

DFT calculations of solute-vacancy binding in Zirconium-based Zr–Nb–Sn alloy

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ABSTRACT

The energetic properties of ternary Zr–Nb–Sn Zirconium-based alloy with concentration of dissolved alloying elements $\sim 1.5\%$ are studied by using density functional theory. The possibility of alloying additions separated by different distances to dissolve/segregate in a host matrix is analyzed with the help of mixing energy and solute–solute binding energy. The ability of solutes to trap single vacancy is discussed by studying formation energy of a vacancy, located on a different distances from both solute atoms and the corresponding solute–solute–vacancy binding. This study provides an insight into the details of vacancy energetics in Zirconium-based alloys exploited in nuclear-power plants.

1. Introduction

The metallic materials employed in water-cooled reactor cores as cladding of nuclear fuels must possess several requirements. They prevent the contact of the cooling water with the fuel (uranium dioxide pellets), and also avoid the release of fission products produced in the fuel during irradiation. The materials therefore should present good resistance to the corrosion, good mechanical properties, good thermal conductivity and low absorption cross section for thermal neutrons. Zirconium-based alloys are actively utilized in the nuclear-power industry as tubes for the fuel cladding for light water nuclear reactor: either pressurized water reactors (PWRs) or boiling water reactors (BWRs) [1–5] due to low thermal neutron capture cross-section and acceptable mechanical properties with good corrosion resistance [6–10]. Nuclear-grade Zirconium-based alloys typically consist of more than 95 weight percent Zirconium and less than 2% of Tin, Niobium, Iron, Chromium, Nickel and other metals, which are added to improve mechanical properties and corrosion resistance (see recent work Ref. [11] and citations therein). Among them one can issue ZIRLO™ with the typical chemical composition (% in weight): 0.5–2 Niobium, 0.7–1.5 Tin, 0.07–0.14 Iron and 0.03–0.14 of at least Nickel and Chromium and the balance essentially Zirconium [12,13]. It was shown that the ZIRLO™ alloy is gaining great importance comparing to Zircaloy-2 and Zircaloy-4 due to optimum corrosion performance and has proven itself as a successful alloy for PWR fuel cladding and structural applications [14].

An exploitation of these alloys in aggressive environment of the nuclear reactor leads to local rearrangement of the alloying elements

in a host matrix due to both generation of point defects in cascades of atomic displacements [15–17] and ballistic mixing caused by irradiation influence [18]. Non-equilibrium point defects can be captured by sinks (grain boundaries, phase interfaces, loops, etc.) or by solute alloying additions. These microstructural transformations can significantly affect both physical and mechanical properties of the irradiated alloy [19,20]. Hence, a detailed study local rearrangement of Nb and Sn atoms and their ability to localize point defects in hexagonal close-packed (hcp) Zirconium matrix remains an actual task in the nuclear materials science.

In order to understand the effects of alloying additions Nb and Sn on diffusion in Zirconium-based alloys, a detailed knowledge of the interaction between solute atoms and solute-vacancy binding are necessary. The solute-vacancy binding energy directly influences solute diffusion. In an alloy with dilute solute concentrations, the solute-vacancy binding energy controls the probability of having a vacancy at a lattice site neighboring a solute atom. Therefore, energetic binding between a solute atom and a vacancy is a key factor in the quantitative understanding solute diffusion. Despite its importance, this interaction is notoriously difficult to experimentally measure accurately but can be readily calculated by using first-principles electronic structure methods such as density functional theory (DFT) [21].

It was shown before that in binary Zirconium-based Zr – Nb alloys Niobium atoms tend to segregate from the solid solution by forming their own body centered cubic (bcc) phase [22–24]. By *ab-initio*

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calculations it was found that the corresponding bcc phase becomes energetically more stable comparing to hcp phase if the concentration of Niobium exceeds 20% [24,25]. At the same time Tin atoms in binary Zr – Sn alloys are dissolve inside Zirconium matrix [22,24,26,27] and Zirconium-based Zr – Sn alloys are characterized by the hcp structure independently on the concentration of Tin [24].

In this article we continue to study energetics of defects in Zirconium-based alloys provided in Refs. [24,28]. There we have shown that in hcp binary Zirconium-based Zr – Nb alloys dissolved Niobium atoms cannot localize around themselves vacancies and their small clusters. In hcp binary Zirconium-based Zr – Sn alloys Tin atoms serve traps for vacancies and their clusters. The main aim of this work is to characterize the energetics of solute-vacancy binding in hcp ternary Zirconium-based Zr – Nb – Sn alloys as a prototype model of ZIRLO™ in order to characterize the interaction between solute additions Nb and Sn and to define the energetically most favorable position of a vacancy nearby these solutes. Results of these calculation will generalize known data about solute-vacancy binding in Zirconium-based materials employed in water-cooled reactor cores as cladding of nuclear fuels.

