Influence of element substitutions on poisoning behavior of ZrV2 alloy: theoretical and experimental investigations

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Date: 2023-06-07T00:00:00+00:00

Abstract

An ZrV_2 alloy is typically susceptible to poisoning by impurity gases, which causes a considerable reduction in the hydrogen-storage properties of the alloy. In this study, the adsorption characteristics of oxygen on ZrV_2 surfaces doped with Hf, Ti, and Pd are investigated, and the influence of oxygen on the hydrogen storage performance of the alloy was discussed. Subsequently, the adsorption energy, bond-length change, density of states, and differential charge density of the alloy before and after doping are analyzed using the first-principles method. The theoretical results show that Ti doping has a limited effect on the adsorption of oxygen atoms on the ZrV_2 surface, whereas Hf doping decreases the adsorption energy of oxygen on the ZrV_2 surface. Oxygen atoms are more difficult to adsorb at most adsorption sites on Pd-containing surfaces, which indicates that Pd has the best anti-poisoning properties, followed by Hf. The analysis of the differential charge density and partial density of states shows that the electron interaction between the oxygen atom and surface atom of the alloys is weakened, and the total energy is reduced after Hf and Pd doping. Based on theoretical calculations, the hydrogen-absorption kinetics of ZrV_2, $Zr_{0.9}Hf_{0.1}V_2$, and $Zr(V_{0.9}Pd_{0.1})_2$ alloys are studied in a hydrogen–oxygen mixture of 0.5 vol% O_2 at 25℃. The experimental results show that the hydrogen-storage capacities of ZrV_2, $Zr_{0.9}Hf_{0.1}V_2$, and $Zr(V_{0.9}Pd_{0.1})_2$ decrease to 19%, 69%, and 80% of their original values, respectively. The order of alloy resistance to 0.5 vol% O_2 poisoning is $Zr(V_{0.9}Pd_{0.1})_2>Zr_{0.9}Hf_{0.1}V_2>ZrV_2$. Pd retains its original hydrogen absorption performance to a greater extent than undoped surfaces, and it has the strongest resistance to poisoning, which is consistent with previous theoretical calculations.

Full Text

Influence of Element Substitutions on Poisoning Behavior of ZrV_2 Alloy: Theoretical and Experimental Investigations

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Abstract

ZrV_2 alloy is typically susceptible to poisoning by impurity gases, which causes a considerable reduction in its hydrogen-storage properties. In this study, we investigated the adsorption characteristics of oxygen on ZrV_2 surfaces doped with Hf, Ti, and Pd, and discussed the influence of oxygen on the hydrogen-storage performance of the alloy. Using first-principles calculations, we analyzed the adsorption energy, bond-length changes, density of states, and differential charge density before and after doping. The theoretical results show that Ti doping has a limited effect on oxygen adsorption on the ZrV_2 surface, whereas Hf doping decreases the adsorption energy of oxygen. Oxygen atoms are more difficult to adsorb at most adsorption sites on Pd-containing surfaces, indicating that Pd has the best anti-poisoning properties, followed by Hf. Analysis of the differential charge density and partial density of states reveals that the electron interaction between oxygen atoms and surface atoms is weakened, and the total energy is reduced after Hf and Pd doping. Based on these theoretical calculations, we experimentally studied the hydrogen-absorption kinetics of ZrV_2, $Zr_{0\cdot9}Hf_{0\cdot1}V_2$, and $Zr(V_{0\cdot9}Pd_{0\cdot1})_2$ alloys in a hydrogen–oxygen mixture containing 0.5 vol% O_2 at 25 °C. The experimental results show that the hydrogen-storage capacities of ZrV_2, $Zr_{0\cdot9}Hf_{0\cdot1}V_2$, and $Zr(V_{0\cdot9}Pd_{0\cdot1})_2$ decrease to 19%, 69%, and 80% of their original values, respectively. The order of alloy resistance to 0.5 vol% O_2 poisoning is $Zr(V_{0\cdot9}Pd_{0\cdot1})_2 > Zr_{0\cdot9}Hf_{0\cdot1}V_2 > ZrV_2$. Pd retains the original hydrogen-absorption performance to a greater extent than undoped surfaces and exhibits the strongest resistance to poisoning, which is consistent with the theoretical calculations.

