Interaction of O–Y and O–Y–Ti clusters embedded in bcc Fe with He, vacancies and self-interstitial atoms

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Abstract
Calculations based on density functional theory are performed to investigate the interaction of O–Y and O–Y–Ti clusters in bcc Fe with He atoms, vacancies (v) and self-interstitial atoms (SIA). The four different cluster structures studied in our previous work (J. Phys.: Condens. Matter 31 095701) are considered. He, v and SIA are inserted on different positions inside and in the environment of the clusters, the total energy of the corresponding supercell is minimized and the binding and incorporation energy of the three kinds of defects is determined. He in the center of a cage-like (CL) cluster is more stable than on interfacial vacant sites (IVS). In CL O–Y clusters He on an IVS is more stable than in the cluster structure with oxygen in the center, whereas there is no significant difference between the two kinds for clusters with Ti. Up to a distance of 1.5 times the iron lattice constant from the cluster center He is not stable on most of the octahedral and tetrahedral interstitial sites in the Fe matrix near the interface. Instead He is shifted towards positions closer to the cluster. Relaxation occurs to known IVS as well as to previously unknown interfacial interstitial sites. Moreover, two or three He atoms are placed on sites found to be stable after adding a single He. The corresponding binding and incorporation energies obtained after relaxation are nearly equal to the sum of the values for the interaction with a single He atom. However, placing He dimers or trimers in the environment of a vacancy may also lead to relatively low values of the incorporation energy. Also, barriers for jumps of He atoms between interfacial sites and the center of CL clusters are determined. In the CL O–Y cluster the barriers are lower than in the CL O–Y–Ti cluster, i.e. trapping and release of He is easier in the former than in the latter. v and SIA interaction with the clusters is also attractive. The binding energy of v strongly depends on the site where v is inserted while in all studied cases the SIA is annihilated at the cluster-iron interface. Present results clearly demonstrate that the oxide-based nanoclusters are strong traps for irradiation induced defects which is in agreement with experimental findings.

Keywords: density functional theory calculations, oxide dispersion strengthened steels, interaction with He, vacancies and self-interstitial atoms

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
1. Introduction

Oxide dispersion strengthened (ODS) Fe–Cr steels or Nanostructured Ferritic/martensitic FeCr Alloys (NFA) are prime candidates for structural materials in nuclear fission and fusion reactors due to their exceptionally high temperature stability, yield and creep strength as well as their high radiation tolerance. These properties stem mainly from the presence of nanometer size O–Y and O–Y–Ti particles, which are embedded in the FeCr matrix. In particular, nanoclusters can act as sinks for radiation induced defects such as the transmutation product He, vacancies and self-interstitial atoms (SIA). In this manner, void swelling due to He-vacancy interactions and He segregation at dislocations and grain boundaries can be reduced [1–7].

Important experimental techniques to characterize the influence of radiation-induced defects on structural properties are transmission electron microscopy (TEM), atom probe tomography (APT), small-angle neutron scattering (SANS), and positron annihilation spectroscopy (PAS) as well as mechanical testing such as nanoindentation. The application of APT and TEM to analyze He-ion irradiated NFA by Edmondson et al [8] showed that about 50% of the He bubbles are located on nanoclusters, the rest on coarse precipitates, dislocations, grain boundaries, and on matrix sites. Compared to conventional FeCr steels, the trapping of He by the nanoparticles of the NFA may lead to a reduced susceptibility to He embrittlement. Nanoindentation-based analysis of comprehensive experimental data on radiation induced hardening led to the conclusion that the nanoclusters are the most important sinks for point defects created by Fe-ion implantation into different kinds of NFA, followed by grain boundaries and dislocations [9].

Atomic-scale theoretical investigations and computer simulations can essentially contribute to the understanding of the interaction of the nanoclusters with He atoms, vacancies, and SIA. Several authors performed density functional theory (DFT) calculations in order to investigate the He storage in the pure oxides Y₂O₃, Y₂Ti₂O₇, and Y₂TiO₅ [10–17]. These studies revealed that in these oxides the He incorporation energy is significantly lower than in pure Fe. Moreover, a few models on the interaction of He, vacancies and SIA with O–Y and O–Y–Ti clusters in bcc Fe were considered. The focus of the works of Brodrick et al [18] Peng et al [19] and Yang et al [20] was on the trapping of vacancies, SIA, or He at the interface between the nanocluster and bcc Fe. For this purpose, these authors considered supercells with planar interfaces between Y₂O₃ or Y₂Ti₂O₇ and bcc Fe. Sun et al [21] investigated the interaction of one or more He atoms with a cubic O–Y–Ti model in bcc Fe while Danielson et al [22] considered the incorporation of a single He atom into the O–Y–Ti cluster model of Barnard et al [23]. The O–Y models of Sun et al [21] and Barnard et al [23] are based on the atomic structures of Y₂O₃ and Y₂Ti₂O₇, respectively. Gan et al [24] considered different cluster models that consist of ‘reference units’. These are bcc Fe unit cells that do not only contain Fe but also a vacancy, an O atom, a Y atom, and up to three Ti atoms. He was added to these model systems in order to investigate He cluster nucleation and growth.

In the present work the most stable atomic configurations obtained in [25] for two O–Y and two O–Y–Ti cluster models are considered and their interaction with He, a vacancy and a SIA is studied by DFT calculations. In this manner the influence of cluster composition as well as morphology can be revealed. The binding and incorporation energy of the defect species are determined for the different cluster models. For this purpose the He atom, the vacancy, or the SIA are initially set on selected sites inside or near the cluster, and after relaxation the final structure and energetics is analyzed. Also, the interaction of two or three He atoms with O–Y and O–Y–Ti clusters is investigated and selected barriers for He migration are calculated. Besides the energetics, i.e. binding and incorporation energy, these barriers are important quantities in order to understand the evolution of the He storage by the clusters at finite temperatures.

2. Cluster models and possible sites for He, vacancies and SIA

In our recent work [25], different structural models for O–Y and O–Y–Ti clusters in bcc Fe were considered and for a given composition the most stable atomic configuration was obtained by DFT calculations. Due to limitations of computational resources the largest clusters investigated in [25] mainly consist of (i) 6 O atoms, 9 vacancies and 6 Y atoms, and (ii) 7 O, 9 v, 3 Y, and 3 Ti. In this context all sites of the underlying perfect bcc lattice which are not occupied by metal atoms (Fe, Y, Ti) are counted as vacancies. That means that all O atoms are assigned to vacancies. The above definition of vacancies is not strictly necessary. However, such a definition may be helpful to better understand the properties of the clusters. The equivalence of investigations the cluster energetics using or not using v was shown in [25]. Two kinds of clusters were studied: (i) cage-like (CL) clusters with a vacancy in the center surrounded by an octahedron of Y and Ti atoms, and (ii) clusters with oxygen at this central site. The first model is directly derived from the atomic structure of the oxides Y₂O₃ and Y₂TiO₇, whereas the second was obtained in [25] and has a core similar to the rock-salt structure. Compared to the pure oxides the two models are depleted in oxygen. The energetic properties of both types of clusters are very similar: If Ti is not present clusters with oxygen in the center are slightly more stable than the corresponding CL structures. The opposite holds for clusters with Ti. Figure 1 illustrates the relevant atomic configurations obtained by the DFT calculations in [25]. In the present work the interaction of He with these clusters is investigated. Possible He sites are classified in the following manner.

(a) He on a vacancy site in the center of CL clusters: This position corresponds to an octahedral interstitial site in bulk Y₂O₃ or Y₂Ti₂O₇.
(b) He on a vacancy site at the cluster-iron interface: Both in CL clusters and in clusters with oxygen in the center (OC) vacant bcc sites which are not assigned to oxygen atoms are available there.

(c) He on interstitial sites: In the interface region He might occupy tetrahedral and octahedral interstitial sites in the underlying bcc lattice. It is known from literature that He is an interstitial foreign atom in bcc Fe, whereby the tetrahedral site is most stable followed by the octahedral site [11, 15, 21, 26–28]. Present investigations are limited to such interstitial sites with a distance of less or equal than 1.5 \( a \) to the center of the cluster, where \( a \) is the lattice constant of bcc Fe.

The possible positions of He atoms are also shown in figure 1. After He is placed on a given position the system is relaxed by DFT calculations. In some cases the assumed He site may be really stable in others it may be unstable. Based on results on the interaction of a single He atom with the cluster, in a further step two or three He atoms are placed on selected sites and the energy of the supercell is minimized using DFT. Besides the sites found to be stable after adding a single He to the cluster, some additional configurations are studied in which two or three He atoms are placed into the environment of these sites.

The relaxed atomic configurations of the clusters with one, two or three He atoms are shown in the supplemental material \(^4\) (stacks.iop.org/JPhysCM/31/485702/mmedia). Three possible sites (A, B, C) for an additional vacancy (v) or an additional SIA are shown in figure 1 as well. The relaxed cluster configurations with v or SIA are also provided in the supplemental material \(^5\).

3. DFT calculations

We carried out spin-polarized calculations in the framework of DFT as implemented in Vienna \textit{ab initio} simulation package (VASP) [29–31]. Projector-augmented-wave (PAW) type pseudopotentials [32, 33] with the Perdew–Burke–Ernzerhof (PBE) [34] parametrization for exchange and correlation terms are considered to treat positive cores and valence

\(^4\) See supplemental material for data on relaxed configurations, incorporation and binding energy values.

\(^5\) See footnote 4.
electrons, with a plane wave cutoff of 500 eV. All our cluster models are embedded in a supercell with 128 bcc lattice sites. In selected cases, a supercell with 250 bcc lattice sites is considered in order to find out whether possible interactions between the periodic images are relevant for results obtained for the smaller cell. Brillouin zone integration is performed using a gamma-point centered Monkhorst–Pack scheme [35]. Based on convergence tests, we use uniform sampling of $3 \times 3 \times 3$ $k$-points for the smaller supercell and $2 \times 2 \times 2$ sampling for the larger cell. The integration in the $k$-space is done with a Methfessel–Paxton [36] smearing width of 0.2 eV.

After placing He into the supercell according to one of the above mentioned models the position of atoms as well as the volume and shape of the supercell are relaxed, so that the force on atoms and the total stress/pressure on the supercell are minimized. In the present calculation the accuracy level of residual force on any atom and of the total energy change between successive ionic iterations are set to $10^{-2}$ eV Å$^{-1}$ and $10^{-5}$ eV, respectively.

The interaction between He and a cluster containing O, Y, and Ti can be characterized using the binding energy of He to the cluster. The binding energy of mHe atoms is given by

$$E_{\text{b}}^\text{nate} = E_{\text{bind}}(O, Y, Ti; mHe) - E_{\text{bind}}(O, Y, Ti)$$  \hspace{1cm} (1)

where $E_{\text{bind}}(O, Y, Ti; mHe)$ and $E_{\text{bind}}(O, Y, Ti)$ are the total binding energies of the cluster with and without mHe. In the present work the cases $m = 1, 2, 3$ are considered. For the cluster configurations shown in figure 1 the quantity $E_{\text{bind}}(O, Y, Ti)$ was determined in [25]. The general relation for the total binding energy of an embedded cluster that consists of $n$ monomers, e.g.: a certain amount of O, Y, Ti, He atoms and vacancies, is defined by

$$E_{\text{bind}}(X_1 + X_2 + \ldots + X_n) = E(X_1 + X_2 + \ldots + X_n) + (n - 1)E^0 - \sum_{i=1}^{n} E(X_i),$$  \hspace{1cm} (2)

$E(X_1 + X_2 + \ldots + X_n)$ and $E(X_i)$ denote the total energy of supercell with the $X_1 + X_2 + \ldots + X_n$ cluster and the total energies of supercells with the monomers $X_i$, respectively, while $E^0$ is the total energy of a supercell containing perfect bcc Fe. By definition $E_b$ and $E_{\text{bind}}$ are negative if attraction dominates. The data for $E(X_i)$ are determined assuming O on an octahedral interstitial site in bcc Fe, and Y, Ti as well as the vacancy on a bcc lattice site [25]. In a similar manner the binding energy of an additional vacancy (v) or an additional SIA to the cluster is given by

$$E_{\text{b}}^\text{v} = E_{\text{bind}}(O, Y, Ti; v) - E_{\text{bind}}(O, Y, Ti)$$  \hspace{1cm} (3)

and

$$E_{\text{SIA}}^\text{v} = E_{\text{bind}}(O, Y, Ti; SIA) - E_{\text{bind}}(O, Y, Ti).$$  \hspace{1cm} (4)

