

# Stability and kinetics of helium interstitials in boron carbide from first principles



Anton Schneider<sup>a,\*</sup>, Guido Roma<sup>a,\*</sup>, Jean-Paul Crocombette<sup>a</sup>, Vianney Motte<sup>b</sup>,  
Dominique Gosset<sup>b</sup>

<sup>a</sup> DEN-Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay, F-91191 Gif sur Yvette, France

<sup>b</sup> DEN-Service de Recherches de Métallurgie Appliquée, CEA, Université Paris-Saclay, F-91191 Gif sur Yvette, France

## ARTICLE INFO

### Article history:

Received 8 June 2017

Received in revised form

7 September 2017

Accepted 13 September 2017

Available online 18 September 2017

### Keywords:

Density functional theory

Boron carbide

Helium

Stability

Kinetics

Nudged elastic bands

## ABSTRACT

When boron carbide is used in nuclear reactors as a neutron absorber, helium concentrations on the order of a few atomic percent can be attained. It is thus of primary importance to know the distribution and kinetics of helium atoms in boron carbide. In spite of a variety of experimental works devoted to the characterization of the microstructure and He bubbles in boron carbide irradiated in reactor, there is a serious lack of knowledge concerning the basic mechanisms governing helium kinetics. This study is devoted to the stability and mobility of helium interstitial atoms in carbon rich boron carbide. The lowest energy He insertion sites were screened through density functional theory and the most probable migration paths and energy barriers were investigated using the nudged elastic bands (NEB) approach. The results suggest that in a wide range of temperatures He interstitials undergo 2D diffusion confined between two  $\langle 111 \rangle$  planes. The onset of 3D diffusion is expected, according to our calculations, with an activation energy close to 2 eV.

Our result is in qualitative agreement with the observation of flat bubbles with  $\langle 111 \rangle$  orientation, although a quantitative comparison with He diffusion data is hindered by discrepancies and microstructure issues in available experimental results.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to boron high neutron absorption cross section, boron carbide is used in shutdown and control rods of various types of nuclear reactors; moreover, due to the absence of a resonance region in the neutron absorption cross section, it is the best candidate for control rods of fast breeder reactors. The nuclear reaction taking place when neutrons are absorbed by the  $^{10}\text{B}$  isotope leads to the productions of large quantities of helium and lithium. In most cases the lifetime of the rods is limited by the swelling and microcracking occurring in the material, in particular due to the accumulation of helium bubbles [1].

Flat He bubbles preferentially oriented in the  $\langle 111 \rangle$  planes in irradiated boron carbide were reported already in the early seventies [2,3]. A transition from flat to equiaxed bubbles was reported at temperatures around 1500° C [4]. Other works reported

spherical bubbles [5–7] even at relatively low temperature, probably due to different irradiation and annealing conditions. In the following decades additional works provided further evidence for  $\langle 111 \rangle$ -oriented flat bubbles, with a more refined quantitative analysis of bubbles sizes as a function of temperature and discussed the conditions in which they are expected [8–10]. The earliest studies did not observe bubbles at grain boundaries [2], and concluded that He diffusion was accelerated along them, but this was due to open porosity of the samples. In more recent works He bubbles were detected at grain boundaries and it was then considered that He is trapped there [10,11]. Whether single He atoms also tend to segregate and get trapped at grain boundaries, or trapping occurs only for He clusters above a given threshold size, is not clearly understood yet.

It is clear that, in order to establish more reliable models for He clustering and release from boron carbide under irradiation, reliable data on diffusion activation energy are desirable. Diffusion of He in boron carbide has first been discussed by Clayton [12] in the framework of He release from  $\text{B}_4\text{C}$  specimens irradiated in reactor at room temperature: with strong assumptions concerning the

\* Corresponding author.

E-mail address: [guido.roma@cea.fr](mailto:guido.roma@cea.fr) (G. Roma).

spatial distribution of He, a diffusion activation energy of  $1.26 \pm 0.13$  eV has been estimated. However, considering the results of later works on dose dependences and bubbles formation, one would rather suppose that a large portion of He was trapped in grain boundaries and the measured activation energy might be associated with the release of single He atoms from trapped bubbles. More involved diffusion models [13] considered indeed both He diffusion in the matrix and He detrapping from so called “accumulation centers”, it is however unclear which are the activation energy values used. The activation energy given by Clayton was used in another model of He release [14], but the diffusion prefactor was significantly reduced in order to reproduce experimental results.

In this paper we investigate the elementary diffusion mechanisms and activation energy for interstitial He atoms from first principles calculations based on density functional theory. We focus mainly on the  $B_4C$  stoichiometry —using the  $B_{11}C$ -CBC structure described later— but, for the sake of comparison, the boron rich  $B_{12}$ -CBC configuration was also tackled.

We predict the relative stability of substitutional and interstitial He insertion sites and find minimum energy paths between the most stable ones. The paper is organised as follows: section 2 is devoted to the technical details of our approach; section 3 is subdivided in subsection 3.1, which describes the stability of insertion sites, subsection 3.2 which discusses the diffusion mechanisms, and subsection 3.3 on the role of the electronic charge density. In section 4 we discuss the results in connection with experimental results. The main results are summarized in the final section 5.