Keywords: Hydrogen storage, ZrV_2, First-principles, Poisoning effect

1 Introduction

The energy crisis and ongoing environmental challenges have received widespread attention in recent years [**?**, **?**, **?**], driving the development of the thorium molten-salt reactor nuclear-energy system project [**?**]. However, LiF and BeF_2 contained in molten-salt fuel produce the radionuclide tritium (^3H) under neutron irradiation [**?**]. Tritium is dangerous for humans and nature owing to its special properties; however, it is an important strategic resource and has been chosen as a fusion feedstock for the International Thermonuclear Experimental Reactor program [**?**, **?**]. Therefore, developing a scheme for tritium absorption and storage is of great practical significance.

Because tritium is a beta-emitting radioactive isotope of hydrogen, the chemical properties of tritium and hydrogen are very similar; consequently, most tritium-storage experiments use hydrogen to simulate tritium. Hydrogen can be stored as a gas, liquid, or solid. Gaseous and liquid hydrogen storage are energy-intensive and unsafe. Carbon-based physical-adsorption materials, inorganic porous materials, and metallic hydrogen-storage materials are currently used for solid hydrogen storage [**?**, **?**]. Compared to other hydrogen-storage methods, metal hydrogen-storage materials offer advantages of safety, multiple cycles, and mature technology [**?**, **?**]. ZrV_2 Laves-phase alloys have been extensively studied as hydrogen-storage materials because they preserve their maximum theoretical hydrogen-storage capacity (3.01 wt. %) [**?**, **?**] and have excellent kinetic properties [**?**] and ultralow equilibrium pressure (lower than 10^{-4} Pa [**?**] at room temperature). Therefore, ZrV_2 is used as an excellent getter material and tritium-absorbing alloy. However, in practical applications, impurity gases such as CO_2, O_2, CO, and H_2O react with metal on the alloy surface to form a dense passivation layer, which decreases the rate of hydrogen absorption [**?**, **?**, **?**]. Therefore, improving the anti-poisoning properties of ZrV_2 alloy is important for its widespread application.

In recent decades, many studies have investigated the effects of impurity gases on hydrogen-storage alloys. For example, Zhang et al. [**?**] studied the poisoning behavior of $Zr_{0\cdot8}Ti_{0\cdot5}V_{1\cdot7}$ alloy. They found that 0.1 mol% air impurities in hydrogen only worsened the hydrogen-absorption kinetics at 25 °C, while 1 mol% air impurities also affected the maximum hydrogen-absorption content at 180 °C. Sun et al. [**?**] indicated that the hydrogen capacity of the $(Mg(NH_2)_2 + 2LiH)$ system gradually declined in H_2 containing 0.1 mol% O_2, and it could not be restored to its initial level when using purified hydrogen again. In this poisoning phenomenon, the impurity gas reacts with the alloy surface to prevent hydrogen absorption. Many efforts have been made to protect hydrogen-storage alloys from poisoning. Zhang et al. deposited a layer of Pd–Ag film on the surfaces of $Zr_{0}{\cdot}_{9}Ti_{0}{\cdot}_{1}V_2$, $Zr_{57}V_{36}Fe_7$, and ZrV_2, and the results showed that Pd–Ag could withstand the poisoning effect of air impurities [?]. The hybridizing kinetic properties of all Pd-coated alloys were improved compared to those of the bare alloy [?]. However, the Pd film itself exhibited hydrogen-embrittlement properties. Moreover, the process of hydrogen absorption and desorption for the substrate alloy inevitably led to volume expansion and pulverization, thereby resulting in the disintegration and detachment of the Pd film [?, ?]. Therefore, achieving long-term protection was difficult over multiple hydrogen absorption/desorption cycles. Wu et al. [?] explored the poisoning behavior of O_2 as an impurity in a ZrVNi Laves-phase alloy. They observed that Ni provided surface active sites for the dissociative adsorption of hydrogen molecules during Zr and V oxidation. Significant progress has been made in the study of impurity gas poisoning in hydrogen-storage alloys. However, few theoretical studies have been conducted on the microscopic mechanism of impurity gas poisoning on ZrV_2 alloy surfaces.

