A First-Principles Study of Hydrogen Desorption from High Entropy Alloy TiZrVMoNb Hydride Surface

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Abstract: The desorption behaviors of hydrogen from high entropy alloy TiZrVMoNb hydride surface have been investigated using the density functional theory. The (110) surface has been determined to be the most preferable surface for hydrogen desorption from TiZrVMoNb hydride. Due to the high lattice distortion and heterogeneous chemical environment in HEA hydride, hydrogen desorption from the HEA hydride surface is found to be complex. A comparison of molecular and atomic hydrogen desorption reveals that hydrogen prefers to desorb in atomic states from TiZrVMoNb hydride (110) surface rather than molecular states during the hydrogen desorption process. To combine as H2 molecules, the hydrogen atoms need to overcome attractive interaction from TiZrVMoNb hydride (110) surface. These results suggest that the hydrogen desorption on TiZrVMoNb hydride (110) surface is a chemical process. The presented results provide fundamental insights into the underlying mechanism for hydrogen desorption from HEA hydride surface and may open up more possibilities for designing HEAs with excellent hydrogen desorption ability.

Keywords: first-principles calculations; high entropy alloys; hydrogen desorption; surface

1. Introduction

Hydrogen, with its quite plentiful amount, cost-effective renewability, high energy density and zero-emission characteristics, has been considered as a potential substitute for fossil fuels in the past several decades [1–4]. However, developing hydrogen storage materials with a low decomposition temperature and pressure (which are well suited for practical purposes), high recyclability, fast kinetics and high hydrogen storage capacity is one of the most crucial difficulties restricting the utilization of hydrogen energy for real applications [5–7]. Recently, high entropy alloys (HEAs), which are composed of five or more elements with atomic concentrations of 5–35% and tend to form single-phase solid solutions [8–15], have received much attention in the hydrogen storage field [16–19]. A number of investigations have suggested that hydrogen storage properties of HEAs can be enhanced by carefully tuning their constituents [17] and an excellent hydrogen storage performance can be achieved, like high hydrogen storage capacity [19,20], reversibly phase transformation [21], rapid hydrogen absorption [22] and moderate absorption/desorption temperature and pressure [23].

Among the investigations of hydrogen storage of HEAs, efforts have been made to study the desorption properties of HEA hydrides. For HEAs such as TiZrVHfNb [19], TiZrHfMoNb [21], MgZrTiFe0.5Co0.5Ni0.5 [24], TiZrNbHfTa [25], TiZrNbTa [22], TiVZrNb [26], MgTiNbCr0.5Mn0.5Ni0.5 [27], MgVAlCrNi [28] and MgTiVCrFe [29], it has been found that hydrogen desorption happens at temperature of above 200 °C. Recently, several works of research have been devoted to reducing the desorption temperature [23,30–32]. The hydrogen desorption properties of a series of TiZrHfMoNb HEAs with
different Mo concentrations have been investigated experimentally and theoretically by Shen et al. [30], who found that the thermal stability of the TiZrHfMoNb hydrides decrease with increasing Mo concentration, which is mainly attributed to the smaller cell volume of the TiZrHfMoNb hydride for higher Mo concentrations. Nygård et al. [23] proposed that the onset temperature for hydrogen desorption decreases linearly with the valence electron concentration (VEC) parameter and dehydrogenation can occur at room temperature when the total VEC is 6.4 in HEAs. Subsequently, Edalati et al. [31] designed the HEA TiZrCrMnFeNi with a VEC of 6.4 and found that 1.7 wt.% of hydrogen can be absorbed and desorbed at room temperature with fast kinetics and without activation treatment. Montero et al. [32] reported that the addition of only 10% Ta into Ti₀.₃₂₅V₀.₂₇₅Zr₀.₁₂₅Nb₀.₂₇₅ decreases the desorption temperature of the hydride phase by around 100 K. Despite these experimental studies of dehydrogenation of HEAs hydrides, few theoretical simulations of hydrogen desorption properties of HEAs have been reported. To date, there have been some theoretical calculations to study the hydrogen storage properties of HEAs, but most of them are mainly focused on the hydrogen absorption behavior [20,33]. Hence, it is necessary to investigate the underlying mechanism for the dehydrogenation of the HEAs on an atomic level.