To this end we initially discuss mixing and binding of Nb and Sn atoms in hcp Zirconium-based ternary alloys in order to define the optimal distance between both solutes. Next, by using the optimized non-defect crystal structure we will test different spatial configuration of the complex Nb – Sn – vacancy in order to define the energetically most stable one.

The paper is organized in the following form. In the next Section we discuss methods of DFT calculations and main energetic characterized used in our calculations to characterize mixing and binding of solutes and vacancy. Results of *ab-initio* calculations are presented in Section 3 for out of defect ternary alloy (Section 3.1) and Zr – Nb – Sn alloys with vacancy (Section 3.2). Main conclusions are collected in the last Section.

2. Methods

In order to study energetic properties of Zr – Nb – Sn ternary alloys with and without vacancy we perform *ab-initio* calculations within the framework of DFT [21] by using the linearized augmented plane wave method with the generalized gradient approximation [29], which is implemented in software packages Wien2k [30,31]. This method self-consistently includes basic and valence electrons and is widely used to calculate the band structure of solids. The basis function was expanded up to $R_{MT} \times k_{max} = 7$, where k_{max} is the maximal value of the reciprocal lattice vectors. We put $R_{MT} = 2.5$ for all atoms giving the plane wave energy cut-off $E_{cut} = 7.84$ Ryd. Wave function expansion inside the atomic spheres was done up to $l_{max} = 10$. Such values for k_{max} and l_{max} are standard. Deviations from these values should be considered in calculating the systems with elements having large difference in masses. Integration over the Brillouin zone was performed by using 1000 k -points, which is enough for the calculation of metallic structures. The simulations are static calculations, that is, they identify the minimum energy positions for atoms in a given structure and as such relate to zero temperature. The criteria for a successful iteration were selected as a balance between computational cost and numerical accuracy and are: converge for the total energy is less than 0.0001 Ryd and the charge of the crystal is less than $0.001e^-$.

We perform *ab-initio* calculations by studying the hcp super-cell $4 \times 4 \times 2$ containing $N = 64$ atoms inside by replacing two Zirconium atoms by Nb and Sn atoms (substitutional solution) in different places, characterized by the distance d_i between them. By studying a problem of accumulation of vacancies by solutes in a base matrix we cut one Zirconium atom (generation of a vacancy) on a different distances from both solutes. The alloy $Zr_{N-2}Nb_1Sn_1$ with $N = 64$ can be considered as the main system for the practical interest investigation due to its usage in nuclear power industry. The concentration of alloying elements \sim

1.5 at.% is useful, as the weight percent composition in ZIRLO™ for nuclear reactor applications as cladding of nuclear fuels.

First of all we perform optimization procedure for all studied crystals to define the optimal values of lattice constants. By taking into account that Zr atom and both considered solutes Nb and Sn do not differ essentially in atomic volume, next we assume that the structural relation c/a for both alloys $Zr_{N-2}Nb_1Sn_1$ and $Zr_{N-3}Nb_1Sn_1\Box_1$ (\Box denotes a vacancy) does not change crucially from one for pure Zirconium, $(c/a)_{Zr}$ [32]. We have performed a full cycle of DFT calculations for the pure Zirconium and found the optimal value $(c/a)_{Zr} = 1.5925$. Next we put $c/a = (c/a)_{Zr}$ for all calculations allowing one to perform the optimization procedure in order to define the ground-state energy by varying the volume of the supercell only for each considered crystal. The dependence of the total energy of the crystal versus the volume of the super-cell is approximated by the Murnaghan equation of states [33].

In order to characterize the probability of mixing or dissolution of Nb and Sn atoms, located on different distances d_i from each other, in Zirconium-base alloy we calculate the dilute solute mixing energy by using the following relation:

$$E_{mix}|_{d_i} = E_{Zr_{N-2}Nb_1Sn_1}^0|_{d_i} - \frac{N-2}{N} E_{Zr_N}^0 - \frac{1}{N} (E_{Nb_N}^0 + E_{Sn_N}^0). \quad (1)$$

Here $E_{Zr_{N-2}Nb_1Sn_1}^0|_{d_i}$ is the ground state energy of an alloy $Zr_{N-2}Nb_1Sn_1$ which contains $(N - 2)$ Zirconium atoms and two solutes; $E_{X_N}^0$ is the ground state energy for the pure crystal of the element X with N atoms in the corresponding equilibrium crystal structure. Positive values of E_{mix} indicate that there is a thermodynamic driving force for the element to segregate from the host matrix; negative E_{mix} means dissolution of the elements inside the host matrix.

