quantum-mechanics calculations based on the density functional theory (DFT), An et al. [6] proposed a new idea for improving the ductility of the boron carbide materials by replacing the C–B–C chain with a more weakly bonded two-atom chain. The aim of this change is to avoid partial amorphization of the $B_4C$ grains under stress by enhancing the slip between the boron icosahedra. A series of investigations based on DFT calculations of $(B_{11}Cp)Si_2, (B_{10}Si_2)Si_2, B_{12}P_2$, and $B_{12}O_2$ revealed that these compounds with two-atom chains instead of three-atom chains are not likely to form amorphous bands under stress, which normally lead to brittle failure [6–9]. Compared to $B_4C$, these materials have similar boron content and improved ductility characteristics, and are therefore expected to outperform $B_4C$ as neutron absorbers for fast reactors by reducing the pellet fragmentation.

Meanwhile, carbon nanotubes (CNTs) are attracting increasing attention due to their excellent abilities to catalyze the recombination of radiation-induced defects and create exhaust paths for helium and other fission gases in their aluminum composites [10]. Therefore, the CNTs are worth investigating further to see if they have an inhibiting effect on the swelling of the $B_4C$ pellet by efficiently capturing and exhausting the helium gas produced from the $^{10}B(n, a)^7Li$ reaction. Moreover, CNTs could be employed as supplement materials to the carbon content in the carbon-deficient boron compounds such as $(B_{11}Cp)Si_2, (B_{10}Si_2)Si_2, B_{12}P_2$, and $B_{12}O_2$, and provide a neutron-spectrum softening effect. In addition, adding CNTs can enhance the toughness of the $B_4C$ pellets. Hitherto, $B_4C$/CNT composites with up to 10 vol% CNT, which can effectively improve the fracture toughness of the material through a fiber bridging effect, have been reported [11].

Since the helium atoms are generated inside the grains during the neutron irradiation, the efficiency of the CNT helium-atom capturing process is largely affected by the diffusivity of the helium atoms inside the grains. The helium diffusivity in these $B_{12}X_2$ materials is an
important indicator for predicting their performances as neutron absorbers. However, there are only few studies focusing on the effects of neutron irradiation on such materials. Moreover, neutron irradiation experiments are costly and require very long time.

Therefore, in this study, we employed DFT calculations as a preliminary study in order to predict the changes in the helium diffusivity by switching the C–B–C chains to Si–Si, P–P, O–O, and As–As chains. We investigated the helium migration energy in boron-carbide-like crystals that contain two-atom chains, including B$_{12}$O$_2$, B$_{12}$Si$_2$, B$_{12}$P$_2$, and B$_{12}$As$_2$, and compare the results to the helium migration energy in B$_2$C, which has been already calculated in the previous study [12]. It is considered to be the most crucial factor in distinguishing the effectiveness of excluding helium gas from the grains.

2. Computational details

All calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) [13,14]. The Perdew–Burke–Ernzerh variant of the generalized gradient (GGA-PBE) approximation was used to determine the exchange-correlation potentials [15]. Moreover, the electron-ion interactions were described by ultra-soft pseudopotentials [16]. Structural optimizations of the supercells were performed using a plane-wave cutoff energy of 450 eV, and the Brillouin zone was sampled with a single k-point at Γ for the B$_{12}$Si$_2$, and a 2 × 2 × 2 Monkhorst-Pack k-point mesh for B$_{12}$O$_2$, B$_{12}$P$_2$, and B$_{12}$As$_2$ to reach a total energy convergence of 0.01 eV per atom. One helium atom was doped into the interstitial sites of the 2 × 2 × 2 supercells of B$_{12}$O$_2$, B$_{12}$Si$_2$, B$_{12}$P$_2$, and B$_{12}$As$_2$, respectively. The cell parameters for the supercells with a helium interstitial-type defect were calculated with the cell parameters of the aforementioned structure models with one helium atom sitting at the center of the supercell. The lattice parameters after geometry optimizations are shown in Table 1. The lattice parameters of the B$_{12}$Si$_2$ structure showed a relatively large deviation from the experimental value obtained for B$_6$Si due to the lower silicon content, while the results from all other calculations were consistent with the experimental values. Note that the silicon boride compound B$_6$Si is reported to have a complex orthorhombic unit cell with 281 atoms [17]. The silicon borides with rhombohedral boron-carbide-like structures are considered to have extra silicon atoms that substitute boron atoms on the icosahedra [18–20]. In this study, we used the simplified B$_{12}$Si$_2$ structure in order to avoid unnecessary uncertainties.