Generally, the process of the dehydriding reaction can be described as follows [5,34,35]:
(a) hydride decomposition at the hydride/metal interface; (b) diffusion of hydrogen atoms through the hydride product layer to the surface; (c) surface penetration of hydrogen atoms; (d) recombination of chemisorbed hydrogen atoms and physisorption; (e) desorption to the gas phase. Among these steps, surface desorption is one of the critical processes. Thus far, considerable efforts have been made on the dehydrogenation of hydrogen storage materials such as MgH₂ in order to improve its kinetic properties and obtain a lower desorption temperature [36–41]. However, hydrogen desorption from the HEA surface, which is crucial to evaluate its dehydrogenation properties, has not been explored theoretically.

In this study, first-principle calculations based on Density Functional Theory (DFT) are carried out to investigate the hydrogen desorption behavior of HEA TiZrVMoNb. The surface energies of TiZrVMoNb (100), (110) and (111) surfaces are calculated and the preferred surface for dehydrogenation has been determined. To gain a fundamental insight into the state of hydrogen during desorption, atomic and molecular hydrogen desorption are compared. The presented results will advance the understanding of the hydrogen storage properties of HEAs and may promote related experimental and theoretical investigations to improve the desorption ability of HEA hydrides.

2. Computational Details

All the calculations are carried out with spin-polarized effects considered, within the DFT framework as implemented in Vienna Ab Initio Simulation Package (VASP) [42,43]. The interaction between ions and electrons is described using the projector augmented wave (PAW) method [44]. The exchange-correlation energy between electrons is described by the generalized gradient approximation (GGA) [45,46] in the scheme proposed by Perdew-Burke-Ernzerhof [47]. The valence electronic configurations for PAW potentials are 4s¹3d³ for Ti, 5s¹4d³ for Zr, 4s¹3d⁴ for V, 5s¹4d⁵ for Mo, 4p⁶5s¹4d⁴ for Nb and 1s¹ for H. A 2 × 2 × 1 Monkhorst-Pack k-grid for Brillouin zone integrations is employed for the surface of HEA TiZrVMoNb hydride. The convergence criteria for energy and force are 10⁻⁴ and 10⁻³ eV/Å, respectively.

The TiZrVMoNb hydride with a hydrogen-to-metal ratio (H/M) of 2 is considered [25,33] and the lattice constant is calculated to be 4.49 Å. Based on the obtained lattice constant, the (100), (110) and (111) surfaces of HEA TiZrVMoNb hydrides are modeled by repeated slab models, in which one slab consists of seven atomic layers. A vacuum thickness of 15 Å perpendicular to the surface is used to separate the periodically repeated slabs. The five metal elements of Ti, Zr, V, Mo and Nb with respective 14 atoms are distributed randomly on the lattice sites in a slab and the hydrogen atoms occupy all the tetrahedral sites. For each orientation, 40 random configurations with a random
distribution of the five alloying elements are considered and optimized with a cutoff energy of 300 eV for the plane-wave basis set. During structural relaxation, the atoms in the top four layers are allowed to relax while the atoms in the bottom three layers are fixed. For each surface, the total energies of the 40 random configurations are compared and the configuration with the lowest total energy is then chosen for the subsequent calculations. Then, to achieve high accuracy, these three surface models are optimized with a cutoff energy of 500 eV and the final configuration (see Figure 1) is used for the investigation of molecular and atomic hydrogen desorption. The randomization method described above has been used in the literature [33,48].

