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Trapping of He clusters by inert-gas impurities in tungsten: First-principles predictions and experimental validation

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ABSTRACT

Properties of point defects resulting from the incorporation of inert-gas atoms in bcc tungsten are investigated systematically using first-principles density functional theory (DFT) calculations. The most stable configuration for the interstitial neon, argon, krypton and xenon atoms is the tetrahedral site, similarly to what was found earlier for helium in W. The calculated formation energies for single inert-gas atoms at interstitial sites as well as at substitutional sites are much larger for Ne, Ar, Kr and Xe than for He. While the variation of the energy of insertion of inert-gas defects into interstitial configurations can be explained by a strong effect of their large atomic size, the trend exhibited by their substitutional energies is more likely related to the covalent interaction between the noble gas impurity atoms and the tungsten atoms. There is a remarkable variation exhibited by the energy of interaction between inert-gas impurities and vacancies, where a pronounced size effect is observed when going from He to Ne, Ar, Kr, Xe. The origin of this trend is explained by electronic structure calculations showing that *p*-orbitals play an important part in the formation of chemical bonds between a vacancy and an atom of any of the four inert-gas elements in comparison with helium, where the latter contains only $1s^2$ electrons in the outer shell. The binding energies of a helium atom trapped by five different defects (He-v, Ne-v, Ar-v, Kr-v, Xe-v, where v denotes a vacancy in bcc-W) are all in excellent agreement with experimental data derived from thermal desorption spectroscopy. Attachment of He clusters to inert gas impurity atom traps in tungsten is analysed as a function of the number of successive trapping helium atoms. Variation of the Young modulus due to inert-gas impurities is analysed on the basis of data derived from DFT calculations.

1. Introduction

Generation of helium (He) in materials through transmutation nuclear reactions under neutron irradiation, giving rise to radiation swelling and grain boundary embrittlement, is a major factor limiting the lifetime of structural materials in fusion and fission power plants [1]. So far, experimental and theoretical effort has been focused primarily on the synergetic effects associated with the simultaneous accumulation of helium and hydrogen. Effects associated with the incorporation of other inert gases have not received much attention even though the agglomeration of noble gas atoms in metals and alloys is a well-known phenomenon observed in multi-beam ion implantation experiments [2]. One of the new ideas is to consider helium co-implantation with other inert-gas ions to simultaneously model dpa damage and dissolved noble gases, and through that to investigate the effect of neutron irradiation on nuclear fusion reactor components. However, a question arises if other noble gas atoms, such as Ar or Xe, are similar to He in relation to ion implantations. Reliable experimental data on defect energies for these noble gases in fusion structural materials, in particular their binding energies with vacancies or vacancy clusters, are very scarce. The effect of noble gas incorporation in these materials has not been systematically studied even though the agglomeration of noble gas atoms implanted in metals and alloys is often observed by transmission electron microscopy. Traditional view is that any noble gas impurity should be similar to helium, since there is no chemical interaction between an inert gas atom and a solid, and hence the behaviour of noble gas atoms in a material can potentially be explained assuming that local lattice distortion increases monotonically from He to Xe. Therefore, the development of an accurate predictive model based on first-principles calculations for defects formed due to the accumulation of helium and other noble gases in the crystal lattice of iron, steel, a non-magnetic body-centred cubic (bcc) refractory metal or alloy, is an issue of significance for the quantification of radiation damage effects on structural integrity of fusion reactor components [3]. In this paper, we investigate small helium clusters trapped by

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inert-gas impurities in tungsten, and validate our theoretical study by comparison with experimental thermal desorption spectroscopy data.

2. Benchmarking density functional theory (DFT) calculations

First-principles calculations described in this work were performed using density functional theory (DFT) implemented in the Vienna Ab-initio Simulation Package (VASP) code with the interaction between ions and electrons described by the projector-augmented waves (PAW) method [4]. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [5] is used for describing the effects of exchange and correlation in tungsten as well as in all the inert-gas elements through the application of standard PAW potentials. For diatomic noble gas molecules, the PBE model predicts interaction energies and equilibrium distances [6,7] closer to both the theoretical hybrid functional PBE0 and experimental values in comparison with the Perdew–Wang (PW) functional [8] used in previous studies of He in bcc-W [9,10]. It is important to emphasize that the inclusion of *semi-core electrons* in the valence states has a significant effect on the energetic trend of intrinsic radiation-induced self-interstitial atom (SIA) defects in all the bcc transition metals [11,12]. In particular, we find that in all the non-magnetic bcc transition metals the most stable $\langle 1\,1\,1\rangle$ configuration of SIAs cannot be reproduced correctly if the semi-core electrons are ignored, this is especially significant for transition metals of group 6B (Cr, Mo, W). All the total energy calculations were performed using a $4\times4\times4$ (128 atom) bcc super-cell, with plane-wave cut-off energy of 400 eV and k-point mesh with spacing of 0.15 $(\text{Å})^{-1}$. In elastic constant calculations, the k-point mesh spacing was 0.10 $(\text{Å})^{-1}$.