Another characterization of the interaction of mHe with the cluster is possible via the incorporation, solution or formation energy [22]

$$E_{\text{incorp}}^\text{mHe} = E(O, v, Y, Ti; mHe) - E(O, v, Y, Ti) - mE^A(He)$$  \hspace{1cm} (5)

where $E(O, v, Y, Ti; mHe)$ and $E(O, v, Y, Ti)$ are the total energy of the supercell containing the embedded cluster with and without mHe, respectively, and $E^A(He)$ is the total energy of a single He atom (0.00705 eV). The corresponding incorporation or formation energies for v and SIA are

$$E_{\text{incorp}}^\text{incorp} = E(O, v, Y, Ti; V) - E(O, v, Y, Ti) + E^A(Fe)$$  \hspace{1cm} (6)

and

$$E_{\text{SIA}}^\text{incorp} = E(O, Y, Ti; SIA) - E(O, Y, Ti) - E^A(Fe).$$  \hspace{1cm} (7)

Here $E^A(Fe)$ is the energy per atom (or its chemical potential) in perfect bcc Fe. In the literature, energetic representation similar to equations (1) and (5) are used in order to characterize the binding and incorporation of metal atoms in Ge clusters [37, 38].

Following the energetic calculation, we consider CL clusters and determine the migration barrier for He jumps from the center to sites at the cluster-Fe interface. The nudged elastic band (NEB) method [39–41] as implemented in the ‘vstools’ is used to obtain the barriers. In the NEB procedure the minimum energy states before and after a jump are connected by a number of states or images that are constructed along the migration path. Then, for these images a restricted relaxation is performed using the precision criteria for total energy difference and residual force per atom as mentioned above. After determining the minimum energy path by the standard NEB procedure the climbing image NEB method is applied to ensure that the exact saddle point is found.

4. Energetics and structure of relaxed cluster configurations containing one He atom

The center of the CL cluster shown in figure 1(a) is found to be the most stable He site, with a binding energy $E_b^\text{He}$ of $-3.31$ eV and an incorporation energy $E_{\text{incorp}}^\text{He}$ of $1.25$ eV. As already mentioned in section 2 this center position corresponds to an octahedral interstitial site in Y$_2$O$_3$. For a larger CL cluster composed of the same kind of atoms Sun et al. [21] found an incorporation energy of $0.92$ eV for such a He site. The deviation from our result may be due to the different sizes of the clusters as well as the different cell sizes and $k$-point grids used in the corresponding DFT calculations. Danielson et al. [15] and Sun et al. [21] obtained 0.62 and 0.92 eV, respectively, for the same He site in bulk Y$_2$O$_3$. It is worth mentioning that in bulk Y$_2$O$_3$ the tetrahedral interstitial site with four Y atoms in the environment is the most stable He site, followed by the octahedral site surrounded by six Y. A further stable site is obtained by placing He on one of the two equivalent vacancy sites (v1) of the CL cluster shown in figure 1(a). The relaxed configuration is called interfacial vacant site (IVS) and is slightly different from v1. The corresponding binding energy $E_b^\text{He}$ is $-3.18$ eV and the incorporation energy $E_{\text{incorp}}^\text{He}$ is $1.37$ eV. In the following the term IVS is generally used for relaxed positions of He initially placed on a vacant site. The various tetrahedral and octahedral interstitial sites with a distance less or equal than 1.5$a$ from the center of the cluster.
are not stable. Instead relaxation strongly changes the atomic configurations and the He atom is shifted towards the cluster. In three cases (o1b, o2a, t1) the final CL structure and the corresponding energetics is very similar to that obtained in the IVS case. In further nine cases a transformation to OC configurations occurs, with He close to an IVS (see below). Such a drastic structural change is certainly due to the small size of the cluster. Finally (o1a), an atomic configuration with He on an interfacial interstitial site (IIS) in the vicinity of the octahedron edge with two Y, and close to two O atoms, is found with $E_{\text{incorp}}^{\text{He}}$ of $-2.01 \pm 0.25 \text{ eV}$. It should be noticed that in the following the term interfacial interstitial site (IIS) is generally used for relaxed He sites which are neither a center site nor an IVS.

In the case of the OC cluster depicted in figure 1(b) the center is already occupied by an oxygen atom so that He cannot be placed there. He is stable on the three possible vacancy sites: The IVS near v1 has a binding energy of $-2.56 \text{ eV}$ (incorporation energy: $2.02 \text{ eV}$) while for the IVS near v2 and v3 $-2.71 \pm 0.14 \text{ eV}$ and $-2.81 \pm 1.74 \text{ eV}$ are obtained, respectively. Again, the tetrahedral and octahedral interstitial sites are not stable. Placing He on such positions leads to strong atomic rearrangements and often to a shift of He towards the cluster. The corresponding atomic arrangements are very similar to those obtained when CL clusters are transformed to an OC structure after adding He to those sites, as mentioned above. In 9 cases He relaxes to an IVS. In two cases (o3a, t2b) the He binding energy is about $-2.65 \text{ eV}$ (incorporation energy of $1.91 \text{ eV}$) and the structures correspond to that of the IVS near v1. After relaxation of o1b, o2a, o3b, t1, t2a, and t2c He binds with $-2.75 \text{ eV}$ to the OC cluster and the atomic configurations are similar to the IVS near v2. He placed on o3c relaxes to a IVS close to v3 with $-2.81 \pm 1.74 \text{ eV}$. In other two cases (o1a, o2b) He occupies interfacial interstitial sites (IIS) in the environment of an octahedron edge formed by two Y atoms, with and without two O atoms in the vicinity. The energetics of these configurations is similar, with $E_{\text{incorp}}^{\text{He}}$ of $-2.10 \pm 0.46 \text{ eV}$ and $-2.07 \pm 0.48 \text{ eV}$.