![Figure 1. Schematic view of the geometrical structures for the (100), (110) and (111) surfaces of HEA TiZrVMoNb hydrides.](image)

3. Results and Discussions

3.1. Surface Energies of the Clean HEA TiZrVMoNb Hydrides

To determine the most favorable surface for hydrogen desorption of HEA TiZrVMoNb hydride, three typical surface orientations are considered [49], i.e., (100), (110) and (111) surfaces. Considering the disordering of metal atoms on TiZrVMoNb hydride, the average surface energies ($\gamma_s$) of 40 random configurations for (100), (110) and (111) surfaces are calculated to evaluate the surface stability by

$$\gamma_s = \frac{1}{40} \sum_{i=1}^{40} \frac{E_{\text{slab},i} - NE_{\text{bulk}}}{2A_s}. \quad (1)$$

Here, $E_{\text{slab},i}$ is the total energy of the surface slab for the $i$-th configurations, $N$ is the formula number in the slab, $E_{\text{bulk}}$ denotes the energy per formula in bulk material, and $A_s$ shows the corresponding surface area. The average surface energies are determined to be 3.010, 2.342 and 3.282 J/m² for the (100), (110) and (111) surfaces of HEA TiZrVMoNb hydrides, respectively. It is shown that the (110) surface with the lowest average surface energy is the most stable for hydrogen desorption. The TiZrVMoNb hydride (110) surface, thus, is considered in the subsequent calculations.

3.2. Molecular Hydrogen Desorption

In the literature, it has been reported that the desorption of molecular and atomic hydrogen both exist in the hydrogen desorption process on the surfaces of metal hydrides [50]. Here, molecular hydrogen desorption is first considered. The top site desorption behaviors of H₂ molecule on TiZrVMoNb hydride (110) surface with different initial heights are investigated (see Figure 2). The covalent radii for H, Ti, Zr, V, Mo and Nb are 0.31, 1.60, 1.75, 1.53, 1.54 and 1.64 Å, respectively [51]. In order to take into account both chemisorption and physisorption, which correspond to the strong and weak interaction between hydrogen and metal atoms, respectively, the initial heights of 1.8, 2.5 and 3.0 Å are chosen in our calculations. For each height, a pair of H atoms are moved out from the top layer and an
The $H_2$ molecule is reintroduced parallelly on the top of their nearest metal atoms. Considering the variable and complex chemical environment of HEA hydrides [33], six configurations are taken into account by removing different hydrogen atoms and choosing different nearest-neighboring metal atoms for the $H_2$ molecule location (i.e., different hydrogen atoms are removed in Configurations 1 and 2, as well as in Configurations 3 and 4. As for Configurations 1, 3, 5 and 6, the nearest metal atoms are different). The geometries of the six configurations with different initial heights are then optimized. It turns out that the dehydrogenation behaviors for the $H_2$ molecule on the TiZrVMoNb hydride (110) surface are complex.

The characters of the optimized height are different, as shown in Table 1 and Figure 3. For Configurations 1, 2, 3 and 4 with the nearest-neighboring metal atoms of V element,
the variation of the height is small before and after optimization when the initial height is 3.0 Å. However, the $\text{H}_2$ molecule moves inward to the surface considerably when the initial height is below 2.5 Å after optimization. As for Configurations 5 and 6 with the nearest-neighboring metal atoms of Nb and Zr elements, the $\text{H}_2$ molecule has similarly optimized heights no matter that the initial height is 1.8, 2.5 or 3.0 Å. The possible reason for this is that the electronegativity of Nb (1.6) and Zr (1.33) is weaker than that of V (1.63), which may result in stronger interactions between the hydrogen atoms and Nb or Zr.

