

The effect of local short-range order in disordered V-Ti solid solutions on the vacancy formation energy

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Received April 30, 2025

Revised September 8, 2025

Accepted November 11, 2025

Using *ab initio* modeling methods, we studied the effect of local short-range order in disordered V-Ti solid solutions on the vacancy formation energy. The results show that the vacancy formation energy significantly depends on the arrangement of titanium atoms in the vicinity of the vacancy and decreases with increasing their number. Moreover, the vacancy formation energy from the knockout of titanium atoms is significantly lower than that from the removal of a vanadium atom.

Keywords: V-Ti alloys, solid solutions, vacancies, *ab initio* modeling, vacancy formation energy.

DOI: 10.61011/PSS.2025.12.63110.7962k-25

1. Introduction

Vanadium alloys of the V-Ti system are promising candidates as structural materials for the first wall of a thermonuclear reactor, as they demonstrate a good combination of strength, ductility and radiation resistance, and also have a rapid decrease in induced activity (from a year to several years) [1,2], which solves the problem of recycling these materials. Irradiation of V-Ti alloys leads to the formation of a large number of point defects (vacancies and embedded atoms), and contact with the region of hydrogen-helium plasma leads to high concentrations of hydrogen and helium atoms inside the material, as a result of which they undergo damage such as helium swelling and hydrogen embrittlement [3]. Understanding the physical picture behind these effects is still unsatisfactory because. Experimental investigation of irradiated nuclear energy materials is a very expensive and time-consuming procedure. For this reason, in recent years there has been a tendency to obtain such data using *ab initio* computer modeling. Relevant research for V-Ti alloys has only begun in recent years. The interaction of He with monovacancies and self interstitial atoms (SIA) in pure vanadium and the alloy V-4%Cr-4%Ti was studied in Ref. [4]. It has been shown that the energy of formation and migration of He is higher in the alloy than in pure V. The formation of helium and vacancies at the grain boundary in V was investigated in Ref. [5]. The same group investigated the effect of 26 different transition metal impurities in vanadium on the interaction of hydrogen and helium with vacancies in vanadium [6].

Boev et al. studied the interaction of Ti atoms with vacancies in BCC vanadium in Ref. [7]. It has been shown that the titanium atom and the vacancy strongly attract, in addition, highly stable Ti-vacancy-Ti triple complexes

are formed. Based on these results, which show that vacancies and titanium atoms in the immediate environment interact strongly enough, we decided to study in detail the effect of the short-range order in V-Ti alloys on the energy of vacancy formation under radiation exposure. In the course of this work, the energy of vacancy formation is modeled depending on which atom is removed from the titanium lattice (Ti vacancy) or vanadium (V-vacancy), for various configurations of titanium atoms in the immediate environment. At the first stage, the simulation was carried out using the Monte Carlo method with interparticle EAM potentials proposed for the V-Ti system in Ref. [8] in order to identify the influence of the local short-range order and determine the type of configuration corresponding to the minimum values of the vacancy energy. After that, several configurations of this type with minimal energy were selected, for which a basic calculation of the energy of vacancy formation in the VASP software package was carried out.

2. Calculation method

Solid solutions of V-Ti have a BCC structure, due to which each atom of the lattice is adjacent to 8 atoms of the first environment and 6 atoms of the second environment. For a fixed number of titanium atoms N ($0 \leq N \leq 14$) there are M possible variants of their distribution over the nodes of the first and second environment. These M node distribution options will lead to a set of L ($L < M$ due to the presence of symmetrically equivalent structures) vacancy formation energies. To find this set, Python code was written that generated all the unequal L variants of the distribution N of Ti atoms across 14 nodes of the first and second environment of the vacancy located in the center of $3 \times 3 \times 3$ BCC cell of vanadium. In all generated