In CL cluster containing O, v, Y, and Ti (figure 1(c)) the center site is the most stable position for He with a binding (incorporation) energy of $-2.78 \pm 0.78 \text{ eV}$. This finding matches well with the result of Danielson et al [22] who reported a value of $1.85 \pm 0.2 \text{ eV}$ for the He energy in the center of the same type of cluster. The result may be also compared with the incorporation energy of He on an octahedral interstitial site of bulk Y$_2$Ti$_2$O$_7$. Yang et al [11] and Danielson et al [12] obtained 0.94 and 0.86 eV, respectively whereas Sun et al [14] reported a value of $1.24 \pm 0.0 \text{ eV}$. As in the case without Ti, the incorporation of He into the center of the small cluster embedded in iron requires more energy than placing He on a similar site in the bulk oxide. In contrast to Y$_2$O$_3$ in bulk Y$_2$Ti$_2$O$_7$ the octahedral interstitial site surrounded by six Y atoms is the most stable He site, followed by the tetrahedral site with 4 Y atoms in the environment. He is also stable on the IVS near v1 (figure 1(c)), with binding (incorporation) energy of about $-2.38 \text{ eV}$.

This configuration was also found by Danielson et al [22] who reported a value of $2.26 \pm 0.17 \text{ eV}$ for $E_{\text{incorp}}^{\text{He}}$. Ten tetrahedral and octahedral interstitial sites with a distance less than $1.5 \text{ Å}$ from the center of the cluster are not stable. In two cases (o1b, o2a) after relaxation He occupies the IVS near v1 (see above). Three cases (o1d, o2b, o2c) yield relaxed structures that were also investigated by Danielson et al [22]. In the following their data for $E_{\text{incorp}}^{\text{He}}$ are given in brackets: (i) He on an IIS close to the octahedron edge with 2Y at corners with $E_{\text{incorp}}^{\text{He}}$ of $-2.42 \pm 0.19 \text{ eV}$, (ii) He on an IIS close to the face with 1 Y and 2 Ti at corners with $E_{\text{incorp}}^{\text{He}}$ of $-2.31 \pm 0.21 \text{ eV}$, and (iii) He on an IIS near the octahedron face with 3 Y at corners with $E_{\text{incorp}}^{\text{He}}$ of $-2.26 \pm 0.23 \text{ eV}$ and $E_{\text{incorp}}^{\text{He}}$ of $2.30 \pm 0.24 \text{ eV}$. Hence, the results of present work agree well with literature data. From the five remaining configurations (o1a, t2d, t2b, o3b, o1c) two are similar to that of (i), one is similar to that of (ii), one is similar to that of (iii), and in the last case He is asymmetrical placed on an IIS close to the octahedron face with 2Y and 1 Ti with $E_{\text{incorp}}^{\text{He}}$ of $-2.26 \pm 0.30 \text{ eV}$. In contrast to results for the CL cluster of figure 1(a) the relaxed IIS structure (i) is more stable than He on the IVS. Interestingly, the tetrahedral and octahedral interstitial sites (2a, t2e o3a) with distances 3.714, 3.111, and 4.173 Å from the center of the cluster and closer to Ti atoms than to Y atoms remain stable after relaxation. He on the two tetrahedral interstitial sites (2a, t2c) have a binding (incorporation) energy of $-1.55 \pm 0.30 \text{ eV}$ and $-0.30 \pm 0.42 \text{ eV}$ and He on the octahedral site (o3a) has $E_{\text{incorp}}^{\text{He}}$ of $-0.24 \pm 0.42 \text{ eV}$. Obviously, the presence of Ti reduces the attraction of He by the cluster since such stable sites are not observed in the case of the CL clusters without Ti (figure 1(a)).

In the OC cluster shown in figure 1(d) the IVS near v1 is stable with $E_{\text{incorp}}^{\text{He}}$ of $-2.39 \pm 0.17 \text{ eV}$. The IVS near v2 is also stable with $E_{\text{incorp}}^{\text{He}}$ of $-2.18 \pm 0.27 \text{ eV}$. He on o2a, t1, and t2c relaxes towards the first IVS with very similar structure and energetics. He on o1c and t2b relaxes to an IIS near the octahedron face with 2 Ti and one Y on the corners, with $E_{\text{incorp}}^{\text{He}}$ of $-2.24 \pm 0.21 \text{ eV}$. The remaining seven tetrahedral and octahedral interstitial sites are also not stable and have different energetics ($E_{\text{incorp}}^{\text{He}}$ varies from $-2.68 \text{ to } -1.80 \text{ eV}$) and final atomic configurations.

5. Relaxed cluster structures with two He atoms

Adding two He atoms to the CL cluster of figure 1(a), at the center and at an IVS, results in a binding energy of $-6.51 \text{ eV}$. The comparison with the relaxed configurations after separate addition of a single He to respective sites ($E_{\text{incorp}}^{\text{He}}$ at 3.31 and $-3.18 \text{ eV}$, see above) shows that each He binds more or less separately. A similar result is obtained for two He on the two equivalent IVS: Both He bind with $-6.33 \text{ eV}$ while $E_{\text{incorp}}^{\text{He}}$...
for single He on IVS is \(-3.18\) eV. Inserting one He into the center, the other as an IIS near a octahedron edge with two Y on the corner and two O and two v in the environment leads to $E_{\text{He}}^{3\text{He}} = -5.32$ eV which corresponds to the sum of $E_{\text{He}}^{3\text{He}}$ for separate addition of He to the two sites. Placing two He atoms symmetrically close to v1, with orientation along the (100) direction, yields a binding energy of \(-5.43\) eV which is less than the sum of the values of $E_{\text{He}}^{3\text{He}}$ obtained by adding one He to a vacancy site. The final He arrangement is rather asymmetric with respect to v1. If the He dimer is oriented along (110) a less stable relaxed configuration (\(-5.11\) eV) is obtained, whereby both He atoms are located symmetrically to v1, the orientation is along (110) and parallel to the closest octahedron face.

If two He atoms are inserted into the supercell with the OC cluster shown in figure 1(b), on the IVS near v2 and v3, a binding energy of \(-5.51\) eV is obtained. Adding two He to the IVS near v1 and v3 gives \(-5.39\) eV. The comparison with results of section 4 (IVS near v2: \(-2.71\), IVS near v3: \(-2.81\), and IVS near v1: \(-2.53\), v3: \(-2.81\)) shows that the two He atoms bind separately. One He on the IVS near v2 and one He on an IIS close to two Y on an octahedron edge gives a binding energy of \(-4.92\) eV which is slightly more stable state than one would expect from the sum of the respective values of $E_{\text{He}}^{3\text{He}}$ (\(-2.71\) and \(-2.10\) eV) for two single He on these sites. On the other hand, if two He atoms are placed symmetrically close to v1, with orientation along the (100) directions, a more stable state with a binding energy of \(-5.27\) eV is obtained. More details can be found in the supplemental material.