Table 1. Structural parameters for the molecular hydrogen desorption on TiZrVMoNb hydride (110) surface with different initial heights ($h_{M-H}$) of 1.8, 2.5 and 3.0 Å in the six configurations as shown in Figure 2. Here, $h_{M-H}$ refers to: the vertical distance between the $\text{H}_2$ molecule and the nearest-neighboring metal atom on surface before optimization; $h'_{M-1H}$ and $h'_{M-2H}$: the vertical distance between each atom of the $\text{H}_2$ molecule and the nearest-neighboring metal atom on surface after optimization; $d'_{1H-2H}$: the distance between the two $\text{H}$ atoms of the $\text{H}_2$ molecule after optimization; $d'_{3H-1H}$ and $d'_{3H-2H}$: the distance between each atom of the $\text{H}_2$ molecule and the third hydrogen atom dissociated from the TiZrVMoNb hydride (110) surface, as shown in Figure 5.

| Configuration | $h_{M-H}$ (Å) | $h'_{M-1H}$ (Å) | $h'_{M-2H}$ (Å) | $d'_{1H-2H}$ (Å) | $d'_{3H-1H}$ (Å) | $d'_{3H-2H}$ (Å) |
|---------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1             | 1.8            | 1.727          | 1.282          | 0.816          | 1.992          | 2.617          |
|               | 2.5            | 1.546          | 1.141          | 0.835          | 2.553          | 2.030          |
|               | 3.0            | 3.039          | 3.077          | 0.754          | -              | -              |
| 2             | 1.8            | 1.704          | 1.276          | 0.856          | 1.937          | 2.590          |
|               | 2.5            | 1.705          | 1.299          | 0.855          | 1.970          | 2.592          |
|               | 3.0            | 3.102          | 3.069          | 0.755          | -              | -              |
| 3             | 1.8            | 1.399          | 1.095          | 2.727          | -              | -              |
|               | 2.5            | 1.397          | 1.105          | 2.717          | -              | -              |
|               | 3.0            | 2.939          | 2.879          | 0.753          | -              | -              |
| 4             | 1.8            | 1.364          | 1.149          | 2.614          | -              | -              |
|               | 2.5            | 1.674          | 1.351          | 0.976          | -              | -              |
|               | 3.0            | 3.006          | 3.083          | 0.757          | -              | -              |
| 5             | 1.8            | 1.656          | 1.472          | 0.826          | 2.763          | 2.153          |
|               | 2.5            | 1.643          | 1.048          | 0.843          | 2.731          | 2.230          |
|               | 3.0            | 1.981          | 1.641          | 0.805          | 2.819          | 2.230          |
| 6             | 1.8            | 2.238          | 2.243          | 0.780          | -              | -              |
|               | 2.5            | 2.267          | 2.267          | 0.777          | -              | -              |
|               | 3.0            | 2.251          | 2.249          | 0.784          | -              | -              |

Figure 3. The average optimized height for the molecular hydrogen desorption on TiZrVMoNb hydride (110) surface in the six configurations with the initial heights of 1.8, 2.5 and 3.0 Å. The geometrical structures for the considered six configurations are shown in Figure 2.
It is also noted that the H-H bonds of the H$_2$ molecules in some configurations are broken (see Table 1). In the case of Configurations 3 and 4, the bond lengths of H$_2$ molecules are elongated above 2.614 Å with low optimized heights, and the elongated bond lengths are much larger than that of the free H$_2$ molecule (0.752 Å), which means a break of H-H bonds. One possible explanation is that the relatively small vertical distance between the H$_2$ molecule and TiZrVMoNb hydride surface results in hydrogen bond breaking. In order to further explore the origin of the break of the H-H bond, Configuration 1, without breaking the H-H bond, and Configuration 3, with a broken H-H bond, are analyzed because in both cases the nearest-neighboring metal atoms are V elements. The local distribution of metal atoms around the H$_2$ molecule in the two configurations are compared in Figure 4. It is found that after structural optimization the H-H axes in these two configurations are along the [010] direction. In comparison to the metal atoms along the [100] direction, the metal atoms along the [010] direction are closer to the hydrogen atoms and their electronegativity is relatively weaker, which suggests that the metal atoms along the [010] direction have stronger influences on hydrogen atoms. Hence, the break of the H-H bond may be due to the weaker electronegativity of Zr (1.33) in Configuration 3 (see Figure 4b), as compared with Nb (1.66) in Configuration 1 (see Figure 4a).

Interestingly, a third hydrogen atom has been found to dissociate from the TiZrVMoNb hydride (110) surface when the value of the optimized height is small in Configurations 1, 2 and 5 (see Table 1 and Figure 5). However, this phenomenon does not occur when the value of the optimized height is large, which suggests that the height affects the interaction between the H$_2$ molecule and the TiZrVMoNb hydride (110) surface.

Comparing the cases in the considered six configurations, similar dehydrogenation behaviors have been found in Configurations 1 and 2, in which different hydrogen atoms are desorbed from the surface and the nearest-neighboring metal atoms are V atoms. Similar phenomena also exist in Configurations 3 and 4. On the other hand, Configurations 1, 3, 5 and 6, with the different nearest-neighboring metal atoms, exhibit different dehydrogenation behaviors. Thus, the dehydrogenation property of the TiZrVMoNb hydride (110) surface is strongly dependent on the distribution of metal atoms rather than hydrogens. For most of the considered configurations, the H$_2$ molecules are not parallel to the desorbed surface after structural optimization. For instance, the optimized vertical distance between each atom of the H$_2$ molecule and the nearest-neighboring metal atom on surface is different when the initial height is 1.8 Å in Configuration 1. The tilting of H-H axes in the H$_2$ molecule are mainly attributed to the high lattice distortion [33] and heterogeneous chemical environment in HEA hydrides [52].

**Figure 4.** The local distribution of metal atoms around the desorbed hydrogen atoms in (a) Configuration 1, (b) Configuration 3 for molecular hydrogen desorption. The value in parentheses denotes the electronegativity of the metal atoms. The geometrical structures for Configurations 1 and 3 are presented in Figure 2.
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Interestingly, a third hydrogen atom has been found to dissociate from the TiZrVMoNb hydride (110) surface. The desorbed H atoms and the third dissociated hydrogen atom are represented by dark blue and yellow spheres, respectively.

3.3. Atomic Hydrogen Desorption

Besides the molecular hydrogen desorption, the atomic hydrogen desorption on TiZrVMoNb hydride (110) surface is further explored. As shown in Figure 6, the H2 molecules in the six different configurations discussed in Section 3.2 are separated along the [100] direction by 4 Å with an initial height of 3 Å. The geometries of the six configurations are then optimized. Table 2 lists the structural parameters and energy difference (\( \Delta E = E_{\text{Cont},n} - E_{\text{Cont},1} \), \( n = 1, 2, \ldots, 6 \)) between Configuration 1 and other configurations for atomic hydrogen desorption on TiZrVMoNb hydride (110) surface. It turns out that the dehydrogenation behaviors for H atoms on the TiZrVMoNb hydride (110) surface are complex, like molecular hydrogen desorption.

![Figure 5](image-url)

**Figure 5.** Schematic view of the third hydrogen atom dissociated from the TiZrVMoNb hydride (110) surface. The desorbed H atoms and the third dissociated hydrogen atom are represented by dark blue and yellow spheres, respectively.

![Figure 6](image-url)

**Figure 6.** Schematic view of the considered configuration for the parallel atomic hydrogen desorption on the HEA TiZrVMoNb hydride (110) surface with an initial height \( h_{M-H} \) of 3.0 Å. The desorbed H atoms are represented by dark blue spheres. Here, \( d_{1H-2H} \) is the distance between the two desorbed hydrogen atoms before structural optimization. Here, \( h_{M-H} \) is the vertical distance between the desorbed hydrogen atoms and the nearest-neighboring metal atom on surface before structural optimization.
Table 2. Structural parameters and energy difference ($\Delta E = E_{\text{Conf},n} - E_{\text{Conf},1}$, $n = 1, 2, \ldots, 6$) see Table 1. and other configurations for atomic hydrogen desorption with an initial height of 3.0 Å. See Table 1 for a description of $h'_{M-1H}$, $h'_{M-2H}$, $d'_{3H-1H}$ and $d'_{3H-2H}$. The geometrical structures for the considered six configurations are shown in Figure 2.