In order to define the energetically most favorable spatial configuration of $Zr_{N-2}Nb_1Sn_1$ alloy, characterized by the optimal distance d_{opt} between two solutes we calculate the binding Nb – Sn energy E_{bind}^{Nb-Sn} for different distances d_i between Nb and Sn solute atoms by using the equation:

$$E_{bind}^{Nb-Sn}|_{d_i} = (E_{Zr_N}^0 - E_{Zr_{N-1}Nb_1}^0) - (E_{Zr_{N-1}Sn_1}^0 - E_{Zr_{N-2}Nb_1Sn_1}^0|_{d_i}). \quad (2)$$

The two groups of terms on the right-hand side of this equation represent the energy required to break a host-host bond (first term) and a host-solute bond (second term) by replacing one Zr atom by Nb atom. Hence, the energy E_{bind}^{Nb-Sn} is defined as the difference between the energy of “infinite separation” and nearby located (for different distances d_i between solute atoms) both solutes. Hence, the solute-solute binding energy can be considered as a measure of stability of the complex Nb–Sn, by varying the distance d_i between solute atoms. If the binding energy $E_{bind}^{Nb-Sn}|_{d_i}$ is negative, then the corresponding complex will be energetically more stable than dissolved Nb and Sn atoms, located on very large distance (infinite separation). In the opposite case, this complex will dissolve into separated solute atoms. Therefore, the minimal value of $E_{bind}^{Nb-Sn}|_{d_i}$ defines the optimal distance d_{opt} between solutes.

Next, the obtained energetically most stable configuration of the ternary alloy $Zr(Nb - Sn)|_{d_{opt}}$ is used to study the ability of the complex Nb – Sn to localize (trap) a single vacancy near to itself. To that end we calculate the energy of single vacancy formation $E_f^v|_{p_i}$ and the binding energy between the complex Nb – Sn and a single vacancy $E_{bind}^{NbSn-\Box}|_{p_i}$, depending on the position p_i of a vacancy nearby the complex $(Nb - Sn)|_{d_{opt}}$. The vacancy formation energy, defined by the formula

$$E_f^v|_{p_i} = E_{Zr_{N-3}Nb_1Sn_1\Box_1}^0|_{d=d_{opt}, p_i} - E_{Zr_{N-2}Nb_1Sn_1}^0|_{d=d_{opt}} + \frac{1}{N} E_{Zr_N}^0 \quad (3)$$

can be compared with the energy of single vacancy formation in the corresponding hcp Zirconium phase

$$E_f^v|_{Zr} = E_{Zr_{N-1}\Box_1}^0 - \frac{N-1}{N} E_{Zr_N}^0. \quad (4)$$

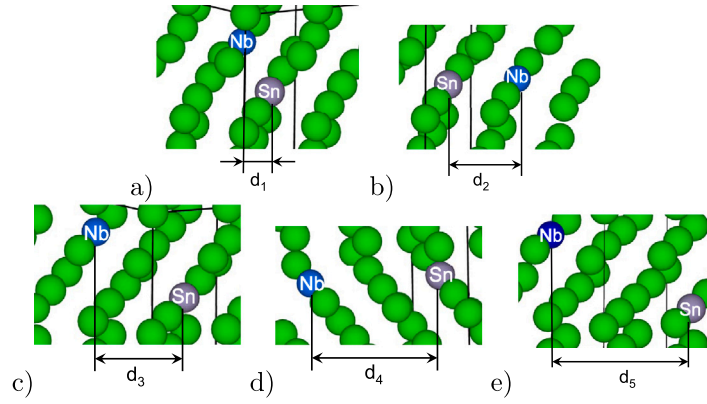


Fig. 1. Fragments of the super-cell of the Zr – 1.5%Nb – 1.5%Sn alloy with different distances between Nb and Sn atoms.

The value $E_f^v|_{Zr}$ can be associated with the formation energy of the single vacancy on a very large (infinite) distance from solute atoms in the same alloy. The corresponding binding energy can be found from the equation:

$$E_{bind}^{NbSn-\square}|_{p_i} = \left(E_{ZrN}^0 - E_{ZrN-1\square}^0 \right) - \left(E_{ZrN-2Nb_1Sn_1}^0|_{d=d_{opt}} - E_{ZrN-3Nb_1Sn_1\square}^0|_{d=d_{opt}, p_i} \right). \quad (5)$$

The minimal negative value of the binding energy corresponds to the most energetically favorable position of the vacancy around solutes.

3. Results and discussions

The main aim of the article is to characterize the ability of the each solute Nb and Sn to localize around itself non-equilibrium vacancy, generated in cascades of atomic displacements. To proceed we calculate the mixing energy of both solutes and the binding solute–solute energy by varying a distance between them and analyze the energy of a single vacancy formation and the binding energy between the pair Nb – Sn and a vacancy.