In the case of the CL-cluster of figure 1(c) adding He at the center and on the IVS near v1 leads to a binding energy of \(-5.18\) eV. This corresponds to the sum of the values of $E_{\text{He}}^{3\text{He}}$ (\(-2.78\) and \(-2.38\) eV) for a single He on the respective sites. Placing the first He at the center and the second on the site t2d leads to a relaxed state, with one He in the center and the other on an IIS close to the two Y at the edge of the octahedron, and to a binding energy $E_{\text{He}}^{3\text{He}} = -5.42$ eV. This corresponds to a slightly more stable configuration than one would expect from the sum of $E_{\text{He}}^{3\text{He}}$ values for single He atoms at one of the two sites (\(-2.78\) and \(-2.42\) eV). Placing two He atoms symmetrically close to v1 and with orientation along the (100) direction yields a binding energy of \(-3.87\) eV. The final arrangement of the two He atoms is asymmetric with respect to the v1 and is located near the 3Ti face of the octahedron. Orienting the He dimer along (110) yields a similar binding energy (\(-3.84\) eV). In the final configuration both He atoms are situated symmetrically to the v1 and the orientation remains along (110) parallel to the 3Ti octahedron face.

After inserting two He on the two IVS of the OC cluster depicted in figure 1(d) a binding energy of \(-4.69\) eV is obtained. This is somewhat more stable than expected from the sum of the values of $E_{\text{He}}^{3\text{He}}$ for the IVS near v1 (\(-2.39\) eV) and v2: (\(-2.18\) eV).

The addition of a He dimer close to v2 near the 2Ti–1Y face of the (distorted) octahedron, with an orientation along the (110) direction, yields a binding energy of \(-4.78\) eV. Interestingly, this configuration is more stable than that with two He on the available IVS near v1 and v2. The relaxed configuration is symmetric with respect to v2, oriented along (110), and is parallel to the 2Ti–1Y face. Putting a He dimer close to v1 near the 3Ti face with orientation along (100) yields even a more attractive state with a binding energy of \(-5.31\) eV. In the relaxed configuration one He atom is close to v1, whereas the other is close to the octahedron edge with two Ti on the corners.

6. Relaxed cluster structures with three He atoms

Placing one He atom at the center and two He on the IVS of the CL cluster of figure 1(a) yields a binding energy for the three He atoms of $E_{\text{He}}^{3\text{He}} = -9.68$ eV which corresponds to the sum of the values of $E_{\text{He}}^{3\text{He}}$ for single He atoms at each of these sites. If one He is at the center, the other on IVS, and the third on an IIS close to the two Y atoms at the corner of an octahedron edge (with two O atoms in the environment) a binding energy of \(-8.50\) eV is obtained. Again, this is nearly equal to the sum of the respective $E_{\text{He}}^{3\text{He}}$ data for a single He atom. The addition of three He atoms symmetrical to v1 and relaxation yields a binding energy of \(-8.41\) eV which is exactly the sum of the binding energy for the relaxed dimer near v1 (\(-5.10\) eV) plus the value of $E_{\text{He}}^{3\text{He}}$ (\(-3.31\) eV) for a single He in the center.

Three He on the three available IVS of the OC cluster of figure 1(b) results in a binding energy of \(-8.11\) eV which is nearly equal to the sum of the respective $E_{\text{He}}^{3\text{He}}$ data for single He addition (IVS near v1: \(-2.53\), IVS near v2: \(-2.71\), IVS near v3: \(-2.81\) eV). One He on IVS near v2 and one on an IVS near v3, and a third on an IIS close to the two Y atoms at the corner of an octahedron edge (with two O atoms in the environment) yields \(-7.61\) eV which is the sum of the respective $E_{\text{He}}^{3\text{He}}$ data (\(-2.71\), \(-2.81\), \(-2.10\)) obtained by adding single He on the corresponding sites. Placing three He atoms in the environment of v1 leads to a symmetrical trimer around this site with an arrangement parallel to the octahedron face. This is a surprisingly stable state with a trimer binding energy of $E_{\text{He}}^{3\text{He}} = -7.97$ eV.

Adding the first He atom to the center of the CL cluster of figure 1(c), the second to the IVS and the third to an octahedral interstitial site (o2b) causes the rearrangement of the oxygen atom close to the third He atom. The second and the third He atoms are arranged in a symmetric manner, leading to a binding energy of \(-7.82\) eV for the three He atoms. This is by about \(0.3\) eV more stable than the sum of the values of $E_{\text{He}}^{3\text{He}}$ obtained for a single He at the center and on the IVS (\(-2.78\) eV, two times \(-2.38\) eV). On the other hand, placing 3 He atoms close to v1 near the 3Ti face of the octahedron yields a configuration with a slightly asymmetric trimer and a binding energy of \(-5.23\) eV.

He on the two available IVS plus one He on the octahedral site o2b yields a relaxed configuration with a binding energy $E_{\text{He}}^{3\text{He}}$ of \(-6.89\) eV and the He atoms are slightly rearranged. The absolute value of $E_{\text{He}}^{3\text{He}}$ is higher than one would expect from data of $E_{\text{He}}^{3\text{He}}$ for one He at the corresponding sites (\(-2.39\), \(-2.18\), \(-1.80\)). After relaxation of three He atoms that were

\footnote{See footnote 4.}
introduced into the OC cluster of figure 1(d) close to v1 near the (distorted) octahedron with 3 Ti atoms, a slightly modified trimer is found with a binding energy of $-6.16 \text{ eV}$ which is more stable than the corresponding trimer in the CL cluster (see above).

7. Discussion of the energetics of He-cluster interaction

Up to a distance of 1.5 $a$ from the cluster center, He is strongly attracted by each of the four different cluster structures considered in this work. Within this region He cannot be stabilized on most of the tetrahedral and octahedral interstitial sites of the underlying bcc lattice but relaxes to positions that are closer to the cluster than the initial sites.