| Configuration | $h'_{M-1H}$ (Å) | $h'_{M-2H}$ (Å) | $d'_{3H-1H}$ (Å) | $d'_{3H-2H}$ (Å) | $\Delta E$ (eV) |
|---------------|-----------------|-----------------|-----------------|-----------------|---------------|
| 1             | 1.100           | 1.818           | -               | -               | 0             |
| 2             | 1.116           | 1.815           | -               | -               | 0.15          |
| 3             | 1.250           | 1.755           | -               | -               | 0.41          |
| 4             | 1.281           | 1.379           | -               | -               | 0.33          |
| 5             | 1.055           | 1.600           | 2.083           | 2.519           | 0.78          |
| 6             | 1.776           | 1.818           | -               | -               | 1.11          |

After structural optimization, the hydrogen atoms are found to locate at different sites. The final positions of the two desorbed hydrogen atoms on TiZrVMoNb hydride (110) surface are illustrated in Figure 7. Figure 8 shows the local distribution of metal atoms around the desorbed hydrogen atoms in the six configurations. In Configurations 1, 2 and 3, the two desorbed hydrogen atoms in each configuration locate at the short bridge site and top site, respectively. In the case of Configuration 4, both of the two hydrogen atoms locate at the short bridge sites. In Configuration 5, one hydrogen atom locates at the long bridge site while the other one locates at the top site after optimization. As for Configuration 6, both of the two hydrogen atoms are located at the short bridge sites. From an overall perspective, the hydrogen atoms do not locate exactly at the top or bridge site and the deviation of the hydrogen atoms is probably due to the random distribution of metal atoms in the HEA hydride. For each configuration, the two desorbed hydrogen atoms exhibit different optimized heights, which are relevant to the electronegativity of their nearest-neighboring metal atoms (see Figure 9). To discuss the effects of the electronegativity of the neighboring metal atoms, the electronegativity of the nearest-neighboring metal atom is considered for the hydrogen atom on the top site; while for the hydrogen atom on the bridge site, the average electronegativity of the two nearest neighboring metal atoms is taken into account. As shown in Figure 9, the higher the electronegativity of nearest-neighboring metal atoms, the larger the optimized heights of the desorbed hydrogen atoms. Since the electronegativity of H (2.2) is larger than that of its nearest-neighboring metal atoms, the metal atoms with higher electronegativity have weaker interactions with hydrogen, resulting in the larger optimized height. Comparing the total energies of the six configurations presented in Table 2, the most preferable desorption configurations are Configuration 1, followed in decreasing order of stability by Configurations 2, 4, 3, 5 and 6, suggesting that the combination of the top and bridge sites may be favorable for atomic hydrogen desorption on TiZrVMoNb hydride (110) surface. In addition, a third hydrogen atom has been found to desorb from the hydride surface for Configuration 5, which is similar to its molecular desorption.

Figure 7. Top view of the TiZrVMoNb hydride (110) surface. The top (T), long bridge (LB), hollow (H) and short bridge (SB) sites are indicated.
Figure 8. The local distribution of metal atoms around the desorbed hydrogen atoms in the six configurations for atomic hydrogen desorption on the HEA TiZrVMoNb hydride (110) surface. Markers 1H and 2H present each of the two hydrogen atoms.

Figure 9. The optimized height of the two hydrogen atoms for the atomic hydrogen desorption on TiZrVMoNb hydride (110) surface in the six configurations with an initial height of 3.0 Å. The parallel axis indicates the electronegativity of the nearest-neighboring metal atoms for the top site or average electronegativity of the two coordinated metal atoms for the bridge site.

