## Interaction of carbon with microstructural defects in a W-Re matrix: an *ab initio* assessment

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#### Abstract

The interaction of carbon atoms with point defects and the core of edge and screw dislocations with Burgers vector  $a_0/2 < 111$  in W and a W-Re matrix is studied by means of the *ab initio* calculations. The structure and energetics of the ground-state atomic configurations are presented and rationalized. It is found that di-vacancies, which are thermally unstable in pure W according to the state-of-the-art *ab initio* calculations, can nucleate at C and Re-C complexes, which fills the gap in the explanation of the emergence of nanovoids observed experimentally under irradiation. Also on the basis of the recent experimental evidence and our calculations, the temperature ranges for manifestation of the yield drop phenomenon, which is related to the obstruction of dislocation motion due to their decoration by impurities such as carbon, are revealed.

Keywords: tungsten, carbon, *ab initio*, dislocations, point defects, interstitial, vacancy, yield drop.

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#### 1. Introduction

Tungsten (W) is the main candidate for plasma-facing components in the demonstration fusion power plant (DEMO) and is chosen as the divertor material for international

thermonuclear experimental reactor (ITER). Carbon (C) atoms are one of the most frequent impurities in commercial tungsten grades. For example, following the official material specifications Plansee-manufactured W contains typically about 92 atomic parts per million (appm) of C with a guaranteed maximum of 458 appm [1]. In the literature, neither before nor after irradiation, the initial distribution of carbon in the W matrix at different temperatures and its redistribution during exploitation of a tungsten component has been reported. However, such information is essential in understanding the evolution of the microstructure of W under neutron or ion irradiation (see for example [2, 3]). In these works it was shown that a) the evolution of the microstructure of W under neutron and ion irradiation is sensitive to the actual carbon content, and b) the experimentally observed microstructure can be reproduced (simulated) correctly only if a certain amount of carbon traps (10-30 appm) is present in the bulk material.

Where it is virtually impossible to study the details of carbon-defect clusters via experimental techniques, accurate *ab initio* simulations offer a possibility to investigate such clusters in detail, i.e., to derive the stable atomic configurations for carbon next to point defects and lattice imperfections. To do so, one calculates the binding energies between carbon and defects/lattice imperfections, which allow the assessment of the carbon (re-)distribution at the thermodynamic equilibrium.

In the literature, *ab initio* calculations have shown that C occupies the octahedral interstitial position in defect-free bcc W [4]. Its migration energy was reported to be 1.46 eV [5], which is 0.20 eV lower than the migration energy of a vacancy in the bulk W [6]. Two interstitial carbon atoms attract each other forming a strong covalent bonding with the maximum binding energy of about 0.4-0.5 eV at a distance of about 2.8 Å [4].

It is known that carbon atoms are strongly bound to point defects, such as vacancies (Va) and self-interstitials (SIAs). For vacancies the binding energy is about 2 eV [4, 7]. Up to four carbon atoms can be trapped at one vacancy site, as it was described in [7]. The interaction of carbon atoms with di-vacancies and larger vacancy clusters has not been assessed so far, however this information is important for the physical understanding of processes leading to the nucleation of vacancy clusters and voids in bcc W under irradiation. In our recent paper [2] we have shown that the formation of voids during neutron irradiation can be explained by the nucleation of small vacancy clusters directly in the displacement cascades. However, the available results [8, 9] of the analysis of electron-irradiated tungsten (with 2.1 MeV electrons at 4.2 K [8] and with 6 MeV electrons [9] followed by the annealing up to 800 and 1000 K, respectively) have also shown the nucleation of vacancy clusters. In the paper [8] it was reported that the electron irradiation lead to the generation of a very small concentration of

isolated vacancies equal to 41 ppm. Upon the annealing of the tungsten samples, the radiationinduced vacancies begin to migrate at the temperatures of about 600-700 K [8, 10, 11] and form small vacancy clusters [8, 9]. Given the repulsion of di-vacancies, as univocally revealed by *ab initio* simulations (see review and results in [12]), there should be a certain mechanism which glues the vacancies together and makes them stable up to the temperatures of about 1000-1150 K, where the next recovery stage is observed. At these temperatures the dissociation of small vacancy clusters becomes possible as it was established during the analysis of the tungsten samples annealed up to 1900 K after the irradiation by 30 keV  $1 \times 10^{20}$  D<sub>2</sub><sup>+</sup> m<sup>-2</sup> ions [11]. The strong affinity of carbon to a single vacancy can be a key in the formation of a stable di-vacancy defect and the further nucleation of larger vacancy clusters.

The attraction of C to SIAs is much weaker than to vacancies and is reported to be 0.62 eV in the work of Becquart et al. [13] and 0.9 eV in the work of Kong et al. [4]. The computational setups in both works were similar (the same pseudopotentials, box size and kpoint mesh) except for a larger cut-off energy (500 eV) and volume/cell shape relaxation used in [4] in addition to structural relaxation only in [13] where a cut-off energy of 350 eV was applied. Besides that, the large spread in these binding energy values can be related to two shortcomings in the respective works. Firstly, the super cells in these works contained 128atoms, whereas the minimum super cell size to reach convergence in formation energy of an SIA is 250 atoms with a  $5 \times 5 \times 5$  k-point mesh [14]. Secondly, the <111> dumbbell/crowdion configuration was used as the ground-state for the SIA. However, the study of Gharaee and Erhart [14] has revealed that there is an alternative equally-stable ground-state configuration for self-interstitials: the so-called bridge interstitial configuration (oriented along <221> crystallographic direction). Note that the energy difference of these configurations with another stable self-interstitial configuration, such as the <110> dumbbell, is about 0.2-0.3 eV. Therefore, besides the application of the larger supercell (250 atoms) the allocation of C next to all three possible configurations should be evaluated consistently to reveal the true groundstate configuration and derive the actual value of the binding energy between a C and SIA.

Limited information is available with regard to the interaction of carbon with intrinsic line and planar lattice defects (imperfections) in W. In the work of Zhou et al. [15], *ab initio* calculations have shown that C is attracted to the grain boundary (GB)  $\Sigma$ 5(310)[001] with a binding energy of 3.15 eV (note that in [15] the correct value for the binding energy is reported in the text while the value of 3.95 eV in the abstract is a typographic error). Based on this value, the equilibrium C population was estimated, which led to the conclusion [15] that in the temperature range 373-973 K and for bulk C concentration of 500-1000 appm almost all C

atoms segregate at the GB interface. We note that such an approach has the shortcoming of assuming an unlimited capacity of the GB interface to accommodate C atoms.

Interstitial impurity atoms attracted to dislocations aggregate in the so-called Cottrell atmospheres, which in turn obstruct the motion of these dislocations [16]. Experimentally, the decoration of dislocations by the impurities manifests in tensile tests via a yield drop. It is explained as follows: the stress required to move the locked dislocations is very high, but once the dislocations escape from the Cottrell atmospheres, the dislocations can glide in a virtually pure crystal. After that, the usual work hardening occurs in the material due to the formation of dislocation networks. Such a behaviour was observed in many metals (Cu, Fe, Al, W, V etc) [17-19], including bcc Fe [17] and W [17, 18], and was attributed to the pinning of dislocation by carbon impurities [17]. The Cottrell atmospheres dissolve at a high temperature, when the entropy contribution to the free energy makes detrapping of carbon atoms from the dislocations possible. For example, in bcc Fe the yield drop disappears at a temperature above 300 °C [17].