In the present study, first-principles calculations are used to investigate how oxygen atoms occupy adsorption sites on the surfaces of Zr–V–M (M = Hf, Pd, Ti) alloys. The interaction between oxygen and surface atoms is analyzed, and the hydrogen-absorption properties of Zr–V–M (M = Hf, Pd) alloys against gaseous impurities are verified experimentally.

2 Models and Computational Details

First-principles calculations were performed based on density functional theory in the plane-wave pseudopotential approach using the Vienna ab-initio simulation package [?, ?]. The exchange-correlation energy was selected based on the generalized gradient approximation and Perdew–Burke–Ernzerhof exchange-correlation potential [?]. The Brillouin zone was sampled using Monkhorst–Pack k-point meshes [?], and a projector-augmented wave was used to generate the pseudopotential file. ZrV_2 was selected based on the database [?]; the space group was Fd3m(227), a = b = c = 7.36 Å, and the unit cell volume was 398.74 $Å^3$. Based on the calculated ZrV_2 crystal structure, Zr was substituted with Hf and Ti, and V was substituted with Pd. The corresponding doped alloy model was obtained, as shown in Fig. 1 [Figure 1: see original paper], and geometric optimization was performed. Based on the calculated crystal structure, a seven-layer slab ZrV_2 surface model was built, separated by a 15 Å vacuum layer, and the lower four layers of the surface were fixed. According to a previous study, the following low-index stoichiometric specific surfaces were selected for cutting from a geometrically optimized bulk: (1) the Zr termination of the $ZrV_2(100)$ surface and (2) the V termination of the $ZrV_2(100)$ surface. The k-point meshes were $(12 \times 12 \times 12)$ and $(5 \times 5 \times 5)$ for the bulk and surface models, respectively. Unit-cell parameters and ion relaxation were allowed during optimization. Based on convergence tests, the energy cutoff was set to

520 eV, the energy convergence standard was 10^{-5} eV, and the force convergence standard was 0.02 eV/Å.

Fig. 1 Schematic of the bulk phase model of the Zr–V–M system: (a) ZrV_2, (b) A-site substitution (ZrVHf), (c) B-site substitution (ZrVPd)

For the optimized results, taking ZrV_2 as an example, the surface energy used to compare the stability of each low-index surface is defined as [**?**]:

$$\gamma = \frac{E_{\text{slab}} - N \cdot E_{\text{bulk}}}{2A}$$

where γ (J/m^2) is the surface energy, E_{slab} (eV) is the total energy of the optimized slab, A (Å^2) is the surface area, N is the number of atoms in the surface model, and E_{bulk} is the total energy per atom of bulk ZrV_2.

The change in surface energy before and after doping is used to reflect the stability of the doped surface. The doping energy is defined as:

$$E_{\text{doping}} = E_{\text{substituted\_slab}} - E_{\text{slab}} + \sum_i \Delta N_i \cdot E_i$$

where $E_{\text{substituted\_slab}}$ is the energy of the doped surface model, ΔN_i represents the change in the number of component i (e.g., when the A site is replaced, the Zr atom decreases and the dopant atom increases), and E_i is the corresponding bulk energy per atom of component i.

Based on the surface-optimization results, the surface with the lowest energy (the most stable surface) was selected for subsequent adsorption studies. The surface of ZrV_2 includes many O atomic adsorption sites. For the Zr termination of the ZrV_2(100) surface ((100)-Zr), there are four highly symmetrical adsorption sites: top, bridge, hollow3, and hollow4. For the V termination of the ZrV_2(100) surface (defined as (100)-V), there are two bridge sites (defined as bridge1 and bridge2) and two top sites (defined as top1 and top2), as shown in Fig. 2 [Figure 2: see original paper]. Adsorption energies are calculated as follows:

$$E_{\text{ads}} = E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate}}$$

where E_{ads} is the adsorption energy, and $E_{\text{slab+adsorbate}}$, E_{slab}, and $E_{\text{adsorbate}}$ are the energies of oxygen on the ZrV_2(100) surface, the ZrV_2(100) surface alone, and the isolated adsorbed oxygen atom, respectively.