The main reason for the He trapping capability of the clusters is the existence of enough open or empty volume inside the CL clusters and at cluster-Fe interfaces. He as an inert gas atom prefers to reside in such regions. The incorporation energy of He on sites near the interface to the iron matrix is lower than in bulk bcc Fe ($4.56 \text{ eV}$) but higher than in bulk Y$_2$O$_3$ (0.62 [15] or 0.92 eV [21]) or Y$_2$Ti$_2$O$_7$ (0.94 [11], or 0.86 [12], or 1.24 eV [14]). This was also pointed out by Sun et al [21] and Yang et al [20]. Such a trend can be explained qualitatively by the electronic structure of the respective solids: In bulk bcc Fe the valence electrons are highly non-localized so that a completely empty volume does not exist, whereas in the bulk oxides the electrons are much more localized due to the predominantly ionic character of the bonds.

In this work, the open or empty volume is also pictured by vacancies in the underlying bcc lattice that are not assigned to an oxygen atom. He at the vacant site in the center of a CL cluster is more stable than on an IVS at the cluster-Fe interface. Due to the small cluster size, the incorporation energy at the center site is somewhat higher than at the comparable site in bulk Y$_2$O$_3$ or Y$_2$Ti$_2$O$_7$. On other stable sites in the interstice between the cluster and the iron matrix (IIS), the absolute value of the He binding energy $E_b$ is often smaller than that on IVS. However, there are also IIS in clusters with Ti, where He is more stable than on an IVS. Comparing He on IVS of CL and OC clusters without Ti, He is found to be more stable in CL clusters, whereas no significant difference exists for the clusters with Ti. In clusters without Ti, He is more stable in the center and on IVS than in those with Ti. In the case of clusters with Ti more different IIS configurations are found than those without Ti.

Separate DFT calculations on the binding energy between He on a tetrahedral interstitial site in bcc Fe and substitutional Y or Ti as well as O on an octahedral interstitial site were performed. It was found that the Y–He pair shows the strongest attraction ($-0.46 \text{ eV}$) followed by the O–He pair ($-0.34 \text{ eV}$) and the Ti–He pair ($-0.14 \text{ eV}$). These findings help to explain qualitatively why clusters without Ti attract He stronger than those with Ti. However, one should also keep in mind that the clusters with Ti contain one more oxygen atom and one less vacant site than those without Ti. As already mentioned above, these vacant sites are most important for the attraction of He.

In bulk bcc Fe the v-He pair has a binding energy of $-2.34 \text{ eV}$. On IVS in clusters with Ti a similar value is obtained ($-2.38 \text{ eV}$ in CL, $-2.18$ and $-2.39 \text{ eV}$ in OC clusters), whereas higher absolute values are found in clusters without Ti ($-3.18 \text{ eV}$ in CL and $-2.53$, $-2.71$, $-2.81 \text{ eV}$ in OC clusters).

In many cases the binding energy of two He atoms to the cluster is about equal to the sum of the $E_b^{\text{He}}$ values for a single He on the respective site. He dimers close to a vacant site are mostly less stable than two He on separate IVS. However, in the OC cluster with Ti opposite results are found. A sum rule also holds for the binding energy of three He if these are on the center site, on an IVS, and on a certain IIS. He trimers close to a vacant site have different energetics so that it is not possible to derive a general rule from the large but limited number of examples considered here. The finding that the addition of two or three He atoms to the environment of a single vacant site is still energetically favorable shows that the cluster structures exhibit a very high He storage capability. Although comprehensive investigations on different sites of one, two, or three He atoms in the region of the clusters were performed in this work, it is obvious that there are still other possible configurations since the potential energy landscape is very complex, in particular in and near clusters with Ti.

The findings obtained with the supercell consisting of 128 bcc lattice sites have been checked by investigating selected cases in a cell with 250 lattice sites. In such a manner the influence of the periodic images can be estimated. The results are provided in the supplemental material. In the larger cell very similar relaxed atomic configurations are found and also the values for binding and incorporation energy are nearly equal. In agreement with results for the smaller supercell very weak or repulsive interaction between the cluster and He is observed if He is apart at more than the distance of 1.5 $a$ from the cluster center. At these sites, the incorporation energy of He is nearly equal to that in pure Fe.

8. He migration barriers near the clusters

8.1. Results

At given temperature the He storage capability of an oxide nanocluster in iron is not only determined by the energetics of the particular stable He site inside the cluster or at the cluster-Fe interface but also by the migration barriers a He atom has to overcome in order to reach these sites. In the following, the focus is on barriers between stable He sites at the interface and the center site in CL clusters.

For clusters without Ti only two stable sites were found at the interface (see section 4). Figures 2(a) and (b) show barriers for the He jump between an IVS and the center and between an IIS (close to an octahedron edge) and the center, respectively. The second migration path is not relevant because of the high barriers. The first one is important since the barrier for He jump to the center is very low (0.07 eV), i.e. only slightly higher than the migration barrier of He in bulk bcc Fe (0.06 eV [26]). Therefore, He can be easily trapped on the center site.

9 See footnote 4.
temperatures relevant for practical applications. On the other hand, leaving the center site is more difficult since the barrier is by about a factor of three higher. Several barriers between stable He sites at the cluster-iron interface and the center site were determined for the CL cluster with Ti. Figures 2(c), (d) and (e) depict barriers for jumps from stable interfacial sites to the center. These sites were also found by Danielson et al [22] (see section 4). Surprisingly the barrier between the IVS and the center site is very high. The most relevant jump is that from the IIS near the octahedron face with 2 Ti and one Y on the corner to the center site, with a barrier of 0.14 eV (IIS relaxed from o2b). The barrier for jumps to the center site from: (i) a He site close to an octahedron edge with 2Y at corners (IIS relaxed from o1a), (ii) a He site in the region of the 2Y–1Ti octahedron face (IIS relaxed from o1c), and (iii) another He site close to the octahedron edge with 2Y at corners (IIS relaxed from o1d) are similar (figures 2(e)–(g)). These jumps are less probable than that shown in figure 2(d) because of the higher barrier of about 0.35 eV. In cases (i)–(iii) the barriers for a jump from the center to a site at the interface are comparable with that in figure 2(d) so that in all these cases He is effectively trapped.

