Substitutional impurities influence on hydrogen sorption properties of titanium and zirconium

T I Spiridonova¹, E V Tuch², A V Bakulin²,³, S E Kulkova²,³*

¹ National Research Tomsk Polytechnic University, pr. Lenina 30, Tomsk, 634050, Russia
² Institute of Strength Physics and Materials Science, pr. Akademichesky 2/4, Tomsk, 634021, Russia,
³ National Research Tomsk State University, pr. Lenina 36, Tomsk, 634050, Russia

E-mail: kulkova@ms.tsc.ru

Abstract. The influence of substitutional impurities on the hydrogen absorption energy in Ti and Zr is investigated by the projector augmented wave method within the density functional theory. Obtained results demonstrate that simple metal atoms are repulsive to H, whereas transition metal atoms attract H and provide traps for H. The relationship between the interaction energy, the lattice distortion and the electronic structure of metals is analyzed.

1. Introduction
Metals of group IVB such as titanium and zirconium are widely used for technological applications in aerospace, marine, chemical, etc. industries. Both metals have high corrosion resistance and good biocompatibility with human tissue that provides their widespread applications in medicine for dental and bone implants, various fixation devices and medical instruments. Besides zirconium and its alloys are very important construction materials for nuclear reactors. The hydrogen is the main factor of degradation of metals and their alloys under working condition. It is known that hydrogen does not dissolve appreciable in metals at room temperature and normal pressure whereas their hydrides can be easily formed. The appearance of hydride phase results in brittle behavior of the metal. This phenomenon is called as hydrogen embrittlement [1]. The increase of temperature leads to better dissolution of hydrogen in the metal matrix and therefore, in particular, titanium exhibits a ductile behavior. It is believed that the alloying allows improving the hydrogen embrittlement and restrain the hydride phase formation. It was reported in [2-4] that substitutional impurities can influence on the terminal solubility of hydrogen in metals due to a trapping of hydrogen. The detailed investigation of influence of simple and transition metals on the solubility of hydrogen in titanium was studied in [5] using the first principles calculations. It was shown that the different mechanisms can be responsible for hydrogen interaction with alloying metals. In particular, the repulsive interaction between simple metals (SM) and hydrogen is due to the hybridization of their orbitals whereas the interaction of H with transition metals (TM) is attributed to the atomic size effect [5]. However, there are contradictory results about preferential position of hydrogen even in pure α-Ti [5, 6]. Thus, the goal of present paper is to study the preferential position for H absorption in both Ti and Zr as well as the influence of substitutional impurities on the hydrogen absorption properties.

2. Calculation method
The calculations of the electronic structure of IV group metals in the hexagonal phase was carried out by projector augmented wave method [7] implemented in VASP code [8] within the generalized gradient approximation for the exchange-correlation functional. The model of the supercell constructed from a $2 \times 2 \times 1$ replication of the conventional hexagonal unite cell, containing 8 atoms of metal, are shown in Fig. 1. The optimization of supercell was performed by keeping its shape, i.e. the supercell was relaxed by changing the lattice constant homogeneously with a ratio of $c/a$ fixed at the experimental values 1.588 and 1.593 for Ti and Zr, respectively. The octahedral (O) and tetrahedral (T) sites for hydrogen atom, shown in figure 1, were considered. One of metal atom which is nearest to H site, was replaced by a metal impurity atom as shown in figure 1. In this case an additional optimization of the atomic positions (after volume optimization) until the forces at each atom $\sim 0.01$ eV/Å, was performed. The total energies were converged up to $10^{-5}$ eV. The $\Gamma$-centered k-points grid $7 \times 7 \times 7$ was applied for the integration over the Brillouin zone. The energy cut-off for plane waves was set as 400 eV.

The binding ($E_b$) and absorption ($E_{abs}$) energies were calculated using the following equation:

$$E_b = E(N-1,X,H) - E(N-1,X) - E(H)$$ (1)

$$E_{abs} = E(N-1,X,H) - E(N-1,X) - 1/2E(H_2),$$ (2)

where $E(N-1,X)$ and $E(N-1,X,H)$ are total energies of system with alloying metal ($X$) without and with hydrogen (H), $E(H)$ and $E(H_2)$ is the total energies of hydrogen atom and molecule, respectively. The factor 2 takes into account the presence of one H atom inside supercell.