Fig. 2 Surface adsorption sites of ZrV_2: (a) Zr-(100), (b) V-(100)

The differential charge density reflects the flow of electrons before and after the formation of the surface structure, which is the difference between the charge densities before and after bonding. In this study, the differential charge is defined as:

$$\Delta\rho = \rho_{\text{slab+adsorbate}} - \rho_{\text{slab}} - \rho_{\text{adsorbate}}$$

where $\rho_{\text{slab+adsorbate}}$ represents the surface after oxygen adsorption, ρ_{slab} represents the unadsorbed pure surface, and $\rho_{\text{adsorbate}}$ represents the isolated adsorbed atoms.

3 Experimental Methods

3.1 Material Preparation

The Zr–V-doped alloys were prepared using vacuum arc melting with the following compositions: ZrV_2, $ZrV_{1\cdot 8}Pd_{0\cdot 2}$, and $Zr_{0\cdot 9}Hf_{0\cdot 1}V_2$. The purity of the raw materials exceeded 99.9%. The alloys were placed in a DHL-400 arc-melting furnace (Shenyang Scientific Instrument Co., Ltd., Chinese Academy of Sciences, China). Each ingot was remelted seven times under the protection of purified argon gas. The alloy ingots were furnace-cooled to 25 °C to obtain as-cast ingots. To obtain alloys with uniform phase structure, the vacuum-encapsulated samples were heated to 1273 K for 168 h in a muffle furnace and then cooled to room temperature to obtain annealed alloys.

3.2 Structure Characterization

The alloy phase compositions and lattice parameters were determined using X-ray diffraction. The X-ray patterns were collected between diffraction angles of 10°–90° (2) in step-scanning mode (step width 0.03°, counting time 0.5 s). The phase distribution was observed using a scanning electron microscope (LEO 1530vp) in backscattered electron imaging mode.

3.3 Hydrogen-Absorption Kinetics of Poisoned Alloys

In this study, poisoning experiments on ZrV_2, $ZrV_{1\cdot 8}Pd_{0\cdot 2}$, and $Zr_{0\cdot 9}Hf_{0\cdot 1}V_2$ alloys were carried out using a comprehensive test device designed and constructed in our laboratory for low-pressure hydrogen-storage performance evaluation. The amount of hydrogen absorbed by the alloys was determined using the volumetric method [**?**]. First, approximately 1 g of bulk sample was selected for testing, and the oxide layer on the surface was removed with 300-mesh sandpaper. Before testing, each sample was activated by heating the sample chamber to 500 °C and evacuating for 2 h. Then, the samples were cooled to 350 °C to continue the activation process. The hydrogen absorption process was repeated until the kinetic curves coincided, indicating that the samples were fully activated. Fully activated samples were then exposed to a hydrogen–oxygen mixture containing 0.5 vol% O_2 at room temperature. The pressure decrease was measured as a function of time and translated into hydrogen absorption capacity, which was expressed as weight percentage (wt.% H).

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4 Results and Discussion

4.1 Oxygen Adsorption Behavior

The two low-index surfaces of ZrV_2 were optimized. According to Eq. (1), the surface energy of (100)-Zr is 2.11 J/m^2, and the surface energy of (100)-V is also 2.11 J/m^2. The two low-index surfaces of ZrV_2 are shown in Fig. 3 [Figure 3: see original paper]. The similar surface energies indicate that different termination surfaces do not significantly affect surface stability. Based on these results, several changes were made to the surface models for element doping. First, the doping element replaces either the A or B site. Second, the relative position of the substituted element in the (100)-V and (100)-Zr planes was chosen to place the doping atoms as close to the outermost layer as possible. Table 1 lists the only few stable configurations after optimization among all combinations (Fig. 4 [Figure 4: see original paper]): Hf substituting for Zr in the first layer of the Zr termination of the ZrV_2(100) surface model (defined as ZrVHf-100Zr1-A); Pd substituting for V in the first layer of the V termination of the ZrV_2(100) surface model (defined as ZrVPd-100V1-B); and Ti substituting for Zr in the first layer of the Zr termination of the ZrV_2(100) surface model (defined as ZrVTi-100Zr1-A).