8.2. Discussion

The results on the barriers for jumps between a stable He site at the interface and the center of CL clusters clearly show preferred minimum energy paths with high importance for He storage. Interestingly, the barrier for a jump to the center of the CL cluster without Ti is lower than for the CL cluster with Ti. Present findings also indicate possible migration paths for He incorporation into larger clusters. However, it must be also noticed that not only the octahedral sites with 6 Y or 3 Y and 3 Ti atoms in the environment can store He (which corresponds to the center site of the CL clusters), but also other sites existing in the interstice of the oxide (Y2O3, Y2Ti2O7) structures, such as tetrahedral and octahedral sites with different atomic environments [12, 14, 15, 21].

9. Relaxed cluster configurations with one additional vacancy

9.1. Results

The calculation of the formation or incorporation energy of single vacancy in bcc Fe yields a value of 2.17 eV which is in agreement with literature data [42, 43].

To investigate the interaction between the vacancy (v) and the clusters shown in figure 1 we have selected three particular bcc sites close to the clusters. The corresponding binding (incorporation) energies of v are given in table 1 and the atomic configurations before and after relaxation are provided in the supplementary material10.

First a vacancy (v) at the bcc site A, at first neighbor distance to an IVS, is considered. The v is weakly attracted by all the four cluster structure. Interestingly, the attraction is somewhat stronger by the clusters with Ti where the v is near the face with 3 Ti atoms on the corner. In the second case, with the v on the site B, and nearly at first neighbor distance to an oxygen atom, or exactly at first neighbor distance to the vacant site assigned to the O atom, the attraction of v is stronger than on site A. The absolute value of the binding energy is higher for the clusters without Ti. In contrast to v on site A, the attraction by OC clusters is stronger than that by CL clusters. Placing the v on site C, nearly at first neighbor distance to two O atoms leads to relatively strong deformations of the CL clusters, whereas the form of the OC clusters is only slightly modified. In these four cases the absolute value of the binding energy is much higher than in the two examples

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10 See footnote 4.
Cluster formation, on three selected bcc sites in the iron matrix near the other authors [42]. In order to assess the interaction of the both atoms of the dumbbell. This agrees well with results of work the value of 3.91 eV was obtained for the SIA formation SIA configuration is the 

\[ \langle 1 \ 0 \ 0 \rangle \]

dependence on the selected v site a weaker or stronger attraction by the clusters is found. Our results agree qualitatively with those of Brodrick et al [18] who found that an interface between Y2O3 and bcc Fe can act as trap for v. If v is placed at first neighbor distance (site A) to an IVS the absolute value of the binding energy is relatively small. The attraction of the v on site A close to the octahedron face with 3 Ti atoms on corners (see figures 1(c) and (d)) is comparable with the binding energy between two vacancies in pure Fe at the first neighbor distance (−0.16 eV, see e.g. [44]). This is not surprising since that v located at this distance from a vacancy that belongs to the cluster. In clusters without Ti the Y atoms seem to weaken the attraction of both vacancies. On site B where the v is close to an oxygen atom the v is bound stronger. From literature it known that in pure Fe a vacancy attracts oxygen strongly (see e.g. [44]) This may be also the reason why on site C the attraction of v is higher than on site B since there are two oxygen atoms in the environment of v. However, not only the O–v interaction is responsible for the value of binding energy but also the other constituents as well as the particular atomic structure of the clusters. Finally, it should be noticed that there are also other non-equivalent sites for v in the vicinity of the cluster which were not studied in this work.

9.2. Discussion

Depending on the selected v site a weaker or stronger attraction by the clusters is found. Our results agree qualitatively with those of Brodrick et al [18] who found that an interface between Y2O3 and bcc Fe can act as trap for v. If v is placed at first neighbor distance (site A) to an IVS the absolute value of the binding energy is relatively small. The attraction of the v on site A close to the octahedron face with 3 Ti atoms on corners (see figures 1(c) and (d)) is comparable with the binding energy between two vacancies in pure Fe at the first neighbor distance (−0.16 eV, see e.g. [44]). This is not surprising since that v located at this distance from a vacancy that belongs to the cluster. In clusters without Ti the Y atoms seem to weaken the attraction of both vacancies. On site B where the v is close to an oxygen atom the v is bound stronger. From literature it known that in pure Fe a vacancy attracts oxygen strongly (see e.g. [44]) This may be also the reason why on site C the attraction of v is higher than on site B since there are two oxygen atoms in the environment of v. However, not only the O–v interaction is responsible for the value of binding energy but also the other constituents as well as the particular atomic structure of the clusters. Finally, it should be noticed that there are also other non-equivalent sites for v in the vicinity of the cluster which were not studied in this work.

10. Relaxed cluster configurations with one additional SIA

10.1. Results

It is well known from literature that in bcc Fe the most stable SIA configuration is the \( \langle 1 \ 1 \ 0 \rangle \) dumbbell [42, 43]. In this work the value of 3.91 eV was obtained for the SIA formation or incorporation energy with a distance of 1.93 Å between both atoms of the dumbbell. This agrees well with results of other authors [42]. In order to assess the interaction of the clusters with a SIA the dumbbell was put, with a certain orientation, on three selected bcc sites in the iron matrix near the cluster. The atomic configurations before and after relaxation are shown in the supplemental material\(^ {11} \). The data on energetics are given in table 2.

In the first case a dumbbell with \( \langle 1 \ 1 \ 0 \rangle \) orientation is placed on the iron site A with a first neighbor distance to an IVS of the cluster, and with about equal distance to the 3 Y atoms on the corners of the corresponding octahedron face. For each of the cluster structures depicted in figure 1 minimization of total energy of the supercell (relaxation) leads to recombination of the SIA with the vacancy on the IVS. That means that one Fe atom of the dumbbell moves to the IVS, the other to the bcc site of the original SIA. The basic atomic configuration of the cluster does not change during the recombination process. The corresponding binding (incorporation) energies of the SIA are given in table 2. Furthermore, a SIA is inserted with \( \langle 1 \ 0 \ 1 \rangle \) orientation on the iron site B having about a first neighbor distance to one oxygen atom, and equal distance to the 2 Y atoms on the corners of the corresponding octahedron edge. Relaxation alters the structure of the clusters significantly so that the original CL or OC pattern is more or less lost, with exception of the OC cluster without Ti. This strong structural change is presumably due to the small size of the clusters. The oxygen atom initially situated closest to the SIA is pushed away and one atom of the dumbbell is shifted towards the vacant site of the underlying bcc lattice that had initially assigned to the pushed oxygen. The other Fe atom occupies the original bcc site of the dumbbell. In dependence on the final position of the pushed O atom the binding (incorporation) energy of the SIA varies. A particularly high absolute value of the SIA binding energy is found for the significantly altered structures. In these cases the SIA incorporation energy is negative or close to zero, which is further evidence that initial cluster configuration becomes unstable during interaction with the SIA (see Brodrick et al [18]). The OC cluster of figure 1(b) is only slightly altered by the addition of the SIA, and here attraction is much lower than in the case where the SIA is placed on site A. In the third case a dumbbell with \( \langle 10 \ 1 \rangle \) orientation is put on the iron site C with about a first neighbor distance to two adjacent O atoms, and equal distance to the 2 Y atoms on the corners of the corresponding octahedron edge. Relaxation alters the structure of the clusters significantly so that the original CL or OC pattern is more or less lost, with exception of the OC cluster without Ti. This strong structural change is presumably due to the small size of the clusters. The oxygen atom initially situated closest to the SIA is pushed away and one atom of the dumbbell is shifted towards the vacant site of the underlying bcc lattice that had initially assigned to the pushed oxygen. The other Fe atom occupies the original bcc site of the dumbbell. In dependence on the final position of the pushed O atom the binding (incorporation) energy of the SIA varies. A particularly high absolute value of the SIA binding energy is found for the significantly altered structures. In these cases the SIA incorporation energy is negative or close to zero, which is further evidence that initial cluster configuration becomes unstable during interaction with the SIA (see Brodrick et al [18]). The OC cluster of figure 1(b) is only slightly altered by the addition of the SIA, and here attraction is much lower than in the case where the SIA is placed on site A. In the third case a dumbbell with \( \langle 10 \ 1 \rangle \) orientation is put on the iron site C with about a first neighbor distance to two adjacent O atoms, and equal distance to the 2 Y atoms on the corners of the corresponding octahedron edge.

\(^ {11} \) See footnote 4.
octahedron edge. Again, except for OC cluster without Ti (figure 1(b)) the relaxation of the supercell leads to changed cluster configurations and almost to a loss of the original CL or OC structure. One of the O atoms is shifted towards the cluster center and also the positions of the other atoms change. One Fe atom of the dumbbell is displaced to the vacant site of the underlying bcc lattice that had initially assigned to the pushed oxygen. The other is shifted to the initial site of the dumbbell. In the case of figure 1(b) the binding energy of the SIA is in the same order of magnitude as that obtained for placing the SIA on site B.

10.2. Discussion

The above results show that there is a strong attraction between a SIA and the cluster structures under consideration. This is mainly due to the availability of open volume or vacant sites. Due to the recombination process the initial SIA disappears, together with a part of the open volume. However, the relaxed cluster structures are still relatively open, so that they can certainly trap a few additional SIA until saturation is reached. Since the studied cluster configurations are small strong modifications of their structure are often observed. This will be certainly not happen for larger clusters. Nevertheless the present study unambiguously demonstrates that SIA can be trapped and annihilated by O–Y and O–Y–Ti clusters in bcc Fe. This is also in qualitative agreement with results of Brodrick et al [18] who found that an interface between Y₂O₃ and bcc Fe can act as trap for SIA.

11. Summary and conclusions

Density Functional Theory calculations were performed in order to study the interaction of O–Y and O–Y–Ti clusters embedded in bcc Fe with He atoms, vacancies (v) and self-interstitial atoms (SIA). He in the center of a CL cluster is more stable than on an interfacial vacant site (IVS) at the cluster-Fe interface. Due to the small size of the investigated clusters the incorporation energy at the center site is higher than at the corresponding site in the bulk oxides Y₂O₃ or Y₂Ti₂O₇. In CL O–Y clusters He on an IVS is more stable than in the configuration with oxygen in the center (OC), whereas there is no significant difference between the two kinds for clusters with Ti. Within a distance of 1.5 a from the cluster center He is not stable on most of the possible octahedral and tetrahedral interstitial sites of the underlying bcc Fe at cluster-Fe interface. Instead, He is strongly attracted by each of the four different cluster structures and is shifted towards positions closer to the cluster. Relaxation to the known IVS as well as to previously unknown IIS is observed. He on such IIS is often less stable than on IVS but in few cases the opposite was found. For two or three He atoms cases corresponding binding and incorporation energies are nearly equal to the sum of the values obtained for the interaction with a single He atom. On the other hand, placing He dimers or trimers in the environment of a vacancy may lead to relatively high (low) absolute values of the binding (incorporation) energy. All these results clearly show the high He storage/trapping capability of the clusters. Despite the comprehensive investigations performed in this work it is obvious that there are still other possible configurations, since the potential energy landscape is very complex, in particular in and near the clusters with Ti.

Moreover, jumping barriers of He between the cluster-iron interface and the center of the CL clusters were determined. Due to the low incorporation energy on the center site the barrier for the jump to this position is lower than that for the backward jump. In the CL O–Y cluster the values of both barriers are lower than in the CL O–Y–Ti cluster, i.e. trapping and release of He is easier in the former than in the latter.

The interaction of an additional vacancy (v) with the different cluster structures is attractive but depends strongly on the site of v. The environment of oxygen atoms leads to strongest attraction which is consistent with the high absolute value of the binding energy of an oxygen-vacancy pair in pure bcc Fe. The recombination of SIA with nearby vacancy shows that the cluster is not only a trap for the v but also for the SIA. The results of the present work confirm findings of few previous theoretical investigations that O–Y and O–Y–Ti clusters embedded in bcc Fe are efficient traps for radiation defects. This is in agreement with experimental observation. New aspects concern results of detailed studies on the influence of different cluster structures (CL and OC) and the calculation of He jump barriers. The role of open volume regions for He storage was highlighted and combined with a qualitative discussion on the basis of the electron structure of bcc Fe and the oxides Y₂O₃ or Y₂Ti₂O₇. Future work is required to investigate the trapping capabilities of more different kinds of oxide clusters, e.g. those with higher oxygen content, and to determine more migration barriers for He, v, or SIA in the environment of the clusters. This could also contribute to develop reliable and sufficiently precise interatomic potentials which would enable the efficient study of large simulation cells and the application of methods like molecular dynamics and Monte Carlo simulations.

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