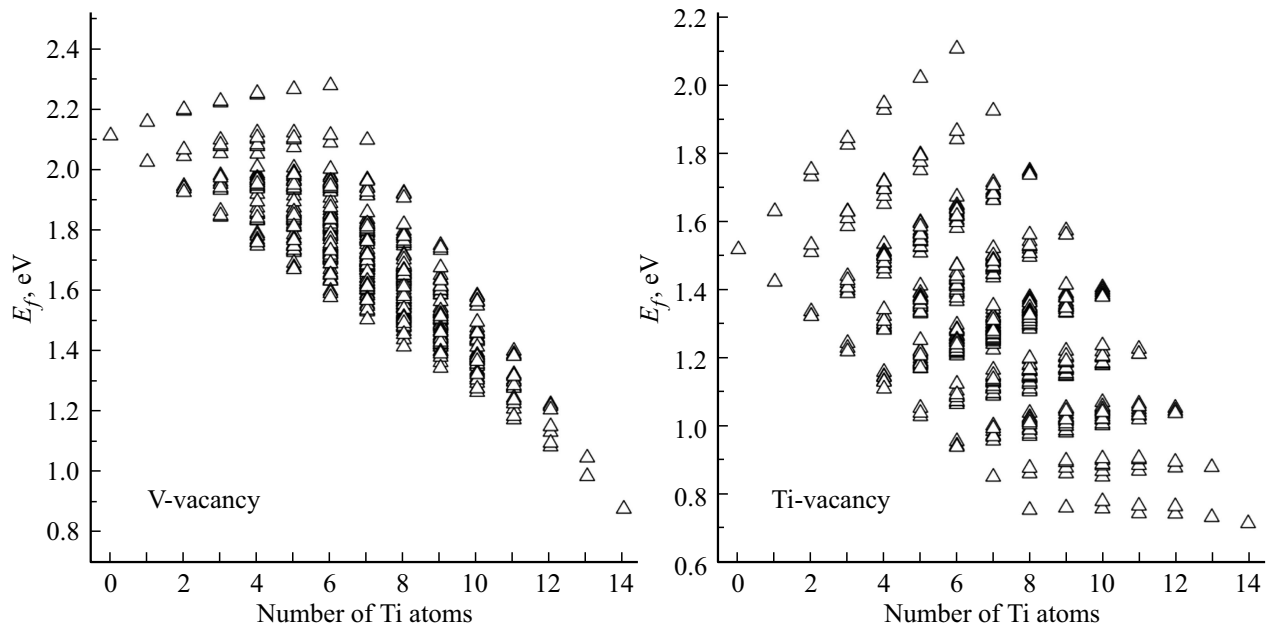


Figure 1. The energy of vacancy formation in the V-Ti BCC cell $3 \times 3 \times 3$ with a different number of titanium atoms in the first and second environment of the vacancy. The following figures show the results obtained with different variants of the distribution of titanium atoms in 14 nodes of the first and second environment.

$3 \times 3 \times 3$ cells, Ti atoms could be present only in the first and second coordination shells around the vacancy; all other atoms in the cell were V atoms. Each structure generated by Python code was read by the LAMMPS molecular dynamics modeling package. In this case, two cases must be considered: the formation of a vacancy as a result of the removal of the atom Ti (Ti-vacancy) with the energy of formation E_f^{Ti} and as a result of the removal of the atom V (V-vacancy) with the energy E_f^{V} . The energy of vacancy formation was calculated using the formulas:

$$E_f^{\text{Ti}} = E_{(n-1)} - E_{(n)} + E(\text{Ti})/n, \quad (1a)$$

$$E_f^{\text{V}} = E_{(n-1)} - E_{(n)} + E(\text{V})/n, \quad (1b)$$

where $E_{(n)}$ is the energy of a cell filled with V and Ti atoms, $E_{(n-1)}$ is the energy of the same cell, but with a vacancy formed by the removal of one of the atoms, $E(\text{Ti})$ and $E(\text{V})$ is the energy of cells filled only with titanium and vanadium atoms, n is the number of atoms in a cell.

When calculating the value $E_{(n)}$, a structural relaxation of the system was performed: the atomic coordinates were adjusted by gradient descent in order to achieve the minimum energy of the system; the cell vectors were independently adjusted to achieve the target pressure in the system (1 atmosphere). After calculating $E_{(n)}$, the central atom of the cell is removed, after which the relaxation calculation is repeated (but without changing the cell vectors) under the same stopping criteria. As a result, we obtain the total energy of the cell with vacancy $E_{(n-1)}$. Basic DFT calculations with higher accuracy were performed using the PAW method, taking into account the generalized gradient approximation in the VASP software package. The

supercell $3 \times 3 \times 3$, consisting of 54 nodes of the BCC lattice, was used as a model. The Monkhorst –Pack scheme with a grid of $4 \times 4 \times 4$ k -points of the Brillouin zone was used for integration in the inverse space and calculation of the electron density. The truncation energy of the plane wave was set to 400 eV. When optimizing the atomic structure, convergence was assumed when the energy change between two electronic self-consistent steps is less than 10^{-6} eV, and the forces on each atom did not exceed $0.01 \text{ eV}/\text{\AA}$. The calculations were performed without spin polarization. We calculated the properties of pure vanadium and titanium with a BCC lattice to assess the reliability of the computational technique. The calculated vanadium lattice parameter (2.99 \AA) deviates from the experimental value (3.02 \AA [9]) by less than 1.5 %, and the titanium lattice parameter (3.252 \AA) has an even better agreement with the experimental value of 3.256 \AA [10].