The formation energies of defects were calculated using the following equation:

$$E_f = E_{\text{def}} - E_{\text{perf}} + n_{\text{He}}\mu_{\text{He}}$$

(1)

where $E_{\text{perf}}$ and $E_{\text{def}}$ are the total energies of the perfect structure model and defective structure model, respectively, and $n_{\text{He}}$ and $\mu_{\text{He}}$ are the number change and chemical potentials of the helium atoms in the structure, respectively, with $\mu_{\text{He}}$ being calculated from an isolated helium atom. The migration energies of helium interstitials were calculated by a transition state search between the decided start and ending defect structures using the method of complete linear synchronous transit/quadratic synchronous transit (LST/QST).

3. Results and discussion

3.1 Interstitial configuration of He in the B$_{12}$X$_2$ materials

Due to structural similarities, the possible interstitial sites of the B$_{12}$X$_2$ crystals (except for B$_{12}$O$_2$) were roughly the same as that of the B$_6$C crystal [12,24], (Figure 1). The interstitial helium atom could be located on both sides of the hexagon, which was formed by four equatorial atoms from the two icosahedra and the two atoms of the chain end, and on the extension line of the two-atoms chain, named $i_6$ and $i_7$, respectively. The space in the middle of the two-atoms chain, named $i_m$, was also investigated. In contrast, the helium interstitials in the B$_{12}$O$_2$ crystal were slightly different, the helium atoms seem not to be able to stably sit on the sites next to the hexagon. Instead, the helium atoms moved to the locations concentrated near the center of the two-oxygen-atom chains during the process of the geometry optimization. The distances between these final locations of the helium atoms to the middle points of the chains were less than 1 Å, and the total energy differences comparing to the defect structures with a helium atom located at the middle points of the chains were as low as 0.03 eV per supercell. Therefore, we did

| B$_{12}$Si$_2$ | B$_{12}$P$_2$ | B$_{12}$As$_2$ | B$_{12}$O$_2$ |
|--------------|--------------|--------------|--------------|
| Expt. $^a$ [18] | Expt. [21] | Expt. [22] | Expt. [23] |
| a(Å) | 5.60 | 5.36 | 5.36 | 5.24 | 5.26 | 5.33 | 5.32 | 5.34 | 5.15 | 5.14 | 5.16 | 147.0 | 129.8 | 130.0 | 122.6 | 121.7 | 122.8 | 130.0 | 129.3 | 130.3 | 102.9 | 102.8 | 103.4 |
| $\alpha$(°) | 68.74 | 69.08 | 69.19 | 69.56 | 69.52 | 69.30 | 70.50 | 70.48 | 70.26 | 62.94 | 63.17 | 62.96 |
| $\Omega$(Å$^3$) | 147.0 | 129.8 | 130.0 | 122.6 | 121.7 | 122.8 | 130.0 | 129.3 | 130.3 | 102.9 | 102.8 | 103.4 |

$^a$The lattice parameters were obtained from rhombohedral B$_6$Si.
not make a distinction between the interstitial sites crowded in the middle of the chains in the calculations. Figure 2 shows a schematic representation of the helium interstitial sites in a \( \text{B}_{12}\text{O}_{2} \) supercell. The sites inside the boron-icosahedra were ignored in this study because these sites have been previously reported as unfavorable for helium atoms [12,24,25]. The results from the calculations of the formation energies for the helium interstitials are listed in Table 2.

In the \( \text{B}_{12}\text{P}_{2} \) and \( \text{B}_{12}\text{As}_{2} \) crystals, the formation energies of helium interstitial atoms at the chain center sites (\( i_{m} \)) were approximately twice as much as those of other sites, which indicates that the \( i_{m} \) sites in \( \text{B}_{12}\text{P}_{2} \) and \( \text{B}_{12}\text{As}_{2} \) were also unfavorable helium interstitial sites. Hence, we excluded them from the migration path calculations. In contrast, the \( i_{m} \) sites of the helium interstitials in the \( \text{B}_{12}\text{Si}_{2} \) and \( \text{B}_{12}\text{O}_{2} \) crystals exhibited similar, relatively low formation energies to those of other sites. Moreover, without any exceptions, the lowest formation energies of the helium interstitial defects in these \( \text{B}_{12}\text{X}_{2} \) crystals were lower than those in the \( \text{B}_{4}\text{C} \) crystal, which indicated that the helium atoms inside the \( \text{B}_{12}\text{X}_{2} \) crystals could migrate to the lattice at a lower temperature than those in \( \text{B}_{4}\text{C} \).

