



Energetic stability of solute–carbon–vacancy complexes in bcc iron

Alexander Bakaev^{a,b,c,*}, Dmitry Terentyev^a, Evgeny E. Zhurkin^b, Dimitri Van Neck^c^a SCK•CEN, Nuclear Materials Science Institute, Boeretang 200, Mol B2400, Belgium^b Department of Experimental Nuclear Physics K-89, Institute of Physics, Nanotechnology and Telecommunications, St. Petersburg State Polytechnical University, 29 Polytekhnicheskaya str., 195251 St. Petersburg, Russia^c Center for Molecular Modeling, Department of Physics and Astronomy, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium

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ABSTRACT

The strong binding between a vacancy and carbon in bcc iron plays an important role in the evolution of radiation-induced microstructure. Our previous *ab initio* study points to the fact that the vacancy–carbon (V–C) pair can serve as a nucleus for the solute-rich clusters. Here, we continue the *ab initio* study by considering the interaction of mixed solute clusters (Mn, Ni and Si) with the V–C pair, and the interaction of typical alloying elements of Fe-based steels (i.e., Mn, Ni, Cu, Si, Cr and P) with di-carbon–vacancy pair (V–C₂). We have identified the sequence of growth of Ni, Si and Mn solute-rich clusters nucleating on the V–C pair. The mixed-solute–V–C configurations are found to be less stable clusters than pure-solute–V–C clusters with the energy difference up to 0.22 eV per four atoms. The V–C₂ pair is found to be as strong nucleation site for the solute-rich clusters as the V–C pair. Only Si solute atom stands out from the trend showing a weaker affinity to the V–C₂ complex by 0.09 eV compared to the attraction to the V–C pair. The overall results point to the importance of taking into account the existence of both V–C and V–C₂ complexes in studying the formation of solute-rich clusters in Fe-based steels for nuclear applications.

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1. Introduction

The safe exploitation of nuclear reactors requires a deep understanding of the complex mechanisms leading to radiation-induced degradation of the structural reactor pressure vessel (RPV) steels. Generally, the effect of radiation consists in [1] (a) agglomeration of in-cascade-created interstitials and vacancies in the form of dislocation loops and nano-voids, (b) enhanced diffusion of solute atoms. The latter can be trapped by the radiation-induced lattice defects, which, in turn, can serve as nucleation sites for the solute-rich clusters. The presence of such objects in the material leads to the obstruction of dislocation movement and, consequently, to the degradation of mechanical properties: increase of the yield stress and embrittlement (reduction of elongation to fracture). The appearance of these undesirable macroscopic effects determines the necessity of the study of nucleation and formation of solute-rich features in the nuclear steels.

The presence of the clusters, containing several different minor alloying elements, in various commercial steels has already been revealed [2–7] using the high precision techniques including atom

probe tomography (APT). Although their density is quite high (up to 10^{24} m^{-3}), their linear size is about one nanometer, which gives no chance to study their internal structure using the transmission electron microscopy (TEM). The recent *ab initio* calculations [8–10] point to the fact that the solute–solute interaction is too weak to explain the nucleation and growth of such complexes. The study of the Fe–Mn–Ni–Cu alloy as a model for the RPV steel has pointed to the association of the solutes with the in-cascade created dislocation loops [11], which was supported by the *ab initio* results showing the high affinity of Mn to the self-interstitial atoms [10] and a possibility of the formation of Ni–Mn <110> mixed dumbbells [11]. The combination of APT and positron annihilation spectroscopy (PAS) methods has revealed [12,13] the formation of solute–vacancy clusters in both Western and Russian RPV steels. Hence, the effect of vacancies on the nucleation and growth of the solute-rich clusters should be elaborated.

In the Fe-based steels the carbon atoms play an important role interacting with vacancies [14,15]. The *ab initio* calculations prove that the dissolved carbon (a) occupies the octahedral interstitial positions in the body-centered cubic iron (bcc Fe) [16], (b) forms stable (immobile) vacancy–carbon complexes which can grow further [16,17]. The stability of the latter together with the mobility and stability of vacancies and vacancy clusters is defined by the carbon concentration and its distribution in the material [18,19].

* Corresponding author at: SCK•CEN, Nuclear Materials Science Institute, Boeretang 200, Mol B2400, Belgium.

E-mail address: alexander.bakaev@ugent.be (A. Bakaev).

In our recent *ab initio* study [20], we have verified the stability of the solute–carbon–vacancies complexes by considering the interaction of the typical alloying elements (Mn, Ni, Cu, Si, Cr and P) in ferritic steels with a vacancy–carbon pair (V–C). It was found that all the considered solutes form stable triple clusters along with the increase of the total binding energy by 0.2–0.3 eV. As a result of the formation of energetically favorable solute–carbon–vacancy triplets, the dissociation energy for vacancy/carbon emission is also increased by ~0.2–0.3 eV, suggesting that the solutes enhance the thermal stability of the carbon–vacancy complex. Association of the carbon–vacancy pairs with multiple (more than two) solute atoms of the same kind was found to be favorable only for Ni, Cu and P and not for Mn, Si and Cr.

The current work is devoted to the further study of the stability of solute–vacancy–carbon complexes in bcc Fe. We study the possible affinity of multiple mixed solute (Mn, Ni and Si) clusters to a vacancy–carbon pair and also consider the solute–V–C₂ complexes. The V–C₂ cluster is essentially more thermally stable (by 1 eV [18]) than the V–C pair and therefore its formation is possible in carbon-rich steels. The sufficient binding energy of the V–C₂ complex, found in [18], implies its stability at least up to 600 K and therefore these complexes are expected to present in the RPV steel matrix under standard exploitation conditions.