Fig. 3 Two low-index surfaces of ZrV_2: (a) the (100)-Zr model, (b) the (100)-V model

Fig. 4 Several doped surface models that remain stable: (a) ZrVHf-100Zr1-A, (b) ZrVPd-100V1-B, (c) ZrVTi-100Zr1-A

Table 1 Surface energy and doping energy for each type of doped surface

Surface type	Surface energy γ (J/m^2)	Doping energy E (eV)
ZrVHf-100Zr1-A		
ZrVPd-100V1-B		
ZrVTi-100Zr1-A		

The results show that the doping energies of ZrVPd-100V1-B, ZrVTi-100Zr1-A, and ZrVHf-100Zr1-A are negative. The system energy decreases due to doping, indicating that the formation of these three structures is most favorable. Pd, Ti, and Hf tend to segregate at the surface, which may affect anti-poisoning behavior.

Based on the surface-optimization results, the adsorption behaviors of the most likely formed Ti-, Hf-, and Pd-doped surfaces were studied. First, the possible adsorption configurations were clarified. The adsorption energies at each highly symmetrical adsorption site on the Zr and V terminations of the ZrV_2(100) surface are listed in Table 2 . Among the various sites, the hollow4 site on (100)-Zr is an unstable adsorption site, whereas the bridge site on (100)-Zr and the bridge2 site on (100)-V are the most stable adsorption sites on the surface. Therefore, oxygen atoms on the surface of the poisoned alloy tend to adsorb at these two sites; they were selected as reference sites for evaluating changes in adsorption energy before and after doping.

Table 2 Adsorption energy of oxygen atoms at different sites on different surfaces of ZrV_2

(100)-Zr		(100)-V	
Adsorption site	Adsorption energy (eV)	Adsorption site	Adsorption energy (eV)
bridge		bridge1	
hollow3		bridge2	
hollow4			

Table 3 shows that when Ti is doped on the ZrV_2 surface, the adsorption energy of oxygen atoms changes from -8.68 eV to -7.7 eV. Therefore, Ti has almost no inhibitory effect on the adsorption energy of oxygen atoms. When Hf is doped on the ZrV_2 surface, the adsorption energy of oxygen atoms changes from -8.56 eV to -1.1 eV. After Pd doping, oxygen atoms cannot be adsorbed on the surface. In particular, the Pd atom located in the first layer of (100)-V destroys one of the two bridge2 adsorption sites close to it, so oxygen atoms can no longer bind there. The oxygen atoms can only adsorb at the remaining bridge2 site or at the more unstable top sites, thereby significantly weakening both the maximum oxygen coverage and the average oxygen atom binding energy.

Table 3 The most stable oxygen atom adsorption energy for each doped surface

Surface types	Adsorption energy (eV)	Adsorption energy difference before and after adsorption (eV)
ZrVHf-100Zr1-A		
ZrVPd-100V1-B	Unable to adsorb	
ZrVTi-100Zr1-A		

The effect of Pd on each adsorption site was studied for the Pd-doped group that exhibited the best anti-poisoning potential. The ZrVPd-100V1-B surface lost its original symmetry due to the introduction of Pd, resulting in new adsorption sites (Fig. 5 [Figure 5: see original paper]). Table 4 lists the adsorption status of all sites on the Pd-doped surface. The results show that Pd segregation to the first layer of the V termination of the $ZrV_2(100)$ surface cancels or weakens the adsorption stability of most bridge sites. This forces oxygen atoms to migrate to more unstable top sites, indicating that Pd has superior anti-poisoning properties.

Fig. 5 Adsorption sites on the ZrVPd-100V1-B surface

Table 4 Oxygen atom adsorption energy at each site on the two doped surfaces of Pd

ZrVPd-100V1-B site	Adsorption energy (eV)	Adsorption energy increments (eV)
top1.1		
top1.2		
top2.1		
top2.2		
bridge1		
bridge2.1		
bridge2.2		

The effects of adsorption and doping on the bond lengths of the system were investigated. First, bridge-site adsorption was examined on the two low-index undoped surfaces. Figs. 6(a) and (b) show O atoms adsorbed on the $ZrV_2(100)$ surface. The adsorbed O atoms (marked by red spheres) have a clear tendency to approach V atoms to form strong bonds. Even for the Zr termination of the $ZrV_2(100)$ surface, V atoms located in the second layer attract surface oxygen atoms inward to form bonds. It can be inferred that V atoms have better oxygen affinity than Zr atoms. Second, for the case of Ti and Hf (A-site) doping, Figs. 6(c) and (d) show that the O–V distance elongates from 2.0 Å to 3.0 Å for Ti doping and from 2.0 Å to 3.33 Å for Hf doping. Compared with Ti, the displacement of the oxygen atom is more pronounced, and the lattice distortion is greater under Hf doping, which breaks the high-symmetry binding site of the O atom and forces it to shift to a more unstable position. Finally, for the case of Pd (B-site) doping, Fig. 6(e) shows that the O–V distance is 1.88 Å before doping and 2.12 Å after doping, indicating that the O atom is weakly adsorbed and easily desorbed under external influence.

Fig. 6 Optimized structures of oxygen adsorption on pristine surfaces: (a) Bridge site of (100)-Zr, (b) Bridge1 site of (100)-V, (c) Bridge site of ZrVTi-100Zr1-A, (d) Bridge site of ZrVHf-100Zr1-A, (e) Bridge1 site of ZrVPd-100V1-B

4.2 Differential Charge Density and Density of States

In the previous section, the ZrVHf and ZrVPd alloys were determined to have the best anti-poisoning effects through analysis of oxygen atom adsorption behavior. Gaining a deep understanding of oxygen adsorption on ZrVHf and ZrVPd alloy surfaces is necessary from an atomic perspective. Therefore, we calculated the differential charge density and density of states (DOS).

The DOS and differential charge density can help us better understand the bonding characteristics between atoms and the difficulty of electron gain and loss between O atoms and doped surface structures. Fig. 7 [Figure 7: see original paper] shows the charge transfer at the Zr/V termination of the $ZrV_2(100)$ surface and the corresponding modified surface before and after adsorption. The green area in the figure indicates charge loss, whereas the red area indicates charge gain. After oxygen adsorption, oxygen atoms tend to gain electrons, and the overlap of electron clouds and electron gain/loss between V–O is more evident than that of Zr–O. Stronger covalent bonds can be formed between V–O, and the bond lengths are shorter compared to those of Zr–O. After elemental substitution, gaps appeared in both the electron gain and loss structures of the doped surface compared to those of the original surface. The decreased ability of doped atoms to lose electrons, as well as weaker interactions with oxygen atoms, leads to a decrease in oxygen atom binding.

Fig. 7 Differential charge density diagrams for each surface: (a) top view of Zr termination of $ZrV_2(100)$ surface model; (b) side view of Zr termination of $ZrV_2(100)$ surface model; (c) top view of Hf-doped $ZrV_2(100)$ surface model; (d) side view of Hf-doped $ZrV_2(100)$ surface model; (e) top view of V termination of $ZrV_2(100)$ surface model; (f) side view of V termination of $ZrV_2(100)$ surface model; (g) top view of Pd-doped $ZrV_2(100)$ surface model; (h) side view of Pd-doped $ZrV_2(100)$ surface model

The DOS is a key parameter for studying atomic bonding and material properties [?]. The bonding properties can be clearly described by the energy-level distribution of electrons. As shown in Fig. 8 [Figure 8: see original paper], the Fermi-energy level is automatically normalized to 0 eV using the software and is marked with a dotted line in the figure. For the Zr termination of the $ZrV_2(100)$ surface in Fig. 8(a), strong orbital hybridization can be observed between the p orbital of the Zr atom in the first layer and the d orbital of the V atom in the second layer at approximately -1.6 eV. After A-site substitution by Hf in Fig. 8(c), the interaction between Zr and V weakens. The Hf atom p orbital hybridizes with the Zr and V atom d orbitals at -1.1 eV. When an O atom is adsorbed on the Hf-doped surface, the electron energy decreases (-3 eV to 0 eV). The interaction between the O atom and surface atoms disappears; thus, chemisorption changes to physical adsorption. The presence of Hf destroys the stable adsorption sites of the O atoms owing to obvious distortion of the surface structure after adsorption.

The electron energy distribution pattern is different for the V termination of the

$ZrV_2(100)$ surface. There is orbital hybridization between the V atom s orbital in the first layer and the Zr atom p orbital in the second layer in the range of -1.5 eV to -1 eV, which is minimized after Pd doping.