The interaction energy between impurity atom and H was calculated as

$$\Delta E = [E(N-1,X,H) + E(N)] - [E(N-1,X) + E(N,H)]$$ (3)

where $E(N)$, $E(N,H)$ are the total energies of supercell with $N$ sites and that with hydrogen.

![Figure 1. Atomic structure of IVB group metal supercell $2 \times 2 \times 1$ with hydrogen at the octahedral and tetrahedral sites (small red balls) and impurity metal (green ball) instead one host atom.](image)

3. Results and discussion

The calculated binding and absorption energies of hydrogen at both O and T sites are given in table 1. It is necessary to note that greater absolute value of the binding or absorption energy means better bonding or dissolving hydrogen in the metal matrix. As can be seen from table 1 the hydrogen prefers to occupy the octahedral site in the hexagonal lattice in case of both considered metals. The difference between H energies at the O and T sites decreases if the relaxation of the atomic positions due to H incorporation in metal matrix was taken into account. The obtained difference in the total energies of Ti with H at the O and T is only 0.16 eV in our calculations that is one order less than the difference $(E_{tot}(T) - E_{tot}(O))$ in [5] where the preference of the T site for hydrogen absorption was found within linear muffin-tin orbital method (LMTO-ASA).

Figure 2 presents the change of the hydrogen absorption energy at both O and T sites if one of Ti atom nearest to the hydrogen position was replaced by simple or 3d transition metals. It is seen that substitutional impurities do not influence on the obtained trend in Ti whereas some impurities such as Sc, V, Cr, Ni can change the preference of considered positions for H absorption in Zr. Figure 2
demonstrates that the transition metal impurities of the middle of 3d-period lead to increase of the hydrogen dissolution in both Ti and Zr matrix.

**Table 1.** Binding and absorption energies for H at both O ad T sites calculated in $2 \times 2 \times 1$ supercell keeping its shape with volume change and with relaxed atomic positions (in brackets).

| Metal | Octahedral site $E_b$ (eV) | Tetrahedral site $E_b$ (eV) | Octahedral site $E_{abs}$ (eV) | Tetrahedral site $E_{abs}$ (eV) |
|-------|--------------------------|--------------------------|-------------------------------|-------------------------------|
| Ti    | $-2.66 (-2.71)$          | $-2.42 (-2.55)$          | $-0.38 (-0.44)$               | $-0.15 (-0.28)$               |
| Zr    | $-2.64 (-2.68)$          | $-2.59 (-2.66)$          | $-0.37 (-0.41)$               | $-0.32 (-0.40)$               |

**Figure 2.** The absorption energies of H at both O and T sites in dependence on substitutional impurity.

The interaction energy between alloying element and hydrogen occupying O and T sites are given in figure 3. Our calculations show that for simple metals $\Delta E$ is positive irrespective of the H site in the metal matrix. The positive values of the interaction energy suppose that considered SM (Al, Si, Ga, Ge) are repulsive to the hydrogen atom. It is seen from figure 3 that $\Delta E(T)$ is larger than $\Delta E(O)$ because the distance between H and SM is shorter when H occupies the T site than the O-site. In general, hydrogen cannot be trapped at both O and T sites with neighboring simple metals in Ti and Zr as well. However, most transition metals have negative $\Delta E$ that means attractive interaction between TM and H at both interstitials whereas the attractive interaction only at the T-site was found in [5]. Consequently, both interstitials having TM as neighbor are trapping sites for H. It is known that the trapping of hydrogen by substitutional impurities was discussed in [2-4]. In particular, the hydrogen trapping by impurities was attributed to size difference between the substitutional impurity and host atoms. It was supposed in [4] that the dissolution of hydrogen reduces the strain in metal matrix due to undersized impurity atom. In order to this effect was more pronounced the H atom should be closer to the impurity atom that suggests the trapping of H. The oversized impurity atom may expand the interstitial sites that makes them more preferential for H occupancy and leads also to trapping of H as was suggested in [2, 3]. It is necessary to note that in both models only structural factors were taken into account.