2. Computational details

The DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP) [21,22] using the projector-augmented wave (PAW) potentials [23,24]. The electron exchange–correlation functional was described within the generalized gradient approximation using PW91 functionals [25], with a Vosko–Wilk–Nusair interpolation [26]. For Fe, Cr, Mn, Si, Ni, Cu, P and C pseudo potentials with 8, 6, 7, 4, 10, 11, 5 and 4 valence electrons were used, respectively. Ionic relaxation was performed using the conjugate gradient algorithm with a force convergence criterion of 0.03 eV/Å. All the calculations were done keeping the cell shape and volume (equal to the equilibrium volume of bulk iron) constant. The energy cutoff for calculations was 450 eV which was checked to be large enough to provide the converged results. A 3 × 3 × 3 k-point mesh was sampled by the Monkhorst and Pack scheme for the systems with 128 atoms. The lattice parameter of pure ferromagnetic Fe is taken to be 2.831 Å following the previous studies [8,9,27].

Given that we perform spin-polarized calculations in the ferromagnetic system and introduce an anti-ferromagnetic impurity (i.e., Mn), one needs to be careful when selecting the initial value of the magnetic moment to ensure that the true minimum energy configuration is obtained after the relaxation. For the configurations involving Mn, we performed additional calculations varying the absolute value and sign of the initial magnetic moment of Mn as some of the results turned out to be particularly sensitive to this choice. Below, we report the results corresponding to the lowest energy configurations only.

To assess the binding energy we apply the standard definition conventionally used in many similar DFT works [8]. The binding energy of n defects $\{A_i\}$ is defined as [8]:

$$E_b(\{A_i\}) = \sum_{i=1}^n E(A_i) - [E(\{A_i\}) + (n-1)E_0], \quad (1)$$

where $E(A_i)$ is the energy of the configuration containing A_i only, $E(\{A_i\})$ is the energy of the configuration with all the n defects and E_0 refers to a configuration containing no defects or impurities, i.e., bulk bcc iron. Following this notation, a positive value implies an attractive interaction and vice versa.

3. Results and discussion

3.1. Stability of mixed solute clusters attached to V–C pair

We have considered the interaction of the solutes of different kind including Mn, Ni and Si with a V–C pair, complementing the results of our previous study [20], where it was established that it is energetically favorable for a V–C pair to accumulate solute atoms of the same kind: up to four of Ni, Cu and P, and up to two atoms of Mn, Si and Cr.

The modeling of the mixed solute clusters has revealed several the most stable configurations which are summarized in the Table 1. Firstly, we have identified the most stable configuration and chemistry for S₂–V–C complex. Then, we have verified the possibility of its growth to the S₃–V–C and S₄–V–C clusters by the consecutive addition of different solute atoms.

We clearly see that the association of the mixed solute clusters to the V–C pair remarkably increases the solute–solute binding. For instance, the binding energy of Mn with the Si–V–C complex raises by 0.03–0.17 eV as compared to the binding energy of the Mn–Si pair [10]. No attractive interaction between the Ni–Mn pair in pure bcc Fe was found [11], while there is an attraction of 0.21–0.25 eV between Ni and Mn in the vicinity of the V–C pair. Similarly, the Ni–Si binding raises from 0.13 eV up to 0.26 eV in the presence of the V–C pair. Further growth of S₂–V–C pairs is most energetically favorable by the addition of extra nickel atoms. Also we have noted, that the total binding energy (sol–sol–sol–sol–V–C) of the Ni–Mn–Ni–Ni–V–C and Ni–Si–Ni–Ni–V–C complexes is by 0.14 and 0.22 eV lower than the total binding energy of the Ni–Ni–Ni–Ni–V–C complex, respectively. This data points to the fact that the growth of solute-rich complexes by adding the mixed kind of atoms is less energetically favorable than keeping the pure solute-rich clusters.

3.2. Stability of mixed solute clusters attached to V–C₂ complexes

In the bcc Fe there are two possible energetically stable V–C₂ spatial arrangements shown in Fig. 1b and c, which will be referred to as ‘linear’ and ‘Γ-shaped’ configurations, respectively. Note that the linear configuration is by 0.4 eV less stable than the other one, hence it is not expected to occur under equilibrium in Fe–carbon alloys, however, due to the strong short-range carbon–solute interaction we shall consider both configurations.

We have scanned all the non-equivalent (i.e., taking into consideration the crystal symmetry) positions for the solute elements (namely, Mn, Ni, Si, Cr, P and Cu) nearby the two considered V–C₂ configurations.

It was revealed that in the case of Γ-shaped V–C₂ complex (see Fig. 1c) all the solutes occupy position #1, i.e., away from the carbon atoms and close to the vacancy. In the case of the linear V–C₂

Table 1

The stable configurations of the S_N–V–C complexes. The complexes where the addition of extra solute shows a negligible binding (less than 0.05 eV) are not shown. The numbers next to the atomic configurations correspond to the ones shown in Fig. 1a.

Atomic configuration of solutes at a V–C pair	Binding energy of the Nth solute to S _{N-1} –V–C (eV)	Atomic configuration of solutes at a V–C pair	Binding energy of the Nth solute to S _{N-1} –V–C (eV)
Mn–Si (1–3)	0.12	Ni–Si (1–4)	0.26
Mn–Si (1–4)	0.26	NiMn–Ni (1–4–3)	0.15
Ni–Mn (1–3)	0.21	NiSi–Ni (1–4–3)	0.09
Ni–Mn (1–4)	0.25	NiMnNi–Ni (1–4–3–2)	0.11
Ni–Si (1–3)	0.15	NiSiNi–Ni (1–4–3–2)	0.09

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