3.1. Mixing and binding of Sn and Nb in hcp Zr-phase

As it was discussed before, in binary Zirconium-based Zr – Nb alloy Niobium atoms tend to segregate from the solid solution, whereas Tin atoms in binary Zr – Sn atoms are dissolve inside Zirconium matrix [22, 22–24,26–28]. At the same time, the atomic volume differences for Zr and Nb atoms $(\Omega_{Nb} - \Omega_{Zr})/\Omega_{Zr} = -0.234$ and Zr and Sn atoms $(\Omega_{Sn} - \Omega_{Zr})/\Omega_{Zr} = 0.156$ indicate, that a compression of lattice induced by Nb atom inside Zr matrix can be compensated by oversized substitutional Sn atom located nearby Nb solute, leading to a decrease in elastic energy of the super-cell. Hence, dissolved Sn and Nb atoms inside hcp Zirconium matrix can fill each other being placed with a fixed distance between them.

In order to define the optimal distance between both solutes in Zr – Nb – Sn alloys we consider five different distances d_i , $i = 1 \dots 5$ between solute atoms Nb and Sn in hcp Zirconium-base super-cell with $d_1 < d_2 < d_3 < d_4 < d_5$: $d_1^{Zr} = a\sqrt{\frac{1}{4}\left(\frac{c}{a}\right)^2 + \frac{1}{3}}$, $d_2^{Zr} = a$, $d_3^{Zr} = a\sqrt{\frac{1}{4}\left(\frac{c}{a}\right)^2 + \frac{4}{3}}$, $d_4^{Zr} = a\sqrt{3}$ and $d_5^{Zr} = a\sqrt{\frac{1}{4}\left(\frac{c}{a}\right)^2 + \frac{13}{3}}$. Typical configurations of the super-cell of the Zr – 1.5%Nb – 1.5%Sn alloy with different distances between Nb and Sn atoms are shown in Fig. 1.

Here we are aimed to define the optimal distance between Niobium and Tin atoms in Zirconium matrix, corresponding to the minimal values of both mixing energy (1) and Nb – Sn binding energy (2) by varying a distance between Nb and Sn atoms, for further investigation of this system with point defects, produced by irradiation. Let us start

with the mixing energy shown in Fig. 2a. In the inset we show the values of the mixing energy of the each solute atom $X = \{Nb, Sn\}$ in the corresponding binary Zirconium-based $Zr_{N-1}X_1$ alloy, defined in the standard manner: $E_{mix}^X = E_{Zr_{N-1}X_1}^0 - [(N-1)E_{ZrN}^0 + E_{XN}^0]/N$. From the inset in Fig. 2a it follows, that the mixing energy of Nb atom in the alloy Zr – Nb takes positive values, meaning that Niobium atom tends to segregate into its own bcc phase rather than dissolve inside the hcp Zirconium matrix. The mixing energy of Tin atom inside Zirconium matrix takes negative value, meaning that Sn atom will dissolve inside hcp structure of Zr – Sn alloy. Obtained results correlate well with previously calculated data [22–24,26,27]. Hence, the chosen values of R_{MT} , E_{cut} and l_{max} are useful for studied crystals. From the main plot in Fig. 2a one sees, that the mixing energy E_{mix} takes negative values for all examined values of the distance between Nb and Sn solutes. Hence, closely located Nb and Sn atoms with high probability will dissolve in Zirconium matrix rather than form precipitates of secondary phases (The cubic $C - 15$ or hexagonal $C - 14$ Laves phases). At the same time, the mixing energy takes minimal value at $d = d_3$ (see the spatial configuration in Fig. 1c), indicating the energetically most favorable distance between Nb and Sn atoms for their dissolution. Hence, one can expect that due to minimization of the elastic energy, caused by the extension of the lattice by oversized Sn atom and lattice shrink in the vicinity of the smaller Nb atom, both atoms with concentration $\sim 1.5\%$ will be located not far from each other in hcp Zirconium matrix.

In order to characterize the stability of the complex Nb – Sn in Zirconium matrix we calculate the corresponding solute–solute binding energy E_{bind}^{Nb-Sn} by the formula (2). From obtained results, shown in Fig. 2b, it follows, that the pair Nb – Sn is unstable if the distances between Niobium and Tin atoms is small due to positive values of the binding energy meaning strong repulsive interaction between atoms. Binding energy decreases with the distance fast, takes minimum value at $d = d_3$ and then increases with the distance d growth. Moreover, it follows, that $E_{bind}^{Nb-Sn}|_{d=d_3} < 0$. The last one means attractive interaction and, therefore, the configuration of the pair Nb – Sn with the distance d_3 is stable. For the large distances $d_i > d_3$ between both solutes the mixing energy $E_{mix} < 0$ does not change essentially (see Fig. 2a) and the binding energy $E_{bind}^{Nb-Sn} \simeq 0$ (see Fig. 2b), meaning that such configurations are energetically comparable with the case of large (infinite) separation of both solutes in Zirconium matrix. From results, coming from Figs. 2a,b one can conclude that atoms Nb and Sn will solute in Zirconium matrix to be separated by the optimal distance $d_{opt} = d_3$. This effect is caused not only by the difference in the atomic volume of both solutes and the base Zr atom, but also by the difference in the number of electrons, included into the crystal structure by replacing Zr atoms by both solutes. The configuration of the alloy $Zr_{N-2}Nb_1Sn_1$ with the distance between Nb and Sn atoms d_{opt} is used as energetically most stable for studying solute–vacancy binding in the next section.

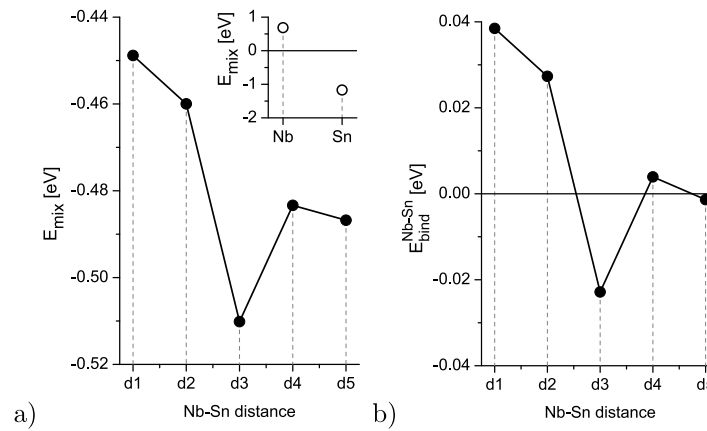


Fig. 2. A dependence of the (a) mixing energy E_{mix} , and (b) binding energy E_{bind}^{Nb-Sn} for the pair Nb – Sn in Zirconium matrix on the distance d_i between Nb and Sn atoms. The inset in Fig. 2a shows the mixing energy of the each solute atom in the corresponding binary Zirconium-based alloy.

3.2. Energetics of ternary Zr – 1.5%Nb – 1.5%Sn alloy with vacancy

In this section we are aimed to define the energetically most favorable position of the non-equilibrium vacancies, produced by cascades of atomic displacements during irradiation influence, around solutes Nb and Sn in hcp Zirconium-based ternary alloy.

First, we compute the formation energy of single vacancy in pure Zirconium crystal $E_f^v|_{Zr}$ by the formula (4) and compare it with the known data obtained by other authors in the framework of different methods in order to verify parameters used in calculations. The calculated within this work value of the formation energy of a single vacancy in pure hcp Zirconium crystal $E_f^v|_{Zr} = 2.11$ eV is in good correspondence with known results of theoretical and numerical study, namely 2.07 eV (Quantum Espresso package [34]); 2.14 eV (Siesta package [35]) and 2.26 eV (molecular dynamics simulation [36]). This once again validates the used parameters for DFT calculations.

To proceed we fix positions of both Niobium and Tin atoms in hcp matrix with the distance between them d_{opt} , defined in the previous section, and perform full the cycle of DFT calculations for this structure with different positions of a single vacancy around the pair Nb–Sn. To that end we consider four different positions of vacancy p_i , $i = 1 \dots 4$ with the distances $d_{\square-Nb}^i$ and $d_{\square-Sn}^i$ from both Nb and Sn solutes, respectively, defined as follows: p_1 : $d_{\square-Nb}^1 = d_2$ and $d_{\square-Sn}^1 = d_5$; p_2 : $d_{\square-Nb}^2 = d_1$ and $d_{\square-Sn}^2 = d_2$; p_3 : $d_{\square-Nb}^3 = d_2$ and $d_{\square-Sn}^3 = d_1$; p_4 : $d_{\square-Nb}^4 = d_5$ and $d_{\square-Sn}^4 = d_2$. Fragments of the super-cell of hcp Zirconium-based ternary alloy $Zr_{N-3}Nb_1Sn_1\square_1$ with vacancy located on different positions (a) p_1 , (b) p_2 , (c) p_3 and (d) p_4 around Nb and Sn atoms are shown in Fig. 3. Here, the configuration p_1 (see Fig. 3a) corresponds to the vacancy position far from Sn atom and nearby Nb atom. In configurations p_2 and p_3 a single vacancy is a nearest neighbor for both solutes: a vacancy is located in a basal plane with Sn atom and in a prismatic plane with Nb atom for p_2 and vice versa for p_3 (cf. Figs. 3b and 3c). In the case p_4 a single being the nearest neighbor for Sn atom locates far from Nb atom (see 3d). The configuration, where the vacancy is located far from both solutes can be associated with the case of vacancy formation in pure Zirconium matrix (infinite separation of the complex Nb – Sn and a single vacancy).