### 3.2 Migration paths and energy barriers

By observing the distribution of stable helium interstitial sites in the \( \text{B}_{12}\text{X}_{2} \) crystals, we found that there were two migration paths to be investigated in order to understand the characteristics of the helium migration in different directions. One of these paths was parallel to the (111) plane, while the other one was along the [111] direction. The two migration paths and the respective calculated energy barriers are illustrated in Figure 3. The migration energy barriers for each path are presented in Table 3. Due to the fact that according to our calculations, the helium interstitials at the \( i_{m} \) sites
in the B$_{12}$Si$_2$ crystal were energetically more favorable than those at the i$_h$ sites, it was assumed the migrations between two i$_h$ sites would pass through the closest i$_m$ sites, which are not shown in Figure 3. However, this does not affect the results from the calculations of the migration barriers.

Schneider et al. [12] performed calculations on the barriers for helium migration in the B$_4$C crystal, and

![Figure 3](image_url)

**Figure 3.** (a) The two helium migration paths [27] and (b) the illustrated migration energy barriers. The excess atoms in the supercell are hidden for convenience.
reported the one for the path parallel to the (111) plane as 1.21 eV and that for the path along the [111] axis as 2.22 eV. The energy barrier for the helium interstitials migrating via the path parallel to the (111) plane in the $B_2O_2$ crystal was calculated to be 1.15 eV, and that for the helium interstitials migrating via the path along the [111] axis in the $B_2Si_2$ crystal was found to be 1.18 eV. This indicated that the helium interstitials could migrate faster in $B_2O_2$ and $B_2Si_2$ than in $B_4C$. Furthermore, due to the strong anisotropy of the migration barriers along the various directions, microstructure optimization, i.e. the fabrication of pellets of $B_2Si_2$ and $B_2O_2$ with the majority of grains aligned in the same direction, could be an effective method to improve the performance of excluding helium atoms from the crystals. In addition, since the rhombohedral $B_4Si$ phase (the structure was simplified to $B_2Si_2$ in this study) decomposes into orthorhombic $B_2Si$ and Si at high temperatures (1100–1390°C [26]), more experimental data are needed in order to assess the effect of this decomposition on the reactor safety when the material is employed in control rods.

In contrast to $B_2O_2$ and $B_2Si_2$, the migration of helium interstitials in the $B_2P_2$ and $B_2As_2$ crystals was found to be isotropic. This was indicated from the fact that the helium interstitial atoms would need to overcome energy barriers of 1.65 and 1.54 eV in $B_2P_2$ and $B_2As_2$, respectively, between the $i_6$ sites, in order to migrate in any direction. It is expected that the flat disk-like helium bubbles may not appear in the neutron-irradiated/helium-implanted $B_2P_2$ and $B_2As_2$ crystals since they should be initiated by the anisotropic helium diffusion.

4. Conclusions

In summary, the migration barriers of helium interstitial atoms in the $B_2X_2$ crystals ($X = O, Si, P, As$) were studied using DFT calculations. The results from the DFT analysis indicated a low helium migration barrier in the direction along the [111] axis of $B_2Si_2$ and the path parallel to the (111) plane of $B_2O_2$. Hence, it is expected that the grain-orientation-optimized pellets of $B_2Si_2$ and $B_2O_2$ would exhibit a better performance of excluding helium gas than that of $B_4C$. In contrast to $B_4C$, $B_2Si_2$, and $B_2O_2$, the helium migration barriers of $B_2P_2$ and $B_2As_2$ were isotropic, which could result in different morphology in the neutron-induced helium bubbles.

All in all, our work suggests that the $B_2Si_2$ and $B_2O_2$ crystals would potentially have a better performance in inhibiting the volume expansion due to the faster helium exhaust. However, further experiments are needed in order to perform a comprehensive evaluation of the ability of $B_2X_2$ crystals to substitute $B_4C$ as neutron absorbers in fast reactors.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Table 3. The calculated migration barriers (in eV) of helium interstitial atoms in each path.

| Migration path     | $B_2Si_2$ | $B_2P_2$ | $B_2As_2$ | $B_2O_2$ | $B_4C$ [12] |
|--------------------|-----------|-----------|-----------|----------|-------------|
| Along (111) plane  | 1.95      | 1.65      | 1.54      | 1.15     | 1.21        |
| Along [111] axis   | 1.18      | 1.65      | 1.54      | 3.23     | 2.22        |
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