3. Results and discussion

The results of the molecular dynamic calculation of the energy of vacancy formation are shown in Figure 1. The graphs show L of different values of vacancy formation energies for each number of N Ti atoms distributed between the first and second environment of the vacancy.

As can be seen from the data in Figure 1, the energy of formation strongly depends on both the number of titanium atoms in the immediate environment of the vacancy and the short-range order in their arrangement. The maximum energy of formation E_f^{max} is observed in cases when the Ti atoms closest to the vacancy are located in the second

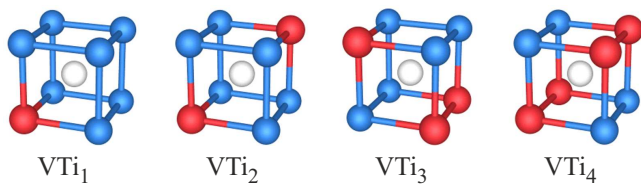


Figure 2. Configurations of four options for surrounding the vacancy with titanium atoms (blue atoms — vanadium, red atoms — titanium, the vacancy is indicated by a light sphere in the center).

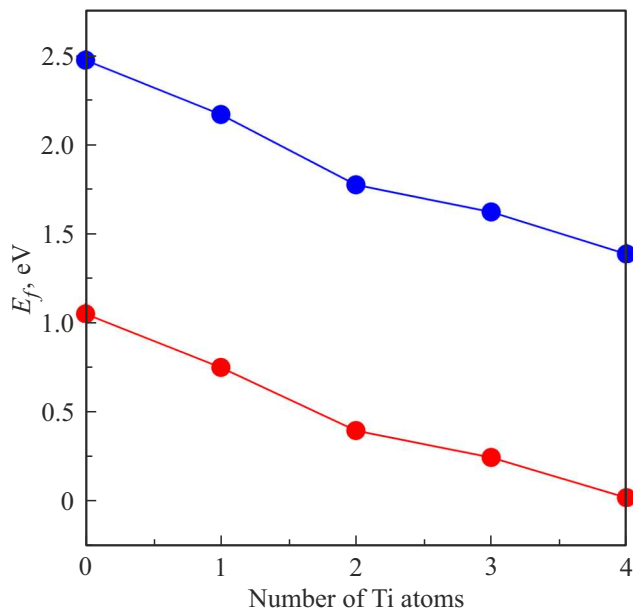


Figure 3. The energy of formation of V-type (blue) and Ti-type vacancies (red) depends on the number of Ti atoms in the immediate environment for the configurations VTi_n shown in Figure 2.

environment in the direction of the sides of the lattice cell. The minimum energy E_f^{\min} is observed when the titanium atoms in the first environment are located along the diagonals of the cell.

These data show a monotonous decrease in the minimum energy of vacancy formation with an increase in the content of titanium atoms among its closest neighbors. It is extremely interesting that the minimum energy of formation of a Ti vacancy is about 1.5 times lower than for a V vacancy. Undoubtedly, under conditions of radiation exposure, configurations with minimal energy of their formation will make the main contribution to the process of vacancy formation. Therefore, the increased probability of the formation of Frenkel pairs (vacancy-embedded atom) at the locations of titanium atoms may play an important role in the processes of radiation degradation of Ti-V alloys.

For refining DFT calculations, 5 configurations were selected, shown in Figure 2. All of these configurations have a minimum energy of formation for a fixed number of

titanium atoms in the first neighborhood of the vacancy according to MC modeling data. In addition, all of them have vacancy formation energies that are almost identical (the difference is less than 0.02 eV) with the minimum vacancy formation energy for a given number of titanium atoms in the first environment. In DFT modeling, volumetric optimization of supercells was performed with a variation of $\pm 5\%$ of the estimated equilibrium value. Three series of optimization calculations were performed for each configuration: for a supercell with a vacancy and for supercells with vanadium and titanium atoms instead of a vacancy. The equilibrium values of the lattice parameter and energy for all cells were calculated using the Birch–Murnaghan’s isothermal equation of state. The energy of vacancy formation was calculated again using the formula (1a, b), and the results are shown in Figure 3.