For benchmarking our DFT-PBE calculations, we have cross-checked the formation energies of intrinsic defects and substitutional and interstitial helium defect configurations, as well as binding energies of He clusters, following reaction $(n-1)\text{He} + \text{He} \rightarrow n\text{He}$ and their interaction with a mono-vacancy, following reaction $\text{He} + (n-1)\text{He-v} \rightarrow n\text{He-v}$, in bcc-W, as shown in Table 1. The results are compared with the corresponding data obtained from DFT calculations for the same 128-atom super-cell but using the PW exchange-correlation functional [9,10]. We find significant differences between the predicted binding energies of 4-He cluster (from $\text{He}_{\text{int}} + 3\text{He}$ reaction): 2.23 eV versus 1.52 eV for PBE versus PW and also for 4-He-atom cluster interacting with a mono-vacancy (from $\text{He}_{\text{int}} + 3\text{H-v}$ reaction): 3.24 eV and 2.61 eV for PBE and PW, respectively. It is interesting that in the assessment of helium cluster behaviour in tungsten [13], the binding energy of 4He-v defect complex was altered from 2.61 eV to the value close to 3.0 eV, which is in better agreement with our DFT-PBE value of 3.24 eV. The relaxation volumes of defects, i.e. volume differences between the fully relaxed defect configurations and perfect lattice structures, are given in the last column of Table 1. The calculated relaxation volumes for vacancies and interstitial helium defects are in good agreement with literature data [14,15]. Table 1 show that the relaxation volume of nHe-v defects changes sign from negative to positive as the number of He atoms, occupying a vacancy, increases. DFT data on relaxation volumes have been used for interpreting lattice expansion of tungsten alloys implanted with He at low temperature.

Table 1
DFT formation and binding energies (in eV) of intrinsic and He defects in bcc-W computed using the PBE exchange-correlation functional (present work), compared with those calculated using the PW functional from Refs. [9,10]. The PBE-predicted relaxation volumes of defects obtained from fully relaxed calculations, in the units of tungsten atomic volume (V_0) in a perfect bcc $4\times4\times4$ bcc super-cell, are given in the last column.

Defect-type	PBE (Present work)	PW ([9,10])	Relaxation volume (V_0)
E_f(vac)	3.24	3.19	−0.37
E_f(SIA$\langle 1\,1\,1\rangle$)	10.06	10.53	1.68
E_f(He_sub)	4.83	4.70	−0.23
E_f(He_tet)	6.22	6.16	0.36
E_f(He_oct)	6.44	6.38	0.37
E_b(2He)	1.03	1.03	0.80
E_b(3He)	1.18	1.36	1.16
E_b(4He)	2.23	1.52	1.65
E_b(5He)	1.59	1.64	2.03
E_b(He-v)	4.63	4.57	−0.23
E_b(2He-v)	3.10	3.11	−0.06
E_b(3He-v)	3.33	3.28	0.14
E_b(4He-v)	3.26	2.61	0.38
E_b(5He-v)	1.88	1.44	0.71
E_b(6He-v)	2.18	2.08	1.10

Formation energies of He in substitutional and interstitial positions in tungsten found in our simulations are in good agreement with literature data. Fig. 1 shows a trend exhibited by these formations energies when going from He to Ne, Ar, Kr and Xe. Our calculations show that the most stable interstitial configuration for the latter four inert-gas elements in bcc-W is the tetrahedral site. The formation energy difference between octahedral and tetrahedral configurations increases from 0.22 eV for He to 0.51, 1.13, 1.25, and 1.62 eV for Ne, Ar, Kr and Xe, respectively, indicating the dominant contribution from lattice distortion to the defect formation energy as the size of an inert gas atom increases from helium to xenon. The octahedral site is a metastable configuration with respect to the tetrahedral one and although it is not the saddle point configuration, the energy difference between the two configurations provides an estimate for the migration barrier of interstitial inert-gas atoms in bcc-W. Energy difference between the two interstitial configurations for inert-gas atoms in tungsten is quite sensitive to size of super-cell used for DFT calculations. A recent study [16] of three inert-gases (He, Ne and Ar) defects in bcc-W modelled using a small 54-atom supercell gives the interstitial energy difference of 0.38 eV for the helium case (in comparison with 0.22 eV found here and in previous studies [9,10]), whilst for neon and argon, this energy difference is 0.62 eV and 1.06 eV compared to 0.51 eV and 1.13 eV found in our 128-atom super-cell study, respectively. Our nudged elastic band calculations give the migration barrier of 0.07, 0.14 and 0.23 eV for the tetrahedral interstitial He, Ne and Ar in a comparison with 0.06, 0.17 and 0.19 eV, respectively, found in [15]. The calculated formation energies of inert-gas atoms in substitutional positions shown in Fig. 1 exhibit a similar monotonic energy trend from He to Xe. The substitutional formation energy is 4.83 eV (compared with 4.70 eV from [9,10]) for He and the corresponding predicted values for Ne, Ar, Kr and Xe are 6.25, 9.28, 9.74 and 10.09 eV, respectively. It is clear from Fig. 1 that these values are not of the same magnitude as the formation energies of inert-gas defects in either of the two interstitial configurations, especially for Ne, Ar, Kr and Xe. As discussed in Refs. [1,17,18], it is not sensible to compare directly the formation energies of substitutional configurations with those obtained for the interstitial sites. Strictly speaking, the definition of the solution energy involves a two-step process: first creating a vacancy and then inserting an inert-gas atom into it. In agreement with a previous study [16], we find, from calculations involving full relaxation of atomic positions that a He defect prefers to occupy a substitutional position rather than an octahedral interstitial configuration away from a vacancy site. For other inert-gas defects, due to the larger distortion around a vacancy associated with the insertion of an inert gas atom into it, the difference between the energies of the two configurations is relatively small although it is still in favor of a substitutional configuration in a similar way as for the He case. Therefore, in the analysis of interaction between a vacancy and an inert-gas impurity we consider the substitutional configuration as the lowest-energy ground state of the system.