Influence of vacancy on helium interaction with α-Zirconium

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Abstract. The first-principle calculations of the interaction between helium and zirconium have been carried out. The main feature of studying such systems is the localization of a He atom in a region near the vacancy in Zr. It has shown that the location of a helium atom in a vacancy vicinity leads to lower formation energy. The calculated density of electron states curves revealed shifts of He 1s state by ~ 0.5 eV towards higher binding energies while located the vacancy vicinity against He-in-vacancy position. Moreover, He 2s states are observed in a region of Zr 4d states from –1.2 to –0.1 eV suggest the hybridization between these states. The crystal orbital Hamilton populations curves have been analyzed to reveal the features of the Zr-He chemical interaction due to the hybridization of He 2s and Zr 4d states.

1. Introduction
Zirconium is widely used as a structural material for active zones of nuclear reactors owing to high corrosion resistivity, high melting temperature, and small neutron capture cross-section [1-3]. During nuclear reactor operation, the particles formed as products of nuclear transmutations are accumulated in structural materials and impair their operational properties [4-6]. Helium is formed in zirconium due to (n, p) and (n, α) nuclear reactions and takes a special place in consideration of such particle-metal interactions [7-8]. During a long-term operation of the nuclear reactors, an appreciable number of vacancies is formed due to elastic collisions of neutrons with zirconium atoms. Helium atoms have low solubility in materials and are trapped by vacancies with a high probability. As a result, helium bubbles and voids are formed that lead to swelling, blistering, and helium embrittlement, irradiation growth, and hardening [9-13].

By now, there is a big amount of theoretical and experimental research dedicated to interactions between helium atoms and metals, such as iron [14-15], titanium [16], and tungsten [17]. The influence of helium and vacancies on the mechanical properties of zirconium and its alloys was investigated from the first principles in [12-13]. In the paper [12] was mentioned the effect of strong hybridization of helium 2s and zirconium 4d states at –1 eV below Fermi energy level. In the present work, we theoretically study the interaction between helium and zirconium in the zirconium–helium and zirconium–helium–vacancy systems with the defect concentration of ~ 3 and ~ 6 at.%.

2. Computational method.
All present calculations were carried out using density functional theory, as implemented in the ABINIT package [18-19] using projector-augmented wave potential [20]. The exchange and correlation interaction were described by the Perdew, Burke, Ernzerhof (PBE) form of general gradient approximation [21]. The cutoff energy for the plane-wave basis was set to 820 eV. Optimization of the lattice parameters and relaxation of the atomic structure was achieved using the
algorithm of Broyden–Fletcher–Goldfarb–Shanno. The atoms in the systems considered were assumed to be in the equilibrium configuration when the force on each atom was less than 50 meV Å⁻¹. The occupation of electron levels was described using a cold smearing scheme with smearing equal to 0.03 eV. For the calculation of a local partial density of electron states the radius of the Zr and He atomic spheres was chosen as 1.169 and 0.689 Å, respectively. The crystal orbital Hamilton populations (COHP) which are helpful to identify the bonding and anti-bonding interactions were computed using the COHP technique [22]. To determine the most stable configurations of the helium positions in interstitial sites we investigate two supercells that consist of 36 and 16 zirconium atoms and the k-point mesh for which were set to 5×5×5 and 5×5×3, respectively. The concentration of both a vacancy and helium atoms in these configurations corresponds to ~ 3 and ~ 6 at.%, respectively. Helium was located in tetrahedral (T1, T2), octahedral (O) sites, and in the basal plane of the interstitial site (BO position). All zirconium atoms nearest to the vacancy are enumerated for discussion convenience. These possible positions have been chosen based on symmetry considerations and presented in Figure 1. The influence of the vacancy on the helium atom position in the zirconium lattice was also studied. It was reached by removing one of the zirconium atoms (marked as “vac” in Figure 1). In a zirconium lattice with the preexisting vacancy, the helium atom can be located in T1 or T2 tetrahedral interstitial sites near the vacancy. Finally, the octahedral site is out of consideration since it is a metastable position: the He atom is moved from O to BO position during relaxation.

![Figure 1](image_url)

**Figure 1.** Supercells of the Zr–He and Zr–He–vac systems with the vacancy and helium concentrations of ~ 3 (a) and ~ 6 at.% (b). The S position (light green circle) corresponds to the helium atom position shifted from the vacancy. a and c are lattice parameters.

### 3. Results and discussion.

In the present paper, we investigated the behavior of helium atom in the presence of the vacancy in zirconium. The formation energy of the Zr–He system is defined as

\[
E_{\text{HE}} = E(\text{Zr}_{N-x}\text{He}) - E(\text{He}) - E(\text{Zr}_N),
\]

the vacancy formation energy and the formation energy of the helium-vacancy complex are defined as

\[
E_{\text{vac}} = E(\text{Zr}_N) - \frac{N-x}{N}E(\text{Zr}_N),
\]

\[
E_{\text{HE-vac}} = E(\text{Zr}_{N-x}\text{He}) - E(\text{He}) - \frac{N-x}{N}E(\text{Zr}_N),
\]

where \(E(\text{He})\) is the total energy of isolated helium atom, \(E(\text{Zr}_N)\) is the total energy of \(N\) zirconium atoms, \(E(\text{Zr}_{N-x}\text{He})\) and \(E(\text{Zr}_N\text{He})\) are the total energy of zirconium and zirconium-helium system with the \(x/N\) vacancy concentration, \(x\) and \(N\) are the numbers of vacancies and zirconium atoms in the supercell, respectively. The results of the calculations are presented in table 1.
Table 1. Results of calculated formation energies and zirconium lattice parameters.

| System   | Unit cell parameters | Formation energy (eV) |
|----------|----------------------|-----------------------|
|          | $a$ (Å)   | $c$ (Å)   | 3 at. % | 6 at. % | 3 at. % | 6 at. % | 3 at. % | 6 at. % |
| Pure Zr  | 3.234   | 5.167   |          |         |          |         |          |         |
|          | 3.231 [12] | 5.169 [12] |          |         |          |         |          |         |
|          | 3.232 [23] | 5.169 [23] |          |         |          |         |          |         |
|          | 3.232 [24] | 5.167 [24] |          |         |          |         |          |         |
| Zr-He$_{T1}$ | 3.234 | 3.233 | 5.211 | 5.272 | 2.699 | 2.685 |          |         |
|          |          |         |         |         |          |         |          |         |
| Zr-He$_{RO}$ | 3.244 | 3.256 | 5.279 | 5.215 | 2.433 | 2.456 |          |         |
|          |          |         |         |         |          |         |          |         |
| Zr-vac   | 3.222 | 3.220 | 5.137 | 5.070 | 1.251 | 1.388 |          |         |
|          |          |         |         |         |          |         |          |         |
| Zr-He$_{ac}$ | 3.226 | 3.236 | 5.166 | 5.028 | 1.330 [12] |          |          |         |
|          |          |         |         |         |          |         |          |         |
| Zr-He$_{8}$ | 3.217 | 3.231 | 5.149 | 5.149 | 1.248 | 1.305 |          |         |

The calculated lattice parameters for pure zirconium are in good agreement with the corresponding calculations of the authors [12]. The calculated formation energy of a single vacancy in supercells with the defects concentration of 3 at.% and 6 at.% is 2.069 eV and 2.106 eV, respectively, which are in good agreement with the results of previous theoretical calculations [12, 23]. It was established that in the case of the non-vacancy systems the minimal formation energy corresponds to the system with helium atom in the BO site. The same result was noted earlier in [12].

Then we considered the behavior of a helium atom located in interstitial sites close to the vacancy. It was denoted that He atoms can be trapped easily by preexisting vacancies. However, it was revealed that the helium atom located in the BO, T1, or T2 site does not move into the vacancy during relaxation, it is stopped in the S position shifted from the vacancy along the hexagonal axis (Figure 1). The difference of formation energy between two helium atom positions is 3 meV and 83 meV for 3 at. % and 6 at.%, respectively. This fact makes the position of the helium atom near the vacancy energetically more favorable in comparison to the position of the helium atom in the vacancy.

To further investigate the interaction between He atom and zirconium atoms, we have calculated local partial densities of electron states (DOS) for the pure zirconium and zirconium–vacancy, zirconium–helium–vacancy systems with two previously mentioned positions of the helium atom and defect concentration of 3 at.% and 6 at.% (Figure 2 and 3, respectively). It is shown from Figure 1 that the zirconium atoms denoted by numbers 4–9 in Figure 1(a)) or 4–6 in Figure 1(b) are the nearest to the vacancy in its basal plane. The zirconium atoms denoted by numbers 1–3 and 10–12 in figure 1(a) or 1–3 and 7–9 in Figure 1(b) are the nearest to the vacancy in the neighbor basal planes. In figures 2 and 3 we presented the local partial density of electron states for the first and sixth Zr atom for both the considered defect concentrations.

From Figures 2(b) and 3(b), it can be seen that the vacancy weakly influences on the electron $s$, $p$, and $d$ states of the metal atoms. For systems with the helium atom located in the vacancy (Figure 2(c) and Figure 3(c)), distinct peaks of the 1s state of helium are visible. In both cases, the helium state is at a distance of ~12 eV to the Fermi level. It is noticed that the lines of zirconium $p$ states are seen in Figure 3(c) at energy ~12 eV. In the case of the helium atom located in the $S$ position, the peak of the He 1s state is shifted toward higher binding due to the interaction between helium and neighbor zirconium atoms. In Figures 2(c) and 3(c), the presence of the $p$ state of helium in the range from ~4 eV to 2 eV is observed. The graphs of $s$ states of helium and zirconium atoms match qualitatively in the energy region from ~4 eV to ~2 eV. This fact reflects overlapping the atomic spheres of zirconium and helium atoms. Similar peaks of the He 2s and Zr 4d DOS are being observed in the energy range from ~1.2 eV to ~0.1 eV. The last-mentioned fact implies the strong hybridization between these states.
**Figure 2.** The local partial DOS of pure Zr (a), Zr–vac (b), Zr–He$_{\text{vac}}$ (c), and Zr–He$_{\text{S}}$ (d) with the defect concentration of 3 at.%. The blue line corresponds to the first Zr atom DOS, the green line corresponds to the sixth Zr atom DOS, red line corresponds to the He DOS. The vertical dashed line is Fermi level ($E_F$).

**Figure 3.** The local partial DOS of pure Zr (a), Zr–vac (b), Zr–He$_{\text{vac}}$ (c), and Zr–He$_{\text{S}}$ (d) with the defect concentration of 6 at.%. The blue line corresponds to the first Zr atom DOS, the green line corresponds to the sixth Zr atom DOS, red line corresponds to the He DOS. The vertical dashed line is Fermi level ($E_F$).
For the detailed analysis of formed hybridized He 2s and Zr 4d states, we calculated COHP curves (figure 4) using the theory of bonding and anti-bonding states. The negative value in COHP curves means anti-bonding states and the positive value suggests bonding states. For Zr–He–vac system there are two the most striking regions with large DOS peaks are at about −0.1 and −1.2 eV (Figures 2(c, d) and 3(c, d)). The COHP value is negative for these Zr–He hybridized states, which corresponds to unstable bonds between the He and Zr atoms.

The COHP value for the helium atom in the vacancy are similar for all neighbor Zr atoms. In the case of the helium atom located in the S position, the strengthening of binding with the atoms 1–3 and the weakening of binding with Zr atoms 4–9 (for the defect concentration of 3 at.%) and 4–6 (for the defect concentration of 6 at.%) are observed. Moreover, Zr atoms 10–12 and 7–9 are located in the second coordination sphere of a He atom for the defect concentration of 3 at.% and 6 at.%, respectively. So, when helium is located in the vacancy there are twelve neighboring Zr atoms around it. When a helium atom is shifted from the vacancy it moves away from Zr atoms 4–9 (4–6) lying in the same basal plane and 10–12 (7–9) lying in the neighbor basal plane for the defect concentration of 3 at.% (6 at.%). Thus, despite the formation of stronger anti-bonding states between He and Zr atoms 1–3 because of the shift of the He atom from the vacancy to S position, this position is energetically more favorable for the helium atom due to significant weakening the interaction of helium atom with nine other neighbor Zr atoms.

**Figure 4.** COHP curves for the He–Zr interaction in the Zr–He–vac systems with 3 at.% (a) and 6 at.% (b) defect concentration. The numeration of Zr atoms is given according to figure 1.

4. Conclusion.
In the present paper, the first-principle study of the features of interaction between helium and zirconium in the zirconium–helium and zirconium–helium–vacancy systems with the defect concentration of −3 and −6 at.% were performed in the framework of the density functional formalism using the projector-augmented wave method. The results of the formation energy calculations revealed that in the case of non-vacancy systems, the helium atom is located in the basal plane site. Concerning systems with preexisting vacancy, we considered the position of the helium atom in vacancy and the position shifted from the vacancy along the hexagonal axis. It was shown that the formation energy for the system with helium atom located in the position shifted from the vacancy along the hexagonal axis is 1.248 eV and 1.305 eV for the concentrations of 3 at.% and 6 at.%, respectively. For the helium-in-vacancy configuration, the value of the formation energy is higher which makes this position energetically less favorable.

To understand the mechanism of the revealed effect the density of electron states was calculated for the considered system. The analysis has shown that the He 1s state shifts from ~13 to ~14 eV below
the Fermi level when the helium atom is displaced from vacancy to the position shifted from the vacancy along the hexagonal axis. Moreover, the He 2s states were found in the energy region of Zr 4d states. According to that fact, the hybridization of He 2s and Zr 4d states is observed. To study the interaction between zirconium and helium atoms the crystal orbital Hamilton populations curves have been calculated for corresponding chemical local bonding. Our calculations revealed the formation of antibonding states between zirconium and helium atoms. While the helium atom is located in vacancy, the anti-binding interaction of the He atom with the twelve nearest Zr atoms is the same. The location of helium in the position shifted from the vacancy along the hexagonal axis leads to strengthening the anti-binding interaction with the three nearest Zr atoms and significant weakening anti-binding interaction with nine other neighbor Zr atoms lying in the basal plane of a vacancy and the neighbor basal plane.

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