Thus, it was found that for both V-type and Ti-type vacancies, the energy of their formation decreases monotonously with an increase in the number of titanium atoms in the immediate vicinity of the vacancy from 0 to 4. At the same time, for V-type vacancies, the decrease occurs from 2.50 eV to 1.48 eV, whereas for Ti-type vacancies, the decrease occurs from 1.05 eV to 0.33 eV. Such a strong difference for the two types of vacancies is probably due to the fact that when titanium is dissolved in BCC-V, the atomic radius of Ti exceeds the atomic radius of vanadium. This follows from the monotonous growth of the lattice parameter BCC of solid solutions of $V_{1-y}Ti_y$ with an increase in the titanium content experimentally detected in Ref. [11] when an impurity titanium atom is placed in it. This result is also confirmed by our *ab initio* calculations. The calculation of the average values of Voronoi polyhedra for Ti and V atoms in the cells under consideration was performed. All the considered cells V-Ti $3 \times 3 \times 3$ were relaxed in VASP at fixed values of the lattice parameters corresponding to the equilibrium values. The results of calculations of the average values of Voronoi polyhedra for titanium and vanadium atoms are shown in Figure 4.

It is clearly seen that the Voronoi polyhedron, built around a single titanium atom, has a volume of 14.5 \AA^3 , whereas a similar polyhedron covering a vanadium atom is only 13.6 \AA^3 . It can also be seen that with an increase in the number of titanium atoms in the environment, the volume of the Voronoi polyhedron increases monotonously, which indicates an increase in local tensile stresses in this region. The established difference in atomic radii leads to the appearance of local stress in the crystal matrix near the atoms of Ti. Local stress leads to a significant decrease in the energy of Ti-vacancy formation compared to the V-vacancy. In addition, the local stress will increase with an increase in the number of titanium impurities in the vicinity of the vacancy, which will lead to a decrease in the energy of its formation. This mechanism fully describes the effect we found. The result found (a sharp decrease in the energy of Ti-type vacancy formation with a large number of nearest neighbors Ti) may be important in the case of radiation exposure to V-Ti alloys. Indeed, with an alloy content

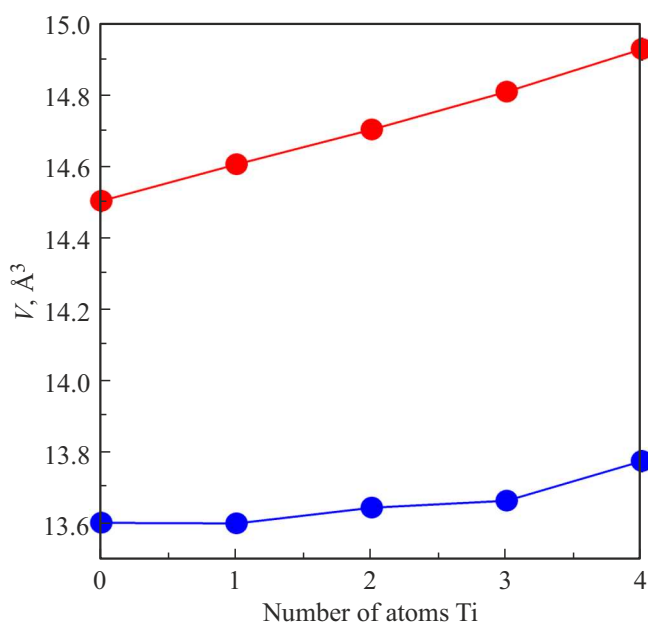


Figure 4. The average volume of Voronoi polyhedra for atoms at various cell nodes in Figure 2. The data for vanadium atoms is marked in blue, and — for titanium atoms is marked in red.

of about 5%, at.% titanium, the probability of detecting 3 atoms of the same grade among the 8 nearest neighbors of a titanium atom is not so small. However, it is clear that the predicted effect will not be easy to detect experimentally. Most likely, it can manifest itself only when studying the radiation effects on V-Ti alloys of various compositions. It is well known that radiation exposure in nuclear reactors is often accompanied by the deposition of various secretions on the surface. It was reported in a recent article in Ref. [12] that TiN emissions were observed when irradiating alloys based on V-Ti with a beam of helium ions at a temperature of 700 °C. It is quite possible that this effect is related to the low energy of formation of radiation Ti vacancies found in our calculations.

Funding

The study was funded by the Russian Science Foundation as part of research project No 25-22-20062.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov