First-Principles Study of the Effect of Titanium Doping on Carbon Monoxide Poisoning Properties of Zirconium-Cobalt Alloys

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Abstract: It is very important to study impurity gas poisoning in ZrCo alloy because it is associated directly with the performance of ZrCo alloy as a hydrogen storage material. In this work, the effects of atomic replacement on the mechanism and properties of CO impurity gas poisoning in doped (Ti) ZrCo hydrogen storage alloys were investigated using the first principles method, based on the pseudopotential plane wave method. The adsorption energy, lattice constant, density of states, and charge density difference of the compounds before and after doping were calculated. Then, surface adsorption models of the ZrCo and Zr0.8Ti0.2Co alloys were established with the assistance of a conventional model. The resulting adsorption energy values of the clean surface and the surface adsorption energy values in the presence of CO impurity gases manifested that the Ti element-doped Zr0.8Ti0.2Co alloy was more susceptible to CO gas poisoning compared to ZrCo, which was consistent with the existing experimental results. In addition, by analyzing the conventional model, the electrons from the doped atoms overlapped with the surrounding electrons of C atoms, the phenomenon of orbital hybridization occurred, and the interactions increased. Consequently, Ti doping was not conducive to ZrCo to improve the ability to resist CO poisoning. The research results of this paper have laid a good foundation for the study of the effect of Ti doping on the antitoxicity performance.

Keywords: ZrCo alloy; elemental doping; CO poisoning; first principles

1. Introduction

Currently, solid hydrogen storage materials are the most widely used materials for storing hydrogen and its isotopes. Compared to gaseous and liquid storage materials, solid hydrogen storage materials offer better safety, higher reliability, and a lower cost [1–4]. Tritium is one of the most important isotopes of hydrogen and can be used as a fuel for fusion reactors. Uranium was once the preferred material for storing tritium due to its high hydrogen absorption capacity and low hydrogen absorption equilibrium pressure at room temperature. Unfortunately, uranium is a radioactive nuclear material, and it will react with hydrogen isotopes to produce high-energy hydride (tritium). In recent years, ZrCo alloy has become an important candidate material for the rapid storage and supplementation of hydrogen isotopes in the International Thermonuclear Experimental Reactor (ITER) due to its good safety and excellent hydrogen storage performance [5].

However, the further application of ZrCo alloys is restricted by its inherent properties, which are important for tritium-related systems such as ITER. The hydrogen-induced disproportionation effect under high-temperature hydrogen pressure (≥400 °C) or the hydrogen absorption and desorption cycle processes result in the significant attenuation
of hydrogen storage capacity [6]. Numerous studies have been conducted on improving the hydrogen storage performance of ZrCo alloys, and many useful results have been obtained [7–12]. For example, Zhang et al. [8] studied the effects of doping elements on the hydrogen storage performance of ZrCo alloys, and the results indicated that the disproportionation rates of ZrCo_{0.8}Fe_{0.2}, Zr_{0.8}Sc_{0.2}Co, and Zr_{0.8}Ti_{0.2}Co showed an upward trend. With the progression of hydrogen storage, the disproportionation rate decreased sharply, and only a few Zr_{0.8}Ti_{0.2}Co alloys showed disproportionation. In addition, the relationship between pressure and time is essentially linear. Kou et al. [9] studied the hydrogen storage properties of ZrCo, Zr_{0.8}Ti_{0.2}Co, and Zr_{0.8}Hf_{0.2}Co using a mental hydrogen storage bed. The pressure, hydrogen concentration, and temperature (PCT) curves showed that the hydrogen storage and disproportionation properties of ZrCo alloy were improved by Hf and Ti doping. Zhang et al. [8] characterized the phase structure of Ti doping on ZrCo alloy and its hydride by X-ray diffraction (XRD) and studied the near equilibrium hydrogen evolution process of the alloy and hydride by differential scanning calorimetry thermogravimetry (DSC-TG). The study found that Ti doping improved the resistance to hydrogen disproportionation and also speculated that Ti doping could change the gap size of the ZrCo alloy and the occupation proportion of hydrogen in the unstable occupied position in lattice, and could reduce the disproportionation driving force to improve the anti-disproportionation ability of the ZrCo alloy.

In magnetic confinement fusion reactor systems such as the ITER project, the deuterium tritium gas in the deuterium tritium fuel circulation system and the recovery system will inevitably contain impurity gases such as He, N\textsubscript{2}, O\textsubscript{2}, \textsubscript{Q}2, \textsubscript{Q}2, N\textsubscript{2}O, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, N\textsubscript{2}, and O\textsubscript{2} and the formation of a dense passivation layer has been shown to hinder the reaction between the hydrogen isotope and the ZrCo alloy, resulting in a significant decrease in the hydrogen absorption rate and hydrogen absorption capacity. Penzhon et al. [14] and Glasbrenner et al. [15] studied the hydrogen absorption properties of ZrCo alloys in impurity atmospheres such as CO, CO\textsubscript{2}, H\textsubscript{2}O, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, N\textsubscript{2}, and O\textsubscript{2} and studied the effects of impurity gases on the surface state of ZrCo alloys using XPS. Prigent et al. [16] compared the effect of CO as an impurity gas on the hydrogen absorption kinetics of Zr-based hydrogen storage alloys such as ZrCo, Zr-Ti-V, and Zr\textsubscript{2}Fe. Li et al. [17] compared the effects of trace element alloying modification and fluorination-electroless plating on the resistance of ZrCo for impurity gas poisoning. In an impurity atmosphere of 3.5% CO + 1% CH\textsubscript{4} + 0.2% CO\textsubscript{2} + 0.2% O\textsubscript{2} + H\textsubscript{2} (volume fraction), the order according to the hydrogen absorption rate followed ZrCo_{Mm0.04} fluorination electroless plating > ZrCo_{Mm0.04} > ZrCo. Guo et al. [18] prepared a Pd and Pd-Ag film-coated ZrCo alloy by electroless plating, which improved the anti-impurity gas poisoning performance of ZrCo alloy. Ti [8] and Hf [19,20] elements are being used to partially replace Zr. Since Zr and Ti are elements in the same main family, the Ti element is used as an additive for Zr-based materials. In addition, both experimental and theoretical studies have shown that Ti doping has a great influence on the storage capacity of hydrogen. However, there have been a few