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Migrating and clustering of He atoms in Ti_3SiC_2: First-principles calculations

Quan Song [a,b], Peng Zhang [a,b], Jun Zhuang [c], Xi-Jing Ning [a,b,*]

[a] Institute of Modern Physics, Fudan University, Shanghai 200433, China
[b] Applied Ion Beam Physics Laboratory, Fudan University, Shanghai 200433, China
[c] Department of Optical Science and Engineering, Fudan University, Shanghai 200433, China

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ABSTRACT

The diffusion path of single He atom in Ti_3SiC_2 was investigated by first principle calculations, showing that the He atoms generated homogenously in the material will quickly migrate into the Si layer at higher temperatures (>500 °C) although a small fraction of them may be trapped by vacancies in the C layer at room temperature. Our further calculations showed that the largest He clusters formed in the Si layer consists of no more than 7 He atoms, corresponding to volume swelling of only 2% at most, and the other He atoms may flow into the grain boundaries because the barrier for a He atom diffusing in the Si layer is only 0.05 eV. These results indicate that Ti_3SiC_2 owns good tolerance of He damage.

1. Introduction

Future fission and fusion reactors (e. g., Gen. IV and ITER) are expected to operate for more than four decades [1–4], which challenges the design of structural materials. The so called MAX phases nano-laminated crystal ceramics with chemical formula $M_{n+1}AX_n$ (n = 1, 2, or 3, M: an early transition metal, A: group IIIA or IVA element and X: carbon or nitrogen), are considered to be promising potential structural materials used in future nuclear reactors because they combine many attractive properties of both metallic and ceramic in nature [5], such as easy machinability, low density, good electrical and thermal conductivity, and damage tolerance [6,7]. Recently, two of the typical MAX materials, Ti_3SiC_2 and Ti_3AlC_2, are arousing great interests of researchers [8–12], and some experiments have shown their excellent tolerance of nanometer scaled amorphization and irradiation induced damages. In many cases, He impurities are produced in nuclear reactors by (n, α) transmutation reactions and lots of earlier experimental observations showed that He could easily migrate, aggregate and form bubbles in metals, resulting in seriously degradation of the materials' mechanical strength and shortening the service time [13]. In fact, He bubbles have been observed in Ti_3AlC_2 irradiated by He ions [14], and therefore the behaviors of He atoms in Ti_3AlC_2 and Ti_3SiC_2 as well as the effects on the MAX phases ceramics should be completely understood at atomic level. Recently, Patel et al. irradiated Ti_3AlC_2 samples with 200 keV He ions (8×10^{17} cm^{-2}; 14 at.%) at 500 °C and found that the Al layers were disordered while the Ti_3C_2 layers remained intact after irradiation [15], revealing the good tolerance of He irradiation. Xiao and Yang et al. via ab initio methods illustrated that H/He most energetically favors near the Al-layer [16,17]. On Ti_3SiC_2, however, very limited experimental studies on the behaviors of He atoms in the material were reported, though some researchers explored the effect of Xe, Kr and Au, heavy ions irradiation, and found irradiation induced hardness and anisotropic swelling [18,19]. Previous theoretical studies mainly focused on the solution energy of a He atom in different sites in Ti_3SiC_2 and the effect on the mechanical properties [20,21].

It is notable that He atoms are generated homogeneously by high energy irradiation in each atomic layer of the MAX phase ceramics used as nuclear structural materials, such as the situation in Ti_3SiC_2 shown in Fig. 1, the generation rate of He atom in the Ti (Ti_I or Ti_{II}) layer is the same as that in the Si or C layer. Thus, in order to predict the final distribution of He atoms in the materials for evaluating the effect on the mechanical properties, we need to know not only the solution energies of He atom in each layer but also the probability for the He atoms diffusing between different layers because if the interlayer diffusion is prohibited, then the total number of He atoms in each layer should be the same and

* Corresponding author at: Institute of Modern Physics, Fudan University, Shanghai 200433, China.
E-mail address: xjning@fudan.edu.cn (X.-J. Ning).

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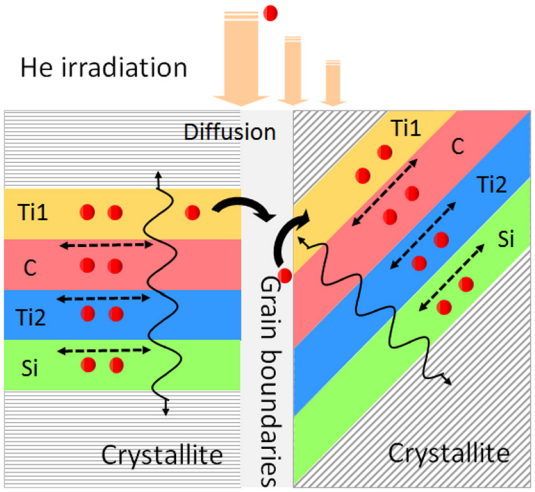

Fig. 1. Schematic of possible migration paths for He atoms generated homogenously in Ti_3SiC_2.

independent of the solution energy. Furthermore, the nuclear irradiation could produce many vacancies in each layer to trap He atoms to form clusters, so the maximum number of the He atoms trapped by a vacancy and the mobility of He atoms within each layer determines how fast the He cluster grows and how many He atoms stay in the atomic layer.