So far, limited information is published regarding the magnitude of the interaction of C with dislocations. A very recent paper by Lüthi et al. [20] reports a binding energy of about 1.6 eV for a carbon located in the prismatic position in the screw dislocation core and the conversion from the so-called 'easy' core to 'hard' core structure, as explained in details in [21]. No binding energy between a C and edge dislocation has been so far reported in W. Even though experimentally, most dislocations have screw character, typically edge dislocations are stronger traps for interstitial impurities than the latter (see for example [22]) and therefore the assessment of the interaction between C atoms and edge dislocations is desirable. Moreover, edge dislocation lines can be taken as the limiting case for large dislocation loops, which are important features in irradiated materials. As such, the binding between a C atom and an edge dislocation provides a measure for the binding between a C and dislocation loop.

Under neutron irradiation, the chemical composition of initially pure W will change due to transmutation and will lead to significant concentrations of Re. Under fusion conditions, the Re content can reach several percents at doses of ~10 dpa (displacements per atom) [23, 24]. According to available *ab initio* calculations, Re interstitials are stable, forming a mixed <221> dumbbell with a binding energy of 0.8 eV, having by 0.05-0.10 eV lower energy than the mixed W-Re dumbbell oriented along the <111> direction. In addition, Re-vacancy (Re-Va) pairs are also stable with a binding energy of 0.2 eV at both first and second nearest neighbour (1nn and 2nn, where nn stands for the nearest neighbour) distances [25]. Also C is attracted to Re, with the energy of 0.2 eV [7]. Re-Va-C<sub>N</sub> complexes have been studied in [7] where it is shown that Re-Va (1nn or 2nn) complexes can attract up to 4 carbon atoms. In [26], it is shown that Re atoms can stabilize vacancy clusters. At this point, no information is available

regarding the interaction between carbon and screw or edge dislocations decorated by Re atoms.

The present work aims at contributing to a consistent physical understanding of the interaction of carbon atoms with point defects and lattice imperfections in tungsten and dilute W-Re alloys. For this, we derive the ground-state configuration of various point defect clusters: Va-Va-Re, Va-Va-C and Va-Re-C, SIA-C and (W-Re dumbbell)-C complexes. In addition we investigate the lowest energy configurations of C and C pairs around both Re-decorated and undecorated screw and edge dislocation lines. The obtained values of the C-dislocation binding energy are used to predict the temperature range, where the yield drop caused by the carbon Cottrell atmospheres, should be observed. The review of a number of tensile tests of different tungsten grades shows a good match between the model prediction and the experimental data.

#### 2. Methodology

The computational analysis was performed using density functional theory (DFT) calculations with the Vienna Ab initio Simulation Package (VASP) [27, 28] applying the projector-augmented wave (PAW) pseudo-potentials [29, 30]. The exchange-correlation effects were treated within the generalized gradient approximation using the parameterization by Perdew, Burke and Ernzerhof [31]. The calculations were performed without spin polarization (non-magnetic). The pseudopotentials with six, seven and four valence electrons were applied for W, Re and C, respectively. The conjugate gradient algorithm was used with force convergence criterion 0.03 eV/Å for the ionic relaxation. The relaxation of the electronic degrees of freedom was performed with a global break condition of  $10^{-4}$  eV. A Methfessel-Paxton smearing of 0.3 eV has been utilized.

For point defect simulations, which included the pairs of substitutional and interstitial defects Re-Va, Re-C, Va-C; triplets of defects Va-Re-C, Va-Va-Re, Va-Va-C, quartets of defects Va-Va-Re-C and purely interstitial defect clusters  $(W-W)_{dumbbell}$ -C,  $(W-Re)_{dumbbell}$ -C, the optimum configurations for the clusters were investigated considering their growth step by step. For example, to find the lowest energy configuration for a Va-Va-C-Re cluster the following 'seeding' ground-state configurations were considered: Va-C-Re (scanning for a lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby), Va-Va-Re (scanning for the lowest energy position for an extra vacancy nearby) and finally the ground-state atomistic structure (having the lowest energy) among them was identified. Such a screening study was firstly performed in  $4 \times 4 \times 4$ 

boxes with a  $3\times3\times3$  k-point mesh. Then the lowest energy configurations were relaxed in a  $5\times5\times5$  box with  $5\times5\times5$  k-point mesh and in a  $6\times6\times6$  box with  $5\times5\times5$  k-point mesh to validate if the convergence of the binding energy of the cluster (calculated as described below) has been finally reached, thus respecting the necessity to apply large boxes for interstitials as discussed in [14].

In order to find the true lowest energy configurations for a carbon atom next to pure SIA and mixed SIA W-Re interstitial configurations three initial 'seeding' configurations <221>, <111> and <110> were considered. In the manuscript, the lowest energy atomic structures and the corresponding binding energies are reported.

For simulations of carbon and rhenium atoms next to screw and edge dislocations the methodology is similar to the one applied in our previous study where the trapping of H and He next to edge and screw dislocations in W has been extensively evaluated [22]. While the exact details for the simulation boxes (including the convergence tests) were given in that work [22], here we report only the main ideas.

A screw dislocation (SD) with Burgers vector (BV)  $a_0/2 < 111$  was modelled using the dislocation dipole approach [32] in a fully (3D) periodic crystal. In this crystal two SDs with antiparallel Burgers vectors b are created in an ideal bcc W crystal, which are forming a dislocation quadruple [33] if replicated, where the latter forms the smallest crystallographic structure with orthogonal basis vectors, which is periodic in all directions. In this work, the dislocation dipole was created with non-orthogonal supercell vectors { $C_1, C_2, C_3$ }:  $C_1 = n \times a_1$ ;  $C_2 = \frac{1}{2}n \times a_1 + m \times a_2 + \frac{1}{2}a_3$ ;  $C_3 = a_3$ , where  $a_1 = \frac{1}{3}[-1-12]$ ;  $a_2 = \frac{1}{2}[1-10]$ ;  $a_3 = [111]$  and (n, m) =(15, 9). The shift along the [1-10] direction of the centers of gravity of th[34]e upward- and downward-pointing triangles, on which the two dislocations constituting the dipole are centered, was accounted for via addition of two components C1 and C2 along a3 (-1/(3m) and -1/(6m), respectively. The simulation box containing 270 and 540 atoms with dimensions  $41.01 \times 38.82 \times 5.49 \text{ Å}^3$  and  $41.01 \times 38.82 \times 10.99 \text{ Å}^3$  (2×b and 4×b distances along [111] direction, respectively) was sampled using a k-point mesh of 1×3×11. Such a crystal allows one to model a reliable core structure with a negligible effect of dislocation self-interaction on the core properties [35]. The box dimensions in the plane perpendicular to the dislocation line are large enough to reach the convergence of the core energy as was confirmed in [36]. Also, a similar modelling crystal was already applied to study the impurity-screw dislocation interaction in [21], to assess the interaction energy between the screw dislocation and a carbon atom in bcc Fe. The convergence of the results of calculation of the binding energy for the defects (C and Re impurity clusters) in the SD core was additionally tested using the box with

the distance of  $8 \times b$  along [111] direction which contained 1080 atoms and was sampled with a k-point mesh of  $1 \times 3 \times 3$ .

