Blocking of annihilation of Frenkel pairs by He atoms

N.N. Degtyarenko, A.A. Pisarev

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, 115409 Kashirskoe sh, 31, Russia

Abstract. The results of DFT modelling of blocking the annihilation of Frenkel pairs at small distances between vacancy and self interstitial atom is performed in application to “subthreshold” radiation defects formation in W. It is shown that even at small distances sufficient for spontaneous annihilation of the Frenkel pair, He atoms can suppress the annihilation near the surface. In some cases an additional vacancy can appear close to the surface thus increasing the radiation damage. It is concluded that He impurities can be an additional reason for subthreshold” radiation damage.

1. Introduction

Radiation damage to metals is a factor of paramount importance in the design and operation of nuclear and thermonuclear reactors. If the radiation damage to materials of nuclear reactors has been studied in great detail, this cannot be said about the study of radiation damage to fusion reactor materials, in which not only neutrons play an active role, but also fast helium ions, as well as deuterium-tritium plasma, which create radiation damage near the surface. An additional feature of radiation damage of fusion reactor materials is extremely large concentrations of hydrogen isotopes (thermonuclear fuel) and helium (a product of the thermonuclear reaction and the decay of tritium). These light impurities interact with radiation defects and influence the damage.

It estimations of the damage rate, the concept of threshold displacement energy (TDE) is often used, suggesting that no primary Frenkel pairs are produced is the energy transferred in collisions is below TDE. Nevertheless, formation of defects at subthreshold energies is often observed in experiments. The concept of TDE is rather uncertain as noted in the review [1], and subthreshold primary damage is possible for several reasons. In addition to factors discussed in [1], one may suggest that hydrogen-defect interaction and helium-defect interaction can influence the survival of primary Frenkel pairs (vacancy and self interstitial atom SIA). At energies close to TDE, the distance between genetically related vacancies and SIA is small, and most of the primary Frenkel pairs annihilate. If, however, hydrogen and helium atoms appear near the pair, these atoms can be trapped in defects preventing annihilation of the vacancy and SIA. In this case primary defects may survive even at subthreshold displacement energies below TDE. This effect is especially important in relation to radiation damage to fusion materials where the concentration of hydrogen and helium is very large.

It was observed experimentally [2, 3] that He and H in solid solution promote formation of voids an interstitial dislocation loops, and this was attributed to interaction of light impurities with point defects. Atomic scale modelling [4] predicted that vacancy formation is facilitated in presence of H interstitials due to decrease of the vacancy formation energy from 2.95 eV to 2.23 eV.
DFT calculations [5] demonstrate that vacancy can be formed spontaneously in presence of several interstitial hydrogen atoms in W.

The powerful method for studying the behavior of point defects in metals is the density functional theory (DFT). Mainly it is used for analyses of defects in the bulk of the metal. There are few works in the literature in which the effect of a surface on the properties of point defects of tungsten is studied, e.g. [6-9]. In this work, we analyze behavior of vacancies and self interstitial atoms near the surface of W in presence of interstitial hydrogen and helium atoms.

2. Method

Ab-initio DFT method was used to analyze structural and electron characteristics of the tungsten crystal bulk and in the near-surface area of tungsten. The calculated super cell contains 128 W atoms (768 electrons) with periodically optimized boundary conditions. The DFT calculations were performed within the framework of the plane wave basis (Quantum Espresso code ver 6.4 [10]) using the correlation functional GGA-PBE (Perdew-Burke-Ernzerhof) with the norm-conserving pseudopotential. To optimize the system energy by the atoms coordinates and parameters of the SuperCell, the iterative quasi-Newtonian method BFGS was chosen, in which the Hessian is calculated approximately based on the steps taken before. All calculations were performed in the spin-polarized approximation for adequate comparison of the calculated energy values of different phases. The cutoff energy was taken to be 720 eV. Convergence threshold on total energy for ionic minimization was \(~5.0\times10^{-6}\) eV. Convergence threshold for electronic selfconsistency was \(5.0\times10^{-7}\) eV. The accuracy of calculating forces was about \(10^{-2}\) eV/Å. Maximum allowable displacement of atoms for iterations was \(5.0\times10^{-4}\) Å. Various initial configurations of primary pair and H2 pair were considered, and results of relaxation were analyzed. The initial distances between a vacancy and SIA were small that is typical for small recoil energies. About 80 calculations were performed to analyze various configurations of defects and impurity atoms.

3. Results

3.1. Recombination of the Frenkel pair in the tungsten bulk.

Figure 1a shows the variant of the initial configuration of defects, which seems to be the most favorable for blocking the recombination of genetically connected vacancies and self interstitial atoms by interaction of the vacancy with He2. Namely, the He2 pair is very close to the primary vacancy, while the primary interstitial W atom is maximally removed from the vacancy (for a given supercell size). Just after the system was allowed to relax, He2 occupies the vacancy. However, the primary SIA, which is relatively far from the vacancy starts to move to the vacancy, pushes the nearest W atoms out of its lattice positions into a nearest interstitial site and occupies the vacant lattice position. This process repeats as a substitution chain and leads to disappearance of the primary vacancy. The He2 pair, which was initially trapped by a vacancy, is pushed out of the primary vacancy into the interstitial position by the last secondary SIA. It follows from these results that the volume of spontaneous recombination of genetically related vacancies and SIA (subthreshold displacement) exceeds the volume of the supercell used in this work, and the presence of impurities in the form of He2 does not prevent spontaneous recombination. In the case of one He atom near the vacancy, recombination is also easy.