In the present work, we first investigated the migration tendency of He atoms generated homogenously in Ti_3SiC_2 by first principle calculations of the diffusion barriers, showing that the He atoms will quickly migrate into the Si layer at higher temperatures (>500°) even if there exist vacancies in the C or Si layers. Then we examined the capacity for a vacancy in the Si or C layer to trap He atoms by calculating the trapping energy to see if the He atoms aggregated in a vacancy in the layers can produce additional vacancy. These results suggest a full picture for the He atoms migrating in the materials.

2. Computational details

Ti_3SiC_2 is a hexagonal crystal structure with space group $P6_3/mmc$ as shown in Fig. 2, where the two types of non-equivalent Ti (Ti_I and Ti_{II}) occupy 2*a* and 4*f* respectively, Si 2*b*, and C 4*f* Wyckoff positions and the possible stable interstitial positions for He atom to stay could be as follows: a hexahedral site I_{Hex1} (I-CSi) surrounded by three Si and two C atoms, a hexahedral site I_{Hex2} (I-SiTi_{II}(Hex)) encompassed by three Si and two Ti_{II} atoms, a octahedral site I_{Oct} (I-SiTi_{II}(Oct)) surrounded by three Si and three Ti_{II} atoms, a tetrahedral site I_{Tetra1}(I-Ti_ITi_{II}) surrounded by one Ti_I and three Ti_{II} atoms, and a tetrahedral site I_{Tetra2} (I-CC) surrounded by four C atoms.

The solution energy of a He atom in the materials is the same as that in [22]:

$$E^s_{He} = E(per + He) - E(per) + E(He_{iso}), \quad (1)$$

where $E(per + He)$ is the total energy of a perfect Ti_3SiC_2 with an interstitial He atom, $E(per)$ the energy of a perfect Ti_3SiC_2, and $E(He_{iso})$ the energy of an isolated He atom. If an atom A of Ti_3SiC_2 is absent to form a vacancy, the formation energy is defined as:

$$E^f_{V_A} = E(V_A) - E(per) + \mu_A, \quad (2)$$

where $E(V_A)$ is the total energy of the system without A atom and μ_A the chemical potential, which are chosen as one of Hexagonal close-packed bulk α-Ti, face-centered diamond-cubic Si and graphite C.

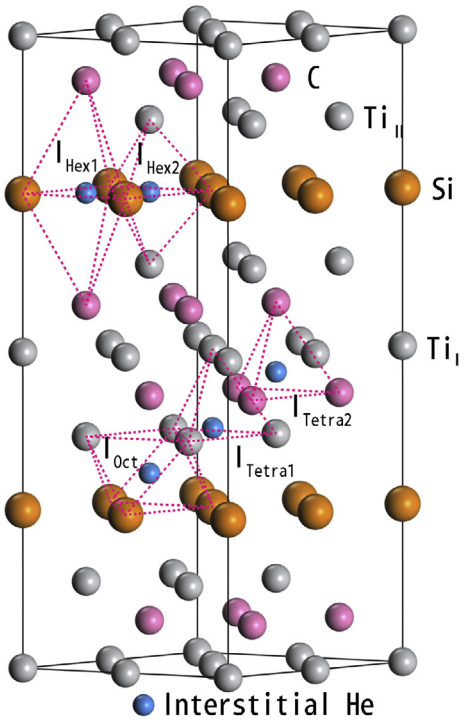

Fig. 2. Layered crystal structure of Ti_3SiC_2 and the possible occupations of He with larger free volume illustrated by red dashed lines are I_{Hex1}, I_{Hex2}, I_{Oct}, I_{Tetra1}, I_{Tetra2}. The Silver, Pink, Orange and Blue ball present Ti, C, Si, and He atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A vacancy in the material may trap more than one He atom. In order to estimate the maximum number of He atoms trapped by a vacancy, we define trapping energy as follows:

$$E_{trap} = E(per + nHe, V) - E(per + (n-1)He, V) - E^s_{He}, \quad (3)$$

where $E(per + nHe, V)$ is the total energy of the system with n He atoms adsorbed in the vacancy, E^s_{He} the lowest solution energy determined by Eq. (1). The maximum number of He atoms trapped by a vacancy is determined when $E_{trap} \geqslant 0$.

The first-principle calculations have been performed within the Vienna ab initio simulation package, where a gradient-corrected form of the exchange correlation functional generalized gradient approximation (GGA-PW91) was employed [23,24]. For detailed calculation settings, the cutoff energy of the plane-wave basis set was 500 eV, systemic calculations have been performed on supercells of $3 \times 3 \times 1$ unit cells containing 108 atoms where $5 \times 5 \times 2$ Monkhorst-Pack k-points sampling for Brillouin zone was chosen. The lattice vectors of the cell and all the atoms were fully relaxed until the convergence was achieved as the force was less than 0.01 eV/Å, whereas the total energy tolerance was set 0.1 meV. The climbing image nudged elastic band (CI-NEB) method was employed to obtain minimum energy path of the He atom when the initial and final configurations were known. The forces on all atoms in each image of the CI-NEB chain were converged to 0.05 eV/Å.

To test the reliability of our calculations method, we optimized the structure of perfect Ti_3SiC_2 to obtain the lattice constants (Table 1), which are in good agreement with previous experimental and theoretical results [20,25–27].

3. Results and discussions

Due to the inert properties, the He atoms generated in Ti_3SiC_2 may diffuse between different atomic layers or within each layer,