The modelling box with edge dislocation (ED) with BV  $a_0/2 <111>$  was created following the method reported in [37]. It was then relaxed using the molecular statics algorithm using the Marinica et al. (version 2) [38] interatomic potential (the details are described in [22]). After the relaxation, the atoms at a distance larger than 11.5 Å from the dislocation core were immobilized. As a result a 1D-periodic crystal with fixed boundary conditions in the *xy* plane was created, which has dimensions of 24.82 × 7.78 × 22.51 Å<sup>3</sup> in the [-1-11] (*x*), [1-10] (*y*) and [112] (*z*) orientations with 246 W atoms in total. Thus, the simulation crystal was cylindrical with the dislocation line as main axis. The details of the convergence test of this box with regards to the study of impurities close to the edge dislocation core are presented in [22].

By applying such crystals, the shortest distance between the single carbon or rhenium atoms and its images due to periodic boundary conditions was equal to 21.98 Å (for  $8 \times b$  box) and 7.78 Å for screw and edge dislocations, respectively. These values are large enough to neglect their self-interaction given that the Re-Re and C-C pair interactions become negligibly small at distances above 3.2 Å (Re-Re repulsion of -0.07 eV at 1nn, -0.02 eV at 2nn and 3nn as calculated in this work) and 4.5 Å [5], respectively.

The strategy to identify the lowest energy configurations for Re, C and Re-C next to the core of dislocations was the following: firstly, the interaction energy map was created for a single C next to a dislocation core. For this, all non-equivalent octahedral positions for a single carbon atom next to the dislocation core were screened to find the total energy minimum. Then the lowest energy positions for a substitutional Re atom next to edge and screw dislocation cores were found. Finally, a) the octahedral positions for carbon atoms were scanned around screw or edge dislocations with Re in the core (the lowest energy substitutional position for Re) and b) the substitutional positions for Re were scanned next to screw and edge dislocation core with carbon located in its lowest energy position (taken from the study of C atoms next to the dislocation core). Finally, among the configurations listed above the lowest energy configurations for a Re-C pair next to edge and screw dislocations were thus identified.

The calculations for point defects were done allowing the cell metrics relaxation (cell volume optimization) following the *ab initio* study of interstitials in W [14] with the initial lattice parameter  $a_0$  equal to 3.172 Å. The test calculations for the same configurations in the crystals with a fixed volume (with the initial lattice parameter mentioned above, in a 5×5×5 box with 5×5×5 k-point mesh and in a 6×6×6 box with 5×5×5 k-point mesh) have shown that the effect of the volume relaxation on the binding energy values in any case is less than 0.02 eV, which is consistent with a previous study of interstitials in W by Gharaee et al. [14]. For

the calculations with dislocations the relaxation of atomic structures only was allowed following our previous study [21]. An energy cut-off of 450 eV was applied for all the calculations to achieve the converged values for the total energy with the absolute error not exceeding 0.01 eV as compared to the same calculations with cut-off energy of 550 eV.

The binding energy  $E_b$  between two defects in a defect cluster was assessed by applying the standard definition used in many DFT works [39-42]:

$$E_b = [E_1 + E_2] - [E_{12} + E_{bulk}], \tag{1}$$

where  $E_1$  and  $E_2$  are the energies of the configurations containing the defects '1' or '2' only,  $E_{12}$  is the energy of the configuration with two defects '1' and '2' forming a joint defect cluster, and  $E_{bulk}$  refers to the energy of the bulk (defect-free) W. Using this convention, a positive value implies an attractive interaction and vice versa. For the description of the defect clusters which consist of more than two defects, the notations of incremental and total energy are introduced. For example, the total binding energy of the cluster with three defects X, Y and Z is referred below as X+Y+Z and has a meaning of the energy needed to separate these defects away from each other, i.e. to form the defects X, Y and Z, not interacting with each other. The incremental binding energy is referred below as X-Y+Z has a meaning of the binding energy of the defect z.

Note that in atomic configurations, where one or several C atoms are located near the SD core, the dislocation core modification (distortion) has been induced, as it will be described later. Therefore, for C-SD binding energy calculations results it will always be reported which dislocation core structure is taken as a reference configuration. Given the complexity of selection of a reference dislocation core structure for Eq. 1, the C-C and Re-C binding energy at the SD core has been calculated using  $4 \times b$  and  $8 \times b$  boxes as a total energy difference between the configurations when C atoms at the SD core are close to each other or are located as far as possible in the simulation box.

The reported ground-state configurations and the corresponding binding and formation energies were calculated using the pseudopotentials without the explicit treatment of semi-core states. All the lowest energy atomic structures, presented in this work, were additionally relaxed using the PBE pseudopotentials with semi-core states enabled. The results have revealed that the effect of semi-core states is negligible showing the energy difference with the pseudopotentials without semi-cores states of less than 0.03 eV. A small impact of semi-core states is consistent with the previous study of various interstitial configurations in W by Gharaee et al. [14].

The visualizations were prepared using the scientific visualization and analysis software OVITO [43].

In order to estimate the detrapping temperatures, at which carbon atoms detach from the dislocations or point-defect clusters due to thermal excitation, we have applied the same approach as used for assessing the trapping of H and He impurities at dislocations in bcc tungsten in [22]. In this approach it is considered that the specimen is heated with a certain heating ramp rate up to high temperature at which the detrapping rate of carbon atoms reaches its maximum for the sinks of a certain kind. The release rate versus time plot can be created to estimate the positions of the release temperature peaks on the basis of a simplified computational analysis using diffusion equations (see e.g. [44]).

It was calculated following the integration of the release equation in the following form:

$$\frac{dC(t)}{dt} = -C(t)v\exp(-\frac{E_b + E_m}{k_B T})$$
(2)

where  $E_b$  is the binding energy between C and the considered defect (taken from the consistent DFT data obtained in this work),  $E_m$  – bulk migration energy (equal to 1.46 eV as reported in the *ab initio* study [5]), C(t) – carbon concentration at the traps (initial concentration at the traps defines the initial condition, i.e., C(0)=C<sub>0</sub>, where C<sub>0</sub> > 0 is selected arbitrary, since it does not alter the position of the peak, k<sub>B</sub> – Boltzmann constant, v – Debye frequency (typical lattice vibration frequency equal to  $10^{13}$  s<sup>-1</sup> was used), T – absolute temperature. The temperature was varying with time as  $T(t) = \alpha \cdot t$ , where  $\alpha = 1; 0.1; 0.01; 0.001$  in order to mimic the heating procedures performed (before the tensile test experiments) at the different heating ramp rates (HRR) of 1.00; 0.10; 0.01; 0.001 K/s, respectively.





Fig. 1. The simulation boxes with a) screw dislocation dipole and b) edge dislocation.

Different colors denote three non-equivalent crystallographic planes along the <111> direction. Enlarged atoms in b) denote the fixed atoms, while small atoms are located in the mobile region, where the structural relaxation was allowed. Two screw dislocation core are

visualized in a) with arrows. The position of the edge dislocation core is shown in b) along with three extra half-planes highlighted with the dashed lines.

#### 3. Results and discussion

#### 3.1 Pair interaction of vacancy, C and Re

The lowest energy configurations for all the pairs with Re, C and Va defects are shown in Fig. 1, while the relevant binding energies are summarized in the Table 1. A carbon atom, located in the nearest octahedral position (see Fig. 1a), is weakly attracted by a Re atom with a binding energy about 0.2 eV. Thereby, the total strain is minimized: the interstitial carbon that expands the lattice and the undersized Re atom fills that strain. A vacancy is a strong binding site for a C atom with an asymmetric configuration similar to Re-C, i.e., with carbon in the nearest octahedral position with regard to the center of the vacancy (see Fig. 1b), which is consistent with a previous work by Liu et al. [45]. In this case, carbon is making five covalent bonds with the nearest atoms (see Fig. 2b)) with a length 2.13-2.14 Å (this is one bond less compared to carbon in an octahedral position with two bonds of 1.95 Å and four bonds of 2.20 Å (see Fig. 2a)), which is very close to the W-C bond length of 2.20 Å in tungsten carbide  $\alpha$ -WC [45, 46]. The latter has a simple hexagonal lattice of tungsten atoms of layers lying directly over one another, where carbon atoms fill half the interstices, thus making tungsten and carbon atoms form a regular trigonal prism.

Vacancies strongly repel each other in tungsten up to 3nn distances, which is consistent with previous *ab initio* studies [12] where this phenomenon was found to be quite independent on the exchange-correlation functional and assumed to be governed by the filling of the d-band [12]. Carbon and Re-C complexes will be considered as one of the candidates for stabilizing di-vacancies in the next section.

There is a relatively weak mutual attraction between a Re atom and vacancies up to 2nn distance (see Fig. 1c). Such an attraction is related to the fact that the atomic radius of Re (137 nm) slightly differs from the one of W (141 nm), therefore the lattice strain for Re and a Va is minimized when the defects are close to each other.

Doir	Binding energy, eV			
Pall	This work	Other works		
Re-C	0.19	0.18 [7]		

Vo C		1.00	1.93 [45]
v a-v	-	1.99	1.97 [7]
	1nn	-0.12	-0.06 [12]
Va-Va	2nn	-0.45	-0.40 [12]
	3nn	-0.12	-0.09 [12]
	1nn	0.23	0.22 [25]
Pe Vo		0.23	0.23 [13]
NC-Va	2nn	0.21	0.22 [25]
	3nn	0.05	

Table 1. Binding energy of point-defect pairs Re-C, Va-C, Va-Va and Re-Va.

#### 3.2 The triplets Va-C-Re, Va-Va-C, Va-Va-Re and quartets Va-Va-Re-C

The results of the search of ground-state atomic configurations for triplets Va-Va-C, Va-Va-Re, Va-C-Re and quartets Va-Va-Re-C are presented in Fig. 1, where also the relevant total and incremental binding energies of different sub-entities are given.

The defect cluster Re-C with a single vacancy, i.e., Va-C-Re was found to be a very stable atomic configuration (see Fig. 1d) in its ground-state. In this case the carbon atoms resides in the octahedral position in the middle between the Va-Re (2nn) pair. In this configuration the minimum energy distances and non-symmetric configurations for Va-C and Re-C pairs are respected. By considering the incremental binding energies presented in Fig. 1d, one can conclude that the Re-C cluster is a very strong trapping site for a vacancy or a carbon atom with a binding energy of about 2.2 eV (by 0.2 eV stronger than a single vacancy).

The addition of impurities, such as C and Re, significantly affects the stability of the divacancies in W as it was revealed analyzing the energetics of triplets Va-Va-C, Va-Va-Re and quartets Va-Va-Re-C. Note that a di-vacancy in impurity-free tungsten (see Fig. 1e, Fig. 1i and Fig. 1n) is an unstable defect (see discussion in the previous section), especially at the 2nn distance (repulsion of -0.45 eV). A single carbon atom was found to glue the di-vacancy in the configuration, where vacancies stand at the 2nn distance (see Fig. 1k), making this defect very resistant against dissociation. The activation energy for the latter process is estimated as 1.17 eV (for Va-Va(2nn) + C binding as obtained at this work) + 1.69 eV (migration energy of the vacancy in bulk W as reported in [47]) = 2.86 eV for the case if the vacancy jumps away from the cluster. Given that the binding energy for C to Va-Va is almost 2.5 eV larger than that of a vacancy to Va-C and migration energies for Va and C in W differ by 0.2 eV [45] only, the dissociation of Va-Va(2nn)-C via the migration of C becomes almost unrealistic. The typical temperature for dissociation of Va-Va(2nn)-C cluster is estimated using the Eq. 2 by applying the dissociation energy of 2.86 eV calculated above. The resulting temperatures are 921; 982 and 1051 K for 0.1; 1 and 10 K/s thermal annealing rates, respectively. Thus, the thermal stability of Va-Va(2nn)-C atomic clusters up to 1050 K provides a possible explanation of the nucleation of small vacancy clusters from single vacancies in the electron-irradiated experiments [8, 9] and their dissociation around 1000-1150 K in the study of thermal annealing (executed with the heating rate of 10 K/s) of D<sub>2</sub><sup>+</sup>-irradiated tungsten samples [11] as described in the Introduction of the current manuscript.

The corresponding pictures, which represent the atomic structures and depleted charge density distribution for a Va-Va(2nn)-C complex as compared to carbon in octahedral positions, Va-C complex and Va-Va(2nn) pair, are shown in Fig. 2. It is clearly seen that in this atomic arrangement the carbon atom effectively cuts the spherical depleted charge density zone into two smaller zones introducing a minimum distortion to the crystal in its position. Moreover, it is apparent that the favourable allocations of C atoms in the matrix are related to the positions where the amount of short W-C bonds (less than the distance of 2.20 Å alike in W-C carbide, as described above) is minimized, which is similar to the behaviour of a H impurity in tungsten (see discussion in [22]). Also note that carbon cancels the repulsive interaction between Va-Va for 1nn and 3nn distances as presented in Fig. 1e and Fig. 1n, but not making it stable because in both cases the carbon atom is too far from either of the vacancies, unlike in the case of Va-Va (2nn)-C.

Rhenium decreases the repulsion between vacancies for Va-Va (1nn and 2nn) defects by about 0.1 eV (see Fig. 11 and Fig. 11), as it was revealed in the analysis of the triplets Va-Va-Re, and makes the 3nn di-vacancy (see Fig. 1p) a weakly stable configuration (Va-Va attraction of less than 0.1 eV), which is consistent with the *ab initio* study [26]. In this, unlike interstitial carbon atoms, a substitutional rhenium atom cannot be allocated in-between vacancies and can not shield the repulsive interaction between them. As a result, a single rhenium atom only cannot make the di-vacancy a stable defect.

The analysis of the quartets Va-Va-Re-C has shown that a Re-C pair stabilizes the divacancy at 2nn and 3nn (see Fig. 1m and Fig. 1q) and zeroes the repulsive interaction for the 1nn di-vacancy (see Fig. 1h). Note that for Va-Va(1nn)-Re-C and Va-Va(3nn)-Re-C a very stable subdefect Va-C-Re (its structure is shown in Fig. 1d) is observed, while the core defect for Va-Va (2nn)-Re-C is obviously Va-Va(2nn)-C (allocated as shown in Fig. 1k). Note that the Va-Va(2nn)-Re-C configuration with Re allocated in the position '#' (see Fig. 1m), which was one of the candidates for the ground state configuration considering the structures of VaVa(2nn)-C and Va-Va(2nn)-Re, is characterized by 0.12 eV, a higher energy (+0.12 eV) than the one shown in Fig. 1m. This is related to a repulsive interaction (of about -0.15 eV) between Re and C at the distance of 2.25 Å.





Fig. 1. Atomic configurations with lowest energy for pairs, triplets and quartets Re, C, Va and Va-Va (1nn, 2nn and 3nn) and relevant total and incremental binding energies (given in eV). The rhenium atom is shown by the red circle, carbon is shown by the shaded circle and the vacancy is represented as a white circle. The matrix W atoms are shown as black circles. The atom marked with '#' is discussed in the text.



(2nn)

Fig. 2. Atomic structures for carbon in octahedral position, carbon next to a vacancy and a divacancy (2nn). W atoms are shown by blue balls while carbon atoms are visualized by the red ones. Three depleted charge density isosurfaces are shown of 0.15 (green), 0.185 (lightred) and 0.22 (lightyellow) e/Å<sup>3</sup>. The bonds between carbon atom and the nearest W atoms are shown. The colour of the bond denotes the bond length and is explained in the legend on the right hand

#### 3.3 Interaction of carbon atoms with self- and mixed-interstitials

The binding energies for C and Re atoms to different ground-state interstitial configurations (SIA, SIA-C defect cluster and mixed W-Re dumbbells) in tungsten are summarized in Table 2, while the corresponding atomic structures are shown in Fig. 3. In the latter figure the depleted charge density isosurfaces are also visualized to highlight the regions favourable for the allocation of carbon impurities. Note that our convergence study (see Table 2) shows that the box size  $5 \times 5 \times 5$  is large enough to study the interaction of single interstitials with C in the W-Re matrix.

The SIA defect (see Fig. 3a) oriented along a <221> direction (the so-called bridge interstitial, referred to in [14] as <11*h*> (*h* ~ 0.5)) was found in this work to be the lowest energy configuration (formation energy equal to 9.81 eV, calculated as  $E_f = E_{boxSIA} \cdot N_{boxSIA} \times E_{coh}$ , where  $E_{boxSIA}$  is the total energy of the crystal with SIA,  $N_{boxSIA}$  is the amount of atoms in this box and  $E_{coh}$  - cohesive energy of W crystal), which is very close to the formation energy of the <111> dumbbell (9.84 eV), while the <110> dumbbell has the highest formation energy among them (10.18 eV). The calculated formation energies are very close (with a difference of less than 0.03 eV) to those reported in [14], thus confirming the accuracy of our calculations and the correctness of the relaxed atomic structures. The carbon atom is most strongly attracted to an SIA oriented along <221> with the energy of 0.73 eV (see Fig. 3b), occupying the position with an open volume created as the result of the shift of the W atom (marked as '\*' in Fig. 3b) towards the [111] direction. In this case, the carbon atom is located in the distorted (in the region of expansion) octahedral position forming six short (of less than 2.3 Å) bonds with nearest tungsten atoms: four bonds of 2.0 Å and two bonds of 2.2 Å as compared to two bonds of 2.0 Å and four bonds of 2.2 Å for the standard octahedral position (see Fig. 2a).

Re is attracted to the W-W dumbbell with the energy of 0.8 eV to an SIA forming a <221>-oriented interstitial, which is consistent with the previous *ab initio* studies [14, 48]. Given a small atomic radius misfit (for Re atom as compared to W as discussed in the section 3.1) a negligible modification of the depleted charge density pattern is observed (see Fig. 3c). If the carbon atom is located in the vicinity of the W-Re interstitial, then the orientation of the W-Re dumbbell changes to <110> (see Fig. 3d). In this configuration, the distance between Re and C atom is large (about 3.4 Å), where their interaction is negligible [7]. In this case, it is apparent that the energy gain for carbon allocated in the expanded octahedral position overcomes the energy loss for the W-Re dumbbell due to a less favourable orientation of

<110> as compared to <221> orientation (energy difference of 0.05 eV, which is consistent with the value reported in [14]). The bond lengths for the C atom to the nearest W atoms in the W-Re dumbbell are the same as for the case of the W-W dumbbell, which explains a negligible difference in the binding energy for these configurations (see Table 2). Also one can note from the results in the Table 2 that the presence of C next to the SIA does not affect the binding energy of Re to the SIA.



c) W-Re bridge interstitial

d) carbon next to W-Re interstitial

Fig. 3. The lowest energy atomic structures for SIAs and W-Re interstitials with and without carbon atom. The W atoms are shown by blue spheres, Re atoms by large red spheres and carbon atoms by small red spheres. The depleted charge density iso-surfaces of 0.22 e/Å<sup>3</sup> are shown. Note that only atoms close to the interstitial defects are visualized. The bonds between carbon (and Re in d) ) atom and the nearest W atoms are shown. The colour of the bond denotes the bond length and is explained in the legend on the right hand side. The range in the legend (for the bond length) was kept the same as in Fig. 2 to allow for a consistent comparison. The atom marked with '\*' is discussed in the text.

Atomic		C to W-Re mixed		Re to W-W SIA		Re to SIA-C pair		
configuration	C to w-w SIA		dumbbell			defect		
Box size, $a_0^3$	$5 \times 5 \times 5$	6×6×6	5×5×5	6×6×6	$5 \times 5 \times 5$	6×6×6	5×5×5	6×6×6
Binding energy, eV	0.73	0.73	0.76	0.75	0.80	0.81	0.84	0.81

Table 2. Binding energy of C and Re atoms to different interstitial ground-state configurations.

# 3.4 Single carbon atoms, pairs of C and Re atoms at screw and edge dislocations

When a single carbon atom is located next to the screw dislocation (SD) core, it induces the localized core structure modification from 'easy' to 'hard' core as was described in the work of Ventelon et al. [20, 21], where such an effect was reported to occur in both bcc W and bcc Fe. The example of the structure of the easy core, which is the ground-state configuration for the undecorated screw dislocation in bcc W, is shown in Fig. 4a, where the atoms form a helix (screw) around the dislocation line. The 'hard' core segment is visualized in Fig. 4b, where the triplets of atoms around the C-decorated dislocation core are located in one [111] plane. Our calculations in the large simulations boxes with a dislocation length up to  $8 \times b$  have shown that a single carbon deflects the dislocation line to the neighbour position, locally converting the dislocation structure into the hard core (see Fig. 4b). Note that the energy loss due to the transformation from the easy to hard core is 0.14 eV/*b* (calculated by the same DFT code VASP in [20]).

The differential displacement maps [49, 50] in Fig. 5 visualize the dislocation core structure in the  $8 \times b$  crystal at different distances along the dislocation line from the C impurity. One can clearly see that the dislocation core structure has a hard core configuration (see Fig. 5b) next to C atom, while at the distance of  $4 \times b$  from it the core converts back to the easy configuration (see Fig. 5f), i.e. becoming similar to what is observed in the crystal with screw dislocation without impurities (see Fig. 5a). Thus, as a result of attractive interaction to the SD, a single C atom causes the deflection (deviation from the straight line) of the SD segment of  $8 \times b$  length.