Spontaneous annihilation of the primary Frenkel pair was analyzed in [11] within the framework of another method. It was estimated that the volume of spontaneous anihilation \(\Omega_{\text{rec}} \approx 200\omega_0\), where \(\omega_0\) is the atomic volume for tungsten. This value is twice the volume of the supercell used here. Annihilation in this volume takes place from any position of SIA.
Figure 1. Configurations of atoms in modeling relaxation of the lattice after production of primary Frenkel pair in the presence of He2 dumbbell. a) – the configuration at the optimization step n = 0 and 47, when the He atoms are trapped by the primary vacancy; b) – the final, optimized configuration, when helium atoms are displaced from the vacancy, and vacancy is filled by the nearest W atom after a chain of substitutions. Symbols (+) – W lattice atoms slightly displaced. Green balls – a pair of He atoms. Red ball – primary SIA. Blue balls – W atoms belonging to the substitution chain. Lilac balls - W atoms surrounding the vacancy. Empty circles – positions where atoms are displaced at n = 47.

3.2. Recombination of the Frenkel pair near surface (100).

In this section we consider the case the upper boundary is free to give the surface of the crystal to relax and the case there are no helium atoms. In the case the surface is close to SIA, there two sinks for SIA: the vacancy and the surfaces. Various configurations of the primary vacancy and primary SIA were considered, and the final state after relaxation depends on the initial position of the primary SIA, orientation of the craudion, formed by primary SIA, and the position of the primary vacancy.

Figure 2. Relaxation of the W lattice in the case a Frenkel pair is created near the (100) surface. There are no helium atoms. a – recombination of a vacancy and SIA due to successive substitutions; b – formation of an adsorbed W atom.
In the case SIA is located on the same atomic layer with a vacancy or deeper in the bulk, SIA creates a crowdion, and one of its atoms recombines with the vacancy as shown in Figure 2a. If SIA is located above the vacancy closer to the surface, then SIA creates a crowdion that moves along the substitution chain to the surface, creating an adsorbed W atom (Figure 2b). Thus, the volume of spontaneous recombination of Frenkel pairs near the surface decreases by about one and a half times, since the areas of the initial location of the interstitial tungsten atom located above the vacancy and closer to the surface fall out of the volume of spontaneous recombination (even without the presence of impurity helium atoms).

3.3 Frenkel pair near the surface (100) in presence of a pair of He atoms.

In this section, initial configurations of the damaged lattice are the same as in the previous section, but the difference is that a pair of He atoms is added. Figure 3 shows the initial configuration corresponding to Fig. 2a, but with two helium atoms near the vacancy, which are trapped by the vacancy almost immediately. The SIA creates a crowdion that do not lead to annihilation of the Frenkel pair as it was without He2. Instead SIA produces a chain of substitutions with neighbor W atoms in the lattice directed towards the surface. As a results, the last W atom rests in adsorption state on the surface (Fig. 3). Thus, the volume of spontaneous recombination of Frenkel pairs near the surface decreases in the presence of impurity helium atoms if to compare with the case described in Section 3.2.

![Figure 3. Blocking of the recombination of the Frenkel pair produced near the (100) surface in the presence of two He atoms near the vacancy. The final stage of optimization. The arrows indicate the displacements of W atoms along the line of the crowdion. The crowdion exit on the surface is seen on the left in the adjacent cell due to the periodicity of the boundary conditions of the supercell.](image)

Figure 3 shows the case similar to that in Fig. 2b, but with two helium atoms near the vacancy. In this case the result of the relaxation is drastic: surface is seriously transformed, an atomic steps on the surface and a second near-surface vacancy are created. One can see in Fig. 4a, that the crowdion line has a smaller angle with the surface than that in Fig. 2b. The last W atom in the chain, which is pushed by the crowdion on the surface, absorbs in a cell different from that in Fig 2b, leaving behind a region of low electron density. Fig.4b shows the electron density isosurfaces for the final stage of structure optimization (given in Fig.4a). The electron density inside closed cavities is less than outside. One can see formation of the second vacancy and serious transformation of the electron density on the surface. Formation of the second vacancy leads to increase of the radiation damage, and appearance of holes and protrusions in the near surface layer.
Figure 4. a - blocking of the recombination of the Frenkel pair created near the (100) surface, in the presence of a pair of He atoms near the vacancy. Cradion disappears on the surface giving an adsorbed W atom and additional secondary vacancy. b - visualization of the electron density distribution for configuration of Fig. 4 a demonstrating formation of an additional vacancy.

Conclusion

Presence of one or two He atoms near the Frenkel pair in W bulk does not influence the annihilation of the vacancy and SIA. Presence of He atoms near the Frenkel pair in areas close to the surface leads to blocking of the annihilation of the vacancy and SIA. The extra W atom adsorbs on the surface. In some cases a second vacancy besides the primary vacancy can appear near the surface giving rise to increase of the lattice damage, serious transformation of the surface, and appearance of holes and protrusions near the surface.

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