In the considered six configurations, all the hydrogen atoms with an initial height of 3 Å move inward to the surface significantly after optimization (see Table 2 and Figure 9), which is different from molecular hydrogen desorption, indicating that hydrogen atoms may prefer to exist near TiZrVMoNb hydride (110) surface. Besides, our results indicate that hydrogen may prefer to desorb in atomic states rather than molecular states.
3.4. A Comparison of Molecular and Atomic Hydrogen Desorption

In order to further compare the atomic and molecular hydrogen desorption, the energy difference ($\Delta E$) between the hydrogen desorption state and the clean TiZrVMoNb hydride (110) surface ($\Delta E = E_{\text{des}} - E_{\text{clean}}$) is calculated. As can be seen from Figure 10, the energy differences for atomic hydrogen desorption are generally lower than those for molecular hydrogen desorption except for Configuration 5, i.e., the energies for atomic hydrogen desorption are smaller than those for molecular hydrogen desorption. These results suggest that atomic hydrogen desorption is more favorable than molecular desorption, which verifies our conjecture in Section 3.3. In the case of Configuration 5, the abnormal phenomenon may be caused by the third hydrogen atom dissociated from the TiZrVMoNb hydride (110) surface, as presented in Figure 5. Combining these results with the observation that the optimized heights in atomic hydrogen desorption are smaller than those in molecular hydrogen desorption, the hydrogen desorption process on TiZrVMoNb hydride (110) surface may be inferred as follows: (a) the hydrogen-metal (H-M) bonds on TiZrVMoNb hydride (110) surface are broken and hydrogen desorb in atomic states near the surface; (b) the hydrogen atoms need to overcome the attractive interaction from TiZrVMoNb hydride (110) surface to combine as H$_2$ molecules. Thus, hydrogen desorption is a chemical process, which is consistent with the cases of other metal hydrides [50,53].

For partly desorbed material, the distribution of metal atoms may not change, i.e., atomic hydrogen desorption may still be preferable to molecular hydrogen desorption, and the hydrogen atoms may need to overcome attractive interaction from hydride surface to combine as H$_2$ molecules.

![Figure 10.](image)

Overall, due to the random distribution of multi-metal atoms, the interactions between hydrogen and the HEA hydride surface are complex and thus result in multiple hydrogen desorption behaviors at different locations on HEA hydride surface. The presented results indicate that the hydrogen desorption properties of high entropy hydrogen storage materials can be tuned by altering the composition of HEAs.

4. Conclusions

In summary, the hydrogen desorption behaviors on TiZrVMoNb hydride surface have been investigated using first-principles calculations. The (100), (110) and (111) surface energies of HEA TiZrVMoNb hydrides are calculated and the TiZrVMoNb hydride (110) surface with the lowest surface energy is predicted to be the most favorable for hydrogen storage materials.
desorption. Based on TiZrVMoNb hydride (110) surface, a comparison of molecular and atomic hydrogen desorption is carried out. For molecular hydrogen desorption, the H-H bonds in H₂ molecules are broken in some cases, due to the different electronegativity of the multi-principal metal atoms. The behaviors of H₂ molecules are found to be more relevant to the distribution of their nearest-neighboring metal atoms than hydrogens. For atomic hydrogen desorption, the hydrogen atoms are found to locate at different sites, and the top and bridge sites are favorable for atomic hydrogen desorption on TiZrVMoNb hydride (110) surface. Besides, the hydrogen atoms have relatively small vertical distances from the surface. A comparison of atomic and molecular desorption behaviors shows that atomic hydrogen desorption is more preferable to molecular hydrogen desorption. The hydrogen desorption process on TiZrVMoNb hydride (110) surface is thus inferred as two steps: (a) the H-M bonds on TiZrVMoNb hydride (110) surface are broken and hydrogen desorbs in atomic states near the surface; (b) the hydrogen atoms overcome attractive interaction from TiZrVMoNb hydride (110) surface to combine as H₂ molecules. The mechanism for hydrogen desorption from HEA surface revealed from this study may be beneficial for related investigations to improve the dehydrogenation ability of HEAs.

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