The ground-state binding energies for C and Re atoms (given different initial C and Re concentrations (12.5%; 25% and 50%) per unit of dislocation length) to edge and screw dislocations in tungsten are summarized in Table 3, while the corresponding lowest-energy stable atomic positions for a single C around edge and screw dislocations are shown in Fig. 6a and Fig. 6b, respectively. As one can see from the binding energy map for a single carbon next

to the SD (see Fig. 6b), the lowest energy configurations are realized when the carbon atom occupies the slightly distorted prismatic sites (marked by 'P', inside the triangles of W atoms, in-between two adjacent [111] planes) inside the hard SD core as shown in Fig. 4b). Six bonds with the length 2×2.13 Å, 2×2.17 Å and 2×2.19 Å with the nearest W atoms can be identified for C at SD in the ground-state configuration (see Fig. 4b). Such lengths for the W-C bonds at the SD are apparently a trade-off between being as close as possible to the optimum W-C bond length of 2.20 Å in tungsten carbide (as discussed in Section 3.1) and minimizing the lattice distortion of the hard core of SD. In this case a single C atom is bound to the SD core in the ground state with the energy of about 1.5-1.6 eV, if the easy core configuration is considered as reference (see Table 3). The octahedral positions next to the SD core offer energetically less favourable sites for C atoms with a binding energy that is lower by 0.3-0.4 eV as compared to the prismatic sites. Both results for the binding energy of a single carbon in prismatic and octahedral sites taking the easy core as a reference are consistent with the earlier study of Lüthi et al. [20]). It was also calculated how strongly C atom is attracted to the SD line taking as the reference configuration a hard core for  $2 \times b$  box size, where the core is purely hard and a mixed hard-easy core in  $4 \times b$  and  $8 \times b$  boxes (i.e. pure hard dislocation core structure at the location of C atom, which gradually reconstructs back to the easy core at a distance of  $4 \times b$  from C atom). For the latter case, it was assumed that the dislocation arms, pinned at the C impurity, bend with a shape of a bow (considering the direction of the dislocation line) [16] deviating from the hard core at the impurity to the easy core at the distance of  $4 \times b$  from the carbon atom (see Fig. 4b). It was, thus, derived that the attraction of C to SD core is about 1.9 eV for hard or mixed core configuration taken as a reference.

In the bulk W the C-C interaction is the strongest when the distance between two carbon atoms in the octahedral positions is equal to the length of b ( $\sqrt{3}/2 \times a_0$ ) along the [111] direction, which is consistent with the results of Kong et al. [4]. The C-C interaction is negligible (being less than 0.05 eV) if the distance between carbon atoms is  $2 \times b$  (and above) along the [111] direction as established in [20] and confirmed in our work. The calculations of C attraction to a C-decorated SD line performed in the  $4 \times b$  crystal (thus excluding any interaction of carboncarbon through the periodic boundaries) have shown that C is attracted to the C-decorated SD with a binding energy of about 2.16 eV, which is larger by 0.2-0.3 eV than reported by Lüthi et al [20]. In the latter paper [20], the C-C binding energy was evaluated by accounting for the total energies of the systems with a single C in  $1 \times b$  and a single or two carbon atoms in  $2 \times b$ boxes (following the procedure presented earlier in [21]), which was positive (0.12 eV), indicating that the carbon atoms weakly attract each other at the SD line, unlike in the bulk W, where the C-C attraction is much stronger (0.4-0.5 eV). In our work, a larger crystal, which was twice and four times as big along the dislocation line, was applied, which allowed one to obtain a converged value of the interaction energy. Thus, a C-C attraction of 0.35 eV (i.e. by ~0.1 eV weaker than C-C binding in the defect-free perfect crystal) was calculated in our work using the difference in total energy between two atomic crystals where C atoms are located close (forming a cluster) and as far as possible along the dislocation line. This finding implies that the C atoms a) can form clusters in the SD core alike in the bulk W, b) will tend to stay next to each other along the screw dislocation line to minimize both the length of the dislocation and the total distortion of the dislocation core (from easy to hard).

A Re atom is weakly attracted to the screw dislocation core with a binding energy of 0.27 eV. No modification of the dislocation core structure is observed (see Fig. 4d), which remains in an easy (non-splitted) core structure in the ground state. However, the transformation into the 'hard' core structure occurs, when C is located next to the Re-decorated screw dislocation as visualized in Fig. 4e. In this case, C occupies the prismatic position similar to the one when there is no Re in the crystal, forming a Re-C bond with a length of 2.09 Å. In this case the Re-C binding energy is 0.16 eV, as the Re-C bond length is by 0.14 Å longer than the Re-C bond for carbon in the octahedral position next to Re in bulk W, where a maximum Re-C binding energy of 0.19 eV is realized (see Fig. 1a). The negligible difference for these two interaction energies implies no effect of the presence of a screw dislocation on the Re-C binding strength. The result above can also be interpreted as C is attracted stronger to a Re-decorated screw dislocation as compared to the undecorated SD (by 0.16 eV), and Re is stronger attracted to the SD if C is present in the dislocation core (by 0.16 eV).

The carbon atoms next to edge dislocations (see Fig. 6a and Fig. 8b) occupy positions that clearly follow the pattern of the depleted charge density distribution visualized in Fig. 7a and Fig. 8a. The charge density distribution is not symmetric along the dislocation line (i.e. along the [112] direction) because the {112} planes visualized in Fig. 8a are not equivalent, which is the case for any six adjacent {112} planes in a bcc lattice. Note that the lowest energy positions for C are located at a distance of about 1 Å from the center of the dislocation (see Fig. 6a and 7c). In this case, the carbon atom is located in a distorted octahedral position (as compared to the octahedral position in bulk W as shown in Fig. 2a), where two short W-C bonds of 1.95 Å for C in the octahedral position in pure W are enlarged to about 2.05 Å in the W crystal with ED, which is getting closer to the optimum W-C bond length of 2.20 Å. Thus, the increased atomic space next to the edge dislocation core (isotropic expansion) creates a favourable site for C (with the binding energy of about 2.1 eV, i.e., by 0.5 eV stronger than the C-screw dislocation binding, taking the easy SD core as a reference), which is very similar to the binding of C to a vacancy (also about 2.0 eV). The ground state configuration for two

carbon atoms next to the edge dislocation is visualized in Fig. 7d and Fig. 8c. In this case the second carbon atom is located at the farther distance of 3.85 Å from the first carbon atom and is located in a slightly larger open volume position, so the interaction energy for the second carbon to the ED core weakly increases by 0.05 eV (see Table 3). Thus, carbon atoms do not tend to form clusters in the ED core.

Rhenium reduces the energy of the crystal with ED by 0.5 eV, if it replaces the W atom in the most compressive region of the dislocation core as shown in Fig. 7b, which is 0.25 eV stronger than the Re-screw dislocation interaction. No modification of the depleted charge density distribution is observed (comparing Fig. 7b and Fig. 4d with Fig. 7a and Fig. 4a, respectively) if Re is located in these positions. The ground state configuration for C next to a Re-decorated edge dislocation is shown in Fig. 7e. In this case the Re-C bond length is 3.17 Å, which is significantly longer than in the case of the screw dislocation, what explains their negligibly small interaction. Consequently, as reported in Table 3, the binding energy of C to an ED does not change if Re is present in the edge dislocation core and Re-edge dislocation binding is not altered if the ED is decorated by a C atom.