According to the above analysis, almost no hybridization orbitals exist between the doped surface atoms and oxygen atoms, which also indicates that doping with Hf and Pd weakens the adsorption effect of oxygen.

Fig. 8 Partial density of states (PDOS) profiles for each surface: (a) Zr termination of $ZrV_2(100)$ surface; (b) Zr termination of $ZrV_2(100)$ surface after oxygen atom adsorption at the bridge site; (c) ZrVHf-100Zr1-A; (d) ZrVHf-100Zr1-A after oxygen atom adsorption at the bridge site; (e) V termination of $ZrV_2(100)$ surface; (f) V termination of $ZrV_2(100)$ surface after oxygen atom adsorption at the bridge site; (g) ZrVPd-100V1-B; (h) ZrVPd-100V1-B after oxygen atom adsorption at the bridge site

4.3 Phase Composition and Microstructure

After homogenization annealing treatment, the Zr–V–M (M = Hf, Pd) series alloys were characterized using X-ray diffraction and scanning electron microscopy. The XRD results are shown in Fig. 9 [Figure 9: see original paper]. All alloys are primarily composed of ZrV_2 and Zr_3V_3O phases. The Zr_3V_3O phase arises from marginal oxidation of the raw material during the annealing treatment, which is similar to results from previous studies [**?**, **?**]. The addition of Hf does not introduce a new phase into the alloy but forms a solid solution. However, particular amounts of Zr_2Pd and Pd_3V phases are observed in the Pd-containing samples. This is determined by the poor solid-solution properties of the Zr–Pd–V system itself, which is consistent with previous reports [**?**]. The difference in the XRD results is mainly related to the solubility of the doped elements relative to Zr or V. Hf can combine with V over a wide range to form HfV_2 belonging to the C15 Laves phase, which remains in the ZrV_2 lattice without precipitation. Pd combines with Zr and V to form PdV_3 with a Pm-3m structure and Zr_2Pd with an I4/mmm structure, respectively, which are not miscible with ZrV_2. No solidification segregation phases were visible in the three alloy samples. The samples did not contain the C14 or C36 Laves phases, thereby indicating good phase uniformity.

Fig. 9 XRD pattern of Zr–V–M (M = Hf, Pd) system alloys

Fig. 10 [Figure 10: see original paper] shows the SEM backscattered electron images of the Zr–V–M (M = Hf, Pd) series alloys. Based on the principle of backscattered imaging, the dark gray areas correspond to the ZrV_2 phase, the white areas to the Zr phase, and the small black areas to the V phase. The energy dispersive spectrometer mapping of the Zr–V–M (M = Hf, Pd) series alloys is shown in Fig. 11 [Figure 11: see original paper]. The results illustrate that Zr, V, Hf, and Pd are uniformly distributed in the selected region of the alloy sample. The characterization results showed that the 1000 °C vacuum heat treatment considerably improved the homogeneity of the alloys, second-phase segregation was weakened, and the doped elements were well incorporated into the matrix.

Fig. 10 SEM backscattered electron images of Zr–V–M (M = Hf, Pd) alloys: (a) ZrV_2 alloy, (b) $ZrV_{1\cdot 8}Pd_{0\cdot 2}$ alloy, (c) $Zr_{0\cdot 9}Hf_{0\cdot 1}V_2$ alloy

Fig. 11 EDS mapping of Zr–V–M (M = Hf, Pd) alloys: (a) ZrV_2 alloy, (b) $ZrV_{1\cdot 8}Pd_{0\cdot 2}$ alloy, (c) $Zr_{0\cdot 9}Hf_{0\cdot 1}V_2$ alloy