## 2. Model structures and methods

Boron carbide has a rhombohedral crystalline structure, which is maintained in a large range of stoichiometry [15]. Here we focus mainly on the carbon rich side, with stoichiometry  $B_4C$  for which we assume the structure shown in Fig. 1,  $B_{11}C$ -CBC, where  $B_{11}C$  icosahedra are connected by CBC chains. The latter structure is considered to be the most stable structure for this stoichiometry [16]; however some disorder, at least in the placement of the icosahedral carbon, is expected [15,17].

In absence of disorder, the icosahedral carbon atom, sitting on a polar site, should induce a monoclinic distortion; only recently an experimental evidence of such distortions was found in the presence of asymmetric twin boundaries [18], while X-ray diffraction (XRD) studies reported a rhombohedral structure. This distortion is very small according to our calculations (less than 12 arcminutes, or  $0.2^\circ$  on the rhombohedral angle in the unit cell). The corresponding lowering of the energy due to the distortion is less than 0.015 eV/atom. Moreover, a test for a He interstitial, reveals a lowering of only 0.05 eV in the formation enthalpy with the distorted cell; this check was made on the interstitial site called *type 2 site* in the following, which is the only one not aligned with the rhombohedral axis. We then decided to keep the rhombohedral structure in our defect calculations, which were performed at the equilibrium volume of the  $B_{11}C$ -CBC structure. We have also checked that full volume relaxation leads to negligible changes in the solution energy for the  $2 \times 2 \times 2$  supercell; in the worst case a difference of 0.11 eV was found and in most other cases it is below 0.04 eV.

Almost all the calculations in this work are based on density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP) [19,20]. A few test calculations, for comparison, were performed with the Quantum-Espresso (QE) package [21]. We chose, for the exchange-correlation, the optB86b + vdW functional [22], containing a Van-der-Waals long-range non-local term and an optimized version of the Bethe 86 exchange term. The projector augmented wave (PAW) method was used for the electronic

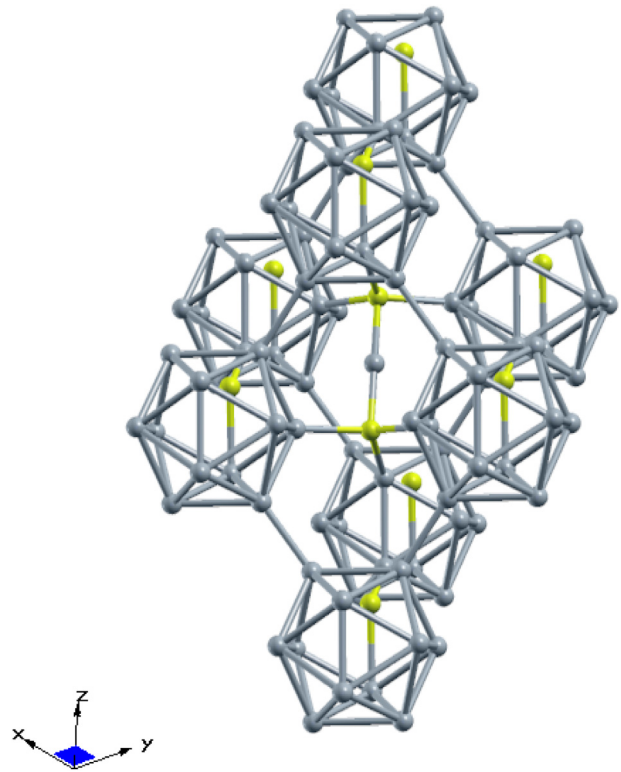


Fig. 1. Rhombohedral structure of  $B_{11}C$ -CBC. Carbon atoms are yellow, boron are gray. The C-B-C chain, connecting six of the eight  $B_{11}C$  icosahedra is clearly visible in the center. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

structure.

Following the relaxation tests that were carried out, the energy cutoff were set to 400 eV for VASP calculations.

A  $3 \times 3 \times 3$  Monkhorst-Pack k-point mesh was used for the 15-atom unit cell for integration over the Brillouin zone. With these parameters the total energy of the unit cell is converged at 0.05 eV. The  $2 \times 2 \times 2$  supercell (120 atoms) and the  $3 \times 3 \times 3$  supercell (405 atoms) were sampled with the  $\Gamma$  point. Atomic relaxations at constant volume were performed down to a maximum atomic force of 0.05 eV/Å.

For comparison, we were led to use the hybrid functional HSE06 [23] with a  $\Gamma$  centered k-point grid in a few cases. Unless stated otherwise, all calculations presented here were performed in a  $2 \times 2 \times 2$  supercell, which turned out to be reasonably well converged for solution and migration energies.

The first step in the systematic study of the helium insertion sites in boron carbide was the study of its possible substitutional sites (i.e., the 15 distinct atomic sites of the defect free boron carbide system). We calculated both the solution energy and incorporation energy for each site. To write the helium incorporation energy in a substitutional site we need the total energies of the system with a vacancy ( $E_{tot}^{vac}$ ), the one of the system containing a substitutional helium atom ( $E_{tot}^{He}$ ) in the vacant site and the He chemical potential  $\mu_{He}$ ; we take the latter as the energy of an isolated He atom (the binding energy of the He-dimer is negligible [24] with respect to formation energies). The incorporation energy is then:

$$E_{inc}^{He} = E_{tot}^{He} - E_{tot}^{vac} - \mu_{He} \quad (1)$$

The results are presented for carbon rich thermodynamical

Download English Version:

<https://daneshyari.com/en/article/5453811>

Download Persian Version:

<https://daneshyari.com/article/5453811>

[Daneshyari.com](https://daneshyari.com)