	С	ED	C at ED	Re at ED	SD	C at SD	Re at SD
С	0.44* 0.34 <sup>4b#</sup> ; 0.45 <sup>4b</sup> 0.47 <sup>8b#</sup> ; 0.44 <sup>8b</sup>	2.07	2.12	2.06	H: 1.89 <sup>2b</sup> ; E: 1.62 <sup>2b</sup> M: 1.88 <sup>4b</sup> ; E: 1.60 <sup>4b</sup> M: 1.89 <sup>8b</sup> ; E: 1.52 <sup>8b</sup>	$\begin{array}{c} 2.17^{2\mathrm{b}}(\geq\!50\%\ c_{C}/\boldsymbol{b})\\ 2.16^{4\mathrm{b}}\left(25\%\ c_{C}/\boldsymbol{b}\right)\\ 2.03^{8\mathrm{b}}\left(\leq\!12.5\%\ c_{C}/\boldsymbol{b}\right)\end{array}$	E: 1.74 <sup>2b</sup> E: 1.73 <sup>4b</sup> E: 1.68 <sup>8b</sup>
Re	0.19 <sup>*</sup> 0.17 <sup>#4b</sup> 0.19 <sup>#8b</sup>	0.51	0.50		$\begin{array}{l} 0.24^{2b} (50\% \ c_{Re}/\boldsymbol{b}) \\ 0.25^{4b} (25\% \ c_{Re}/\boldsymbol{b}) \\ 0.27^{8b} (12.5\% \ c_{Re}/\boldsymbol{b}) \end{array}$	$\begin{array}{c} 0.36^{2b} (\geq 50\% \ c_C/\pmb{b}) \\ 0.38^{4b} (25\% \ c_C/\pmb{b}) \\ 0.43^{8b} (\leq 12.5\% \ c_C/\pmb{b}) \end{array}$	
C at ED			0.04	-0.01			
C at SD						0.12 <sup>2b</sup> [20] 0.34 <sup>4b#</sup> 0.35 <sup>8b#</sup>	0.19 <sup>4b#</sup> 0.16 <sup>8b#</sup>

Table 3. Binding energies of C and Re to screw and edge dislocations undecorated or decorated by C. 'H', 'E' and 'M' stand for the hard, easy and mixed hard-easy screw dislocation core, respectively, taken as a reference for the calculation of the binding energy. The data on C-C and C-Re interaction in the bulk is added for comparison. The crossed cells correspond to the configurations not considered in this work, while the gray-coloured cells show the configurations already reported in another cell in this table.

\* in the 5×5×5 box with crystal orientations [100], [010] and [001], where C atoms are located at the distance of  $1 \times \boldsymbol{b}$ ;

 $^{2b}$ ,  $^{4b}$  and  $^{8b}$  stand for the size of the crystal (along [111] direction) with SD which was used for the calculation of the interaction energy. In this case, the carbon concentration per unit of dislocation length  $C_c/b$  is 50%, 25% and 12.5%, respectively;

<sup>#</sup> the binding energy was calculated as a total energy difference between two configurations, where two entities are as close as possible and as far as possible along [111] direction.



e) single carbon atom next to SD with Re atom in the core

Fig. 4. Atomic configurations for a screw dislocation in W and C, Re and Re-C clusters in the dislocation core. Three depleted charge density isosurfaces are shown of 0.15 (green), 0.185 (light red) and 0.22 (light yellow) e<sup>-</sup>/Å<sup>3</sup>. The range for the legend (for the W-C bond length) was kept the same as in Fig.2. The single dashed lines are added to highlight the structure of the SD core. The blue dotted line in a) and b) indicates the SD line with and without carbon atom.





Fig. 5. Differential displacement maps of a) undecorated and bcdef) C-decorated screw dislocation core structures at different distances from the impurity atom. Three different blackand-white denote three non-equivalent atomic planes along <111> direction. The red cross highlights the position of C atom. Green circles are added to a) b) and f) to visualize the location of the dislocation core. The dashed circles illustrate the dislocation core transition from hard to easy configuration.



Fig. 6. Binding energy map for carbon atoms around a) edge and b) screw dislocations. The dislocation line is perpendicular to the image plane. Black atoms denote the relaxed positions for W atoms before the introduction of a C atom. The symbol '§' indicates the position of the screw dislocation core prior to the introduction of the carbon atom. The octahedral and prismatic sites for a C atom are denoted as 'O' and 'P', respectively.



e) single carbon atom next to ED with Re

atom in the core

Fig. 7. Atomic configurations for edge dislocation in W and C, Re and Re-C clusters in the dislocation core. Three depleted charge density isosurfaces are shown of 0.15 (green), 0.185

(light red) and 0.22 (light yellow) e<sup>-</sup>/Å<sup>3</sup>. The range of the legend (for the W-C bond length) was kept the same as in Fig. 2. The orientation of the crystal shown is the same as in Fig. 6a. The Re atom is shown by the enlarged circle.



Fig. 8. Atomic configurations for an edge dislocation in W and C, Re and Re-C clusters in the dislocation core. Three charge density isosurfaces are shown of 0.15 (green), 0.185 (light red) and 0.22 (light yellow) e<sup>-</sup>/Å<sup>3</sup> in a). The range of the legend (for the bond length) was kept the same as in Fig. 2 to make a consistent comparison. The dashed line represents the ED line. The colour of atoms in a) and c) is related to the location of the particular atom along [112] direction (see the legend). In c) the W atoms are shown with black circles, while coloured (according to the its binding energy to dislocation) circles denote carbon atoms.

### 3.5 Yield drop phenomenon in tungsten

The decoration of dislocations by carbon impurities in materials manifests via the yield drop phenomenon observed during the initiation of plastic deformation. In order to estimate the temperature range for this phenomenon in tungsten, i.e., to derive the temperature for the dissolution of the carbon Cortrell atmospheres, we have summarized the available results of tensile tests (stress-strain curves) for different commercial tungsten grades. The tensile test results for Plansee-manufactured as-received tungsten grades were taken from [18] and represent the experimental data obtained in the range of strain rates  $2 \times 10^{-4}-5 \times 10^{-2}$  s<sup>-1</sup> and temperature range 300-1000 °C: 1) sintered W (averaged grain size of 35 µm, dislocation density not reported), 2) heavily deformed M184 W (average grain size of 35-50 µm, dislocation density not reported), 3) ITER-specification Plansee W (average grain size of 10-50 µm, dislocation density of  $4.5 \times 10^{12}$  m<sup>-2</sup>). The detailed specifications for these W grades are given in [18, 51]. Another set of tensile tests results [52] is for as-received CFETR tungsten (average grain size of 60 µm, dislocation density not reported; the detailed specifications are given in [53]), which is the Chinese first-wall material for thermonuclear reactors). The latter experiments were performed at SCK•CEN [52] via the displacement-controlled tensile tests, which have been done on miniaturized samples (gauge length 5.2 and 15 mm) in the range of strain rates  $6 \times 10^{-5} - 5 \times 10^{-2}$  s<sup>-1</sup> and temperature range 200-600 °C, which spans the low-temperature window for tungsten application in fusion. The results of the tensile tests for Plansee and CFETR tungsten grades are presented in Fig. 10. Most of the tests were done at temperatures below 600 °C and only few test data [18] is available at 1000 °C. The corresponding values for the magnitude of the yield drop (including the results not shown in Fig. 9) are presented in Fig. 11. The general trend is the following: the magnitude of the yield drop decreases with temperature, becoming small above 600 °C and becoming negligible or zero at 1000 °C. Thus, one can expect that carbon atmospheres dissolve (and the yield drop phenomenon disappears) in the temperature range 600-1000 °C.



(a) ITER-specification tungsten. From [52]





(c) Plansee tungsten grades after different mechanical treatment. From [18]

Fig. 10. The results of tensile tests for different tungsten grades.



Fig. 11. The magnitude of the yield drop in different tungsten grades (including a different manufacturing process) depending on the temperature.