The figures 3c,d show the change of volume of both Ti and Zr caused by substitutional impurities and hydrogen. In our calculations H expands the equilibrium volume of Ti (Zr) lattice by 1.46-3.32%, (0.96-2.50%), whereas TM metal with atomic radius less than that of host metal reduces this volume as shown in figure 3c,d. The change of volume is slightly larger in case of H at the tetrahedral site than that for H at the O site that can be indication of the preference of the octahedral site for H absorption. In the presence of H the lattice contraction is reduced due to undersized impurity atom. As can be seen from figure 3c,d the volume change due to TM demonstrates a parabolic behavior as in [5] and reaches a maximum change at Fe, Co. These results coincide well to the interaction energies presented in
Among considered transition metals only Sc has the radius larger that Ti but almost the same as Zr. So, the presence of Sc in Ti matrix increases its volume as seen in figure 3c. Obtained results reveal the attractive H-Sc interaction at both H sites inside metal matrix whereas the repulsive behavior was found in [5] for H at the tetrahedral site. The similar behavior was obtained in our calculation without relaxation of atomic positions around Sc. Thus, it is very important in theoretical calculations to take into account the local strain and the lattice distortion due to substitutional impurity and H absorption. It is necessary to emphasize that the lattice distortion can depend strongly on the concentration of alloying metal and hydrogen. In general, our calculations of the interaction energies between TM and H support also as in [5] the strain field model suggested in [4].

Several words should be said about the electronic structure of system in the presence of H and substitutional impurities. Figure 4 presents the total densities of states (DOS) of Ti with impurity atom (V, Cu) and the system with both V(Cu) and H at the octahedral site. It can be seen that low-lying states are appeared at −7 eV in the DOS curve for system with hydrogen. These states are formed due to interaction of H s-state with s,d-states of host and impurity atoms. These hybridized states represent the covalent bonding between H and TM. It is seen in figure 4 that the total DOS changes only slightly due to the presence of H in Ti-X-H system. The same can be revealed from the local DOS curves of impurity atom and H comparing them in Ti-X-H, Ti-H and Ti-X systems. In this context we support the conclusion of Ref. [5] that the electronic structure may be not the main factor for understanding the microscopic nature of H trapping in metals doped by TM. It should be noted that mentioned above trends are valid for Zr also.

**Figure 3.** Interaction energy between hydrogen and alloying element (a,b) and the change of equilibrium volume relative to that of pure Ti (c) or Zr (d).

**Figure 4.** Total densities of states of Ti-X (dashed lines) and Ti-X-O (solid lines) system for H in the octahedral site.
Figure 5. Local DOS of H in the O (top) and T (bottom) sites and Cu (left) and Ge (right) in Ti-X-H systems. DOS of H in Ti-H and that of TM or SM in Ti-X are given by dots.

In case of simple metals in Ti or Zr matrix there are low-lying states also. Moreover they are common feature of simple metal and also present in Ti-X system due to hybridization of SM \(s,p\)-states with \(s,d\)-states of Ti (Zr). In system with hydrogen (Ti-X-H) these low lying states are split into two bands. It is clearly can be seen in the local DOS of H (figure 5a,b) that there is bonding (at \(-10\) eV) and antibonding (at \(-6.5\) eV) states with gap between them in case of H at the O and T-sites. In spite of the hybridization between SM and H states contributes to the binding energy, however the contribution to kinetic energy due to the Pauli principle, is larger that leads to a positive \(\Delta E\) and to repulsive interaction between the simple metal and hydrogen in Ti-X-H system.

4. Conclusion

The first principles investigation of the influence of substitutional impurities on the H absorption in \(\alpha\)-Ti and \(\alpha\)-Zr was performed. The relationship between impurity trapping of hydrogen and lattice distortion as well as electronic structure was analyzed. It was shown that H prefers to occupy the octahedral position in both metals, however the difference in absorption energies for O and T sites in Zr is lower than that in Ti. The substitutinal impurities do not influence on the obtained trend in Ti whereas the T site may be more preferred for H absorption in Zr in case of some metals such as Sc, V, Cr and Ni. The calculations of the interaction energy show that simple metals are repulsive to H whereas transition metals are attractive to H and may provide its trapping. Different factors are responsible for the SM-H and TM-H interactions: the electronic factor may be a main reason of the repulsive SM-H interaction while the size effect can be responsible for TM-H interaction.

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