In order to characterize the ability of solute atoms Nb and Sn to localize a single vacancy nearby them we calculate the vacancy formation energy $E_f^v|_{p_i}$ and the binding energy $E_{bind}^{NbSn-\square}|_{p_i}$ between the complex $NbSn|_{d_{opt}}$ and the single vacancy \square by using formulas (3) and (5), respectively, for the spatial configurations, shown in Fig. 3. From the naive consideration one can conclude, that in the case of both $E_f^v|_{p_i} < E_f^v|_{Zr}$ and $E_{bind}^{NbSn-\square}|_{p_i} < 0$ the spatial configuration $NbSn\square|_{p_i}$ is stable and the vacancy with high probability will be generated nearby the complex NbSn with the distances $d_{\square-Nb}^i$ and $d_{\square-Sn}^i$ from it. Obtained data for the formation energy $E_f^v|_{p_i}$ and the corresponding binding

energy $E_{bind}^{NbSn-\square}|_{p_i}$ for different spatial configurations p_i with $NbSn|_{d_{opt}}$ are shown in Figs. 4a,b, respectively.

It follows, that for the case p_1 , when the single vacancy is the nearest neighbor for the Nb atom and locates far from Sn atom, the vacancy formation energy $E_f^v|_{p_1}$ is larger than the reference value $E_f^v|_{Zr}$ for the pure Zirconium; the binding energy $E_{bind}^{NbSn-\square}|_{p_1}$ is positive. It means, that the configuration p_1 is unstable, comparing to the infinite separation $NbSn|_{d_{opt}} - \square$. For the fixed distance between Nb atom and vacancy $d_{\square-Nb} = d_2$ a decrease in the distance $d_{\square-Sn}$ from d_5 toward d_1 (compare configurations p_1 and p_3) results in a decrease in both values $E_f^v|_{p_i}$ and $E_{bind}^{NbSn-\square}|_{p_i}$. The last one means that a single vacancy with the high probability will be localized nearby Sn atom. By comparing results for the configurations p_2 and p_3 , where the vacancy is the nearest neighbor for both atoms one gets, that the vacancy position p_3 with $d_{\square-Nb}^3 > d_{\square-Sn}^3$ is more favorable than p_2 one with $d_{\square-Nb}^2 > d_{\square-Sn}^2$ due to both $E_f^v|_{p_2} > E_f^v|_{p_3}$ and $E_{bind}^{NbSn-\square}|_{p_2} > E_{bind}^{NbSn-\square}|_{p_3}$. Herewith, both configurations p_2 and p_3 are less probable, comparing to the case of the infinite separation between the complex NbSn and a vacancy, characterized by $E_f^v|_{Zr}$ and $E_{bind}^{NbSn-\square} = 0$ (shown by solid lines in Figs. 4a,b). Finally, for the fixed distance between Sn atom and vacancy by $d_{\square-Sn} = d_2$ an increase in the distance $d_{\square-Nb}$ from d_1 toward d_5 (compare results for configurations p_2 and p_4) results in a decrease in both values E_f^v and $E_{bind}^{NbSn-\square}$. The last one means, that the vacancy with high probability will be localized far from Nb atom. Moreover, one gets, that for the configuration p_4 , characterized by the vacancy position nearby Sn atom and far from Nb atom, the vacancy formation energy $E_f^v|_{p_4}$ is less than the corresponding value $E_f^v|_{Zr}$ for the pure hcp Zirconium and the binding energy $E_{bind}^{NbSn-\square}|_{p_4} < 0$. It means, that the configuration p_4 is more stable than each p_i , ($i = 1, 2, 3$) and it is energetically more favorable than than configuration with isolated vacancy from the complex NbSn. Hence, in hcp Zirconium-based alloy Zr – Nb – Sn the single vacancy with high energetic probability will occupy the lattice node nearby Tin atom and far from Niobium atom. Obtained results correspond well to known data [24,34–36] in reference points.

4. Conclusions

We have performed atomistic modeling of energetic properties of ternary Zr – Nb – Sn Zirconium-based alloy with concentration of dissolved alloying elements relevant to commercial alloys exploited in nuclear power plants as cladding materials. We have discussed separately alloys without point defects and with a single vacancy, located on different distances from solutes Nb and Sn.

We have found that in ternary hcp Zirconium-based alloy Zr–Nb–Sn with the concentration of alloying elements $\sim 1.5\%$ atoms Nb and

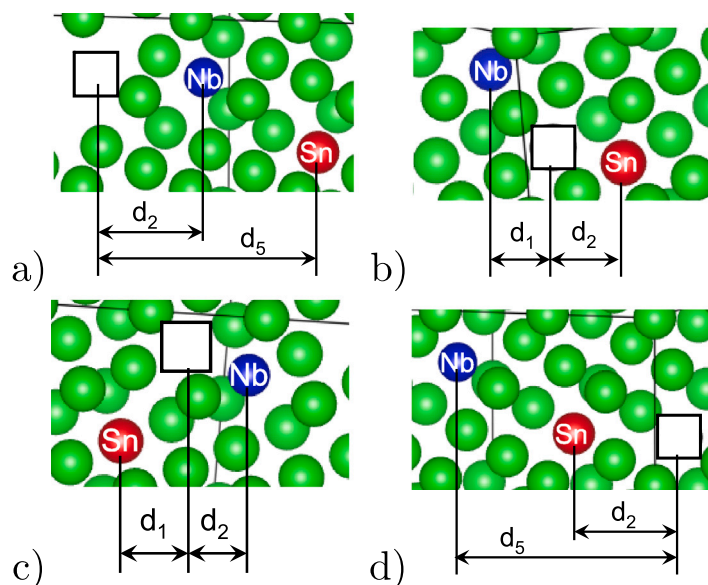


Fig. 3. Fragments of the super-cell of hcp Zirconium-based ternary alloy $Zr_{N-3}Nb_1Sn_1□_1$ with vacancy ($□$) located on different positions (a) p_1 , (b) p_2 , (c) p_3 and (d) p_4 around Nb and Sn atoms.

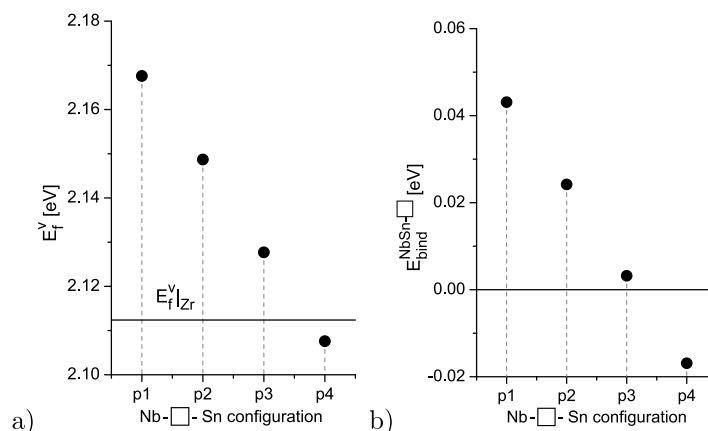


Fig. 4. Formation energy of a vacancy located at different positions around Nb and Sn atoms (a) and the binding NbSn – $□$ energy (b) for different configurations p_i .

Sn with the high probability will not segregate into secondary phase with the equivalent concentration of elements. They will dissolve inside hcp Zirconium matrix to be separated by a distance which is equal to the radius of the second coordination sphere. It is shown, that non-equilibrium vacancies generated in cascades of atomic displacements will segregate nearby Tin atoms and far from Niobium atoms.

Obtained results extend known knowledge about solute-vacancy binding for binary Zirconium-based alloys [24] on the case of ternary Zr – Nb – Sn alloys with dissolved atoms Nb and Sn with small concentration being a prototype model of the ZIRLO™ alloy.

These results can be useful to construct the appropriate empirical interaction potentials for molecular dynamics modeling of cascades of atomic displacements in Zirconium-based alloys and to perform cluster dynamics and rate theory simulations of the dislocation loops evolution in Zirconium-based alloys. We expect that our nontrivial findings will stimulate further theoretical and experimental studies of the point defect redistribution in Zirconium-based alloys.

CRediT authorship contribution statement

Lu Wu: Funding acquisition, Project administration, Supervision. **Vasyl O. Kharchenko:** Conceptualization, Methodology, Software, Writing – original draft. **Xianggang Kong:** Resources, Validation.

Dmitrii O. Kharchenko: Visualization, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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References

- [1] D.O. Northwood, *Mater. Des.* 6 (1985) 58.
- [2] C. Lemaignan, *Zirconium Alloys: Properties and Characteristics*, Elsevier, 2012, pp. 217–232.
- [3] G.K. Dey, S. Banerjee, P. Mukhopadhyay, *J. Phys. Colloques* 43 (1982) 327.
- [4] K. Lingamurthy, I. Charit, *Prog. Nucl. Energy* 48 (2006) 325.
- [5] B.A. Cheadle, The development of Zr-2.5Nb pressure tubes for CANDU reactors, in: 16th International Symposium on Zirconium in the Nuclear Industry, 2010, pp. 67–87.
- [6] N. Kumar, J. Azpunar, Z. He, *J. Nucl. Mater.* 414 (2011) 341.
- [7] B.A. Cheadle, C.E. Coleman, H. Licht, *Nucl. Technol.* 57 (1982) 413.
- [8] K.L. Murty, I. Charit, *Prog. Nucl. Energy* 48 (2006) 325.
- [9] B. Raj, U.K. Mudali, *Prog. Nucl. Energy* 48 (2006) 283.
- [10] N. Selmi, A. Sari, *Adv. Mater. Phys. Chem.* 3 (2013) 168.
- [11] F. Onimus, S. Doriot, J.-L. Bechade, 3.01 - Radiation effects in zirconium alloys, in: R.J.M. Konings, R.E. Stoller (Eds.), *Comprehensive Nuclear Materials*, Elsevier, 2020, pp. 1–56, ed. by J.M.Rudy, Konings, Roger E. Stoller, *Comprehensive Nuclear Materials (Second Edition)* (Elsevier).
- [12] G.P. Sabol, G. Schoenberger, M.G. Balfour, *Improved PWR Fuel Cladding (IAEA-TECDOC-665)*, International Atomic Energy Agency, 1992.
- [13] L. Castaldelli, C. Fizzotti, L. Lunde, Long-term test results of promising new dszirconium alloys, in: D. Franklin (Ed.), *Zirconium in the Nuclear Industry*, ASTM International, West Conshohocken, PA, 1982, pp. 105–126.
- [14] G. Sabol, *J. ASTM Int.* 2 (2005) 1.
- [15] C. Lemaignan, Nuclear materials and irradiation effects, in: D.G. Cacuci (Ed.), *Handbook of Nuclear Engineering*, Springer, Boston, MA, 2010.
- [16] K. Nordlund, S.J. Zinkle, A.E. Sand, et al., *J. Nucl. Mater.* 512 (2018) 450.
- [17] R.E. Stoller, 1.11 - Primary radiation damage formation, in: R.J. Konings (Ed.), *Compr. Nucl. Mater.*, Elsevier, Oxford, 2012, pp. 293–332.
- [18] P. Sigmund, *Particle Radiation and Radiation Effects*; Springer Series in Solid State Sciences, vol. 151, Springer, Berlin/Heidelberg, Germany, 2006.
- [19] S.A. Khandy, J.-D. Chai, *J. Appl. Phys.* 127 (2020) 165102.
- [20] S.A. Khandy, J.-D. Chai, *J. Magn. Magn. Mater.* 502 (2020) 16656.
- [21] P. Hohenberg, W. Kohn, *Phys. Rev. B* 136 (1964) 864.
- [22] S.C. Lumley, S.T. Murphy, P.A. Burr, et al., *J. Nucl. Mater.* 437 (2013) 122.
- [23] M. Cottura, E. Clouet, *Acta Mater.* 144 (2018) 21.
- [24] Lu. Wu, V.O. Kharchenko, D.O. Kharchenko, R. Pan, *Mater. Today Commun.* 26 (2021) 101765.
- [25] V.O. Kharchenko, D.O. Kharchenko, *Condens. Matter Phys.* 16 (2013) 13801.
- [26] C. Li, *J. Nucl. Mater.* 304 (2002) 134.
- [27] H. Zou, G.M. Hood, J.A. Roy, et al., *J. Nucl. Mater.* 208 (1994) 159.
- [28] Lu. Wu, V.O. Kharchenko, Xianggang. Kong, D.O. Kharchenko, *J. Nucl. Mater.* 554 (2021) 153079.
- [29] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [30] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, *Computer Code WIEN2K*, Vienna University of Technology, 2002.
- [31] P. Blaha, K. Schwarz, P. Sorantin, S.B. Rickey, *Comput. Phys. Comm.* 59 (1990) 399.
- [32] G.M. Benites, A. Fernandez Guillermet, G.J. Cuello, *J. Campo, J. Alloys Comp.* 299 (2000) 183.
- [33] F.D. Murnaghan, *Proc. Natl. Acad. Sci.* 30 (1944) 244; *Equilibria* 23 (2002) 134.
- [34] C. Varvenne, O. Mackain, E. Clouet, *Acta Mater.* 78 (2014) 65.
- [35] G. Verite, F. Willaime, C.C. Fu, *Solid State Phenom.* 129 (2007) 75.
- [36] M.I. Mendelev, G.J. Ackland, *Phil. Mag. Lett.* 87 (2007) 349.