The calculated detrapping temperatures for different microstructural features in W are shown in Fig. 12. The data for the SD is presented taking either easy or hard core SD as a reference for the calculations of the binding energy. Given that the carbon atoms, being trapped at the SD, change the dislocation core structure from the easy to hard core configuration, the carbon atoms will be detrapped from the hard-cored SD. Therefore the latter should be considered as the main configuration for the detrapping temperature assessment of screw dislocations. From Fig. 12 one can conclude that the estimated temperature window for the dissolution of carbon-formed Cottrell atmospheres lays within 600-900 °C, which is consistent with the results of tensile tests presented here. Given a typical heating ramp rate of 0.1 K/s, the C-dislocations and edge dislocations, respectively. Thus, with the increasing temperature the carbon atoms undergo detrapping first from screw dislocations and then from edge dislocations. Vacancies, being as equally strong traps for carbon atoms as edge dislocations, are important features for the case of tungsten being irradiated by the neutrons, ions or electrons with an energy that exceeds the threshold for formation of Frenkel pairs.



Fig. 12. The detrapping temperature for carbon from screw dislocation (SD), edge dislocation (ED), vacancy and for breaking the C-C pair in tungsten at the different heat ramp rates. The methodology to calculate the detrapping temperature is described in the text. The indexes 'H' and 'E' denote the binding energy for C to the SD, calculated taking the hard or easy core, respectively. The lines connecting the points with the same heating ramp rate are added as a guide for the eye. The error bars provide the estimation of the possible deviation of the calculated detrapping temperature given a cumulative error on binding plus migration energy of 0.05 eV and 10% error on the frequency *v*.

#### 4 Conclusions

The characterization of the interaction of C with point defect clusters (Va-Va-Re, Va-Va-C, Va-Re-C, SIA-C and (W-Re dumbbell)-C complexes) and dislocations in W and a dilute W-Re matrix has been performed using the DFT calculations. Two types of dislocations, namely screw and edge, with Burgers vector  $a_0/2 <111$ > were considered. The ground-state atomic structures for these defect clusters were identified and the corresponding binding energies were calculated. The results of the simulations were compared with the available experimental evidence for the presence of impurity atoms, such as carbon, in the form of Cottrell atmospheres in different commercial tungsten grades and the results of the study of annealing of electron-irradiated pure W.

On the basis of the DFT calculations, the following four conclusions can be drawn:

1) In a pure W, the C atoms interact strongly with vacancies ( $E_b$ =2.0 eV) in the nearest octahedral position and form a stable cluster with a SIA oriented in the ground-state along <221> direction (bridge interstitial) with a binding energy of 0.73 eV. Whereas, in a W-Re matrix, C can form clusters with substitutional Re atoms (Re-C attraction with  $E_b$ =0.2 eV) and stable V-C-Re complexes, where Re-V are located at the 2nn distance and C atom resides inbetween. The presence of Re atoms barely increases the attraction of C to the W-Re dumbbell by less than 0.05 eV. In a W-Re matrix, the lowest-energy orientation of the W-Re dumbbell is <221>, while the ground state configuration for a C atom at a W-Re dumbbell is realized when the latter is oriented along the <110> direction.

2) The study of Va-Va-Re, Va-Va-C and Va-Va-Re-C clusters showed that the C atoms stabilize the di-vacancy cluster at the 2nn distance and cancel the vacancy-vacancy repulsion at the 1nn and 3nn distances. The single Re atoms cancel the repulsion for di-vacancies at the 1nn and 3nn distances. Re-C clusters stabilize the di-vacancy at the 2nn and 3nn distances and cancel the vacancy-vacancy repulsion at the 1nn distance. Thus, the formation of di-vacancies, nucleated at C and Re-C in tungsten, initiates the formation and growth of vacancy clusters.

3) The C atoms are strongly attracted to dislocations in bulk W. The binding energy of a single C atom to a screw and an edge dislocation are 1.5-1.6 eV and 2.1 eV, respectively, taking the easy SD core structure as a reference. C atoms, if approaching the SD core, induce a SD core transformation from the 'easy' to 'hard' core and occupy the distorted prismatic positions inside the hard dislocation core, shifted to the neighbour position. Once introduced at the SD core, the C atoms are trapped at the SD (with a hard core) with the energy of about 1.9 eV. The latter two findings indicate that the presence of C at the SD core can assist the nucleation of kinks and obstruct their propagation along the SD line. Thus, C atoms would directly affect the dynamics of the screw dislocation motion, which macroscopically is manifested as the yield drop. C atoms are found to be attracted by 0.2-0.5 eV stronger to edge dislocations compared to screw dislocations. The calculations with a pair of C in the cores of SD and ED has shown an attraction in the SD core of 0.3-0.4 eV and a negligible (less than 0.05 eV) interaction of C atoms in the core of the ED. Thus, C atoms tend to form clusters along the screw dislocation line only. The strong C-C attraction in the SD core is rationalized by the minimization of the lattice distortion (transformation to the hard core structure) and the dislocation line length, when C atoms are located next to each other along the dislocation line.

4) The Re atoms are attracted to both edge and screw dislocation with a binding energy of 0.51 and 0.27 eV, respectively. The presence of Re in the dislocation core does not alter the

binding of C atoms to the edge dislocation, while the binding energy for C to the SD line increases by 0.16 eV when the SD is decorated by rhenium.

The results of the DFT calculations, obtained in this work, rationalize the following experimental findings:

1) While the DFT calculations predict the repulsion of the di-vacancy complexes in pure W, the experimental analysis of the thermal annealing of electron-irradiated tungsten samples has shown the nucleation of vacancy clusters [8, 9] at about 600-700 K, which dissolve at the temperatures of about 1000-1150 K as revealed by the analysis of the annealed up to 1900 K tungsten samples after the irradiation by 30 keV  $1 \times 10^{20}$  D<sub>2</sub><sup>+</sup> m<sup>-2</sup> ions [11]. Our *ab initio* simulations explain this experimental data by proposing a mechanism which can glue the divacancies together and allow further growth of the larger vacancy clusters. In our work, C and Re-C complexes were found to stabilize di-vacancies, thus making the vacancy clustering possible. The calculated expected temperature of dissociation of Va-Va(2nn)-C complexes via the emission of vacancy is about 1000-1100 K depending on the heating ramp rate, which fits excellently to the above mentioned experimental findings.

2) The obtained sets of binding energies for C atoms with edge and screw dislocations in W were also used to estimate the temperature ranges for C detrapping from dislocations. The calculated release temperatures have been discussed in the light of available results of uniaxial tensile tests in different commercial tungsten grades, where the yield drop phenomenon is naturally manifested. The available experimental dataset points to the fact that the C atmospheres dissolve between 600 and 1000 °C, while the release temperatures, calculated in the present work based on the strength of attraction of C to dislocations, are found to be in good correspondence with these values, predicting the range for C detrapping between 700 and 900 °C.

3) The exact values of interaction strength for C at point defects and dislocations, calculated in this work, are essential to parameterize reliable Object Kinetic Monte Carlo (OKMC) models of the evolution of microstructure in W under neutron or ion irradiation. The latest OKMC model [3] developed for the W-Re system has shown that taking into account the parameters for C-SIA and C-edge dislocation (the latter is taken as an approximation for large dislocation loops) interactions in W and W-Re, obtained in this work, it is possible to predict correctly the evolution of the radiation-induced microstructure observed experimentally [54-58].

The obtained dataset of binding energies for C at different microstructural features in a W-Re matrix can also be used to fit or validate a W-C or W-Re-C interatomic potentials.

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