4.4 Hydrogenation Properties of the Poisoned Zr–V–M (M = Hf, Pd) Alloys

Zhang et al. [**?**] showed that the hydrogen-absorption ability of $Zr_{0\cdot 9}Ti_{0\cdot 1}V_2$ alloy is minimized when exposed to oxygen, and after regeneration, the oxygen-poisoned $Zr_{0\cdot 9}Ti_{0\cdot 1}V_2$ sample hardly absorbs hydrogen. Therefore, the main simulation results were confirmed by studying the hydrogen-absorption kinetic behaviors of ZrV_2, $Zr_{0\cdot 9}Hf_{0\cdot 1}V_2$, and $ZrV_{1\cdot 8}Pd_{0\cdot 2}$ alloys in a hydrogen–oxygen mixture containing 0.5 vol% O_2 at room temperature. Fig. 12 [Figure 12: see original paper] shows the kinetic curves of the two doped alloys and the ZrV_2 alloy at room temperature. The vertical axis of the curve represents the ratio of the hydrogen absorption H/M after poisoning to the last pure hydrogen absorption H/M before poisoning. The degree of degradation in hydrogen-storage capacity after poisoning differs among the three cases: ZrV_2 retained only 19% of the original capacity, $Zr_{0\cdot 9}Hf_{0\cdot 1}V_2$ retained 69% of the original hydrogen absorption, and $ZrV_{1\cdot 8}Pd_{0\cdot 2}$ retained 80% of the original capacity, which is consistent with the first-principles calculations. Pd maintains the original hydrogen-absorption performance to a greater extent than the Hf-doped and undoped surfaces and exhibits the strongest resistance to poisoning. Table 4 indicates that Pd doping boosts the adsorption energy at five of the seven oxygen atom adsorption sites, and it optimizes the hydrogen absorption after poisoning to a theoretical value of 71%, which is close to the experimental result of 76%. The introduction of Pd and Hf destabilizes the stable oxygen atom adsorption sites, hinders stable O–V bonding, and enhances the total energy of the system, thereby optimizing the anti-poisoning properties relative to the ZrV_2 alloy.

Fig. 12 Hydrogen-absorption kinetics in hydrogen–oxygen mixtures of Zr–V–M (M = Hf, Pd) alloys in 0.5 vol% O_2 at room temperature: (a) ZrV_2 alloy, (b) ZrVHf alloy, (c) ZrVPd alloy

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5 Conclusions

In conclusion, this study investigated the effect of doping elements Hf, Pd, and Ti on the anti-poisoning properties of ZrV_2 alloy using first-principles calculations and experiments. The adsorption behavior was investigated on the most stable (100) surface of ZrV_2 using first-principles calculations, which revealed that the preferential adsorption sites for oxygen atoms are bridge sites. The adsorption behavior of oxygen atoms on the bridge sites of the three doped surfaces was studied. The results indicated that the Pd-doped ZrV_2 alloy surface could not adsorb O_2, and the Hf-doped surface had an adsorption energy of -1.10 eV; thus, Pd exhibited excellent anti-poisoning effects, and Hf was second best. Analysis of the differential charge density and DOS showed that the interaction of the Pd- and Hf-doped atoms with oxygen atoms was reduced, which led to a decrease in the binding force of the oxygen atoms. Based on the first-principles calculations, the kinetic behavior of hydrogen absorption for ZrV_2, $Zr_{0\cdot9}Hf_{0\cdot1}V_2$, and $ZrV_{1\cdot8}Pd_{0\cdot2}$ was studied in a hydrogen–oxygen mixture containing 0.5 vol% O_2 at room temperature. The poisoning experiments showed that the hydrogen-absorption capacities of ZrV_2, $Zr_{0\cdot9}Hf_{0\cdot1}V_2$, and $ZrV_{1\cdot8}Pd_{0\cdot2}$ decreased to 19%, 69%, and 80% of their original values, respectively.

CRediT Authorship Contribution Statement

Shuang Yang: Conceptualization, Methodology, Investigation, Writing – original draft.
Runjie Fang: Conceptualization, Methodology, Writing – review and editing.
Guo Yang: Conceptualization, Methodology, Writing – review and editing, Supervision, Funding acquisition.
Lijun Lv: Writing – review and editing, Supervision, Software.
Xingbo Han: Conceptualization, Methodology, Writing – review and editing, Supervision, Funding acquisition, Software.
Wei Liu: Writing – review and editing, Supervision.
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Pengfei Zhu: Writing – review and editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that may have influenced the work reported in this study.

Acknowledgments

We gratefully acknowledge financial support from the Youth Innovation Promotion Association, Chinese Academy of Science (Grant No. 2019263) and the National Natural Science Foundation of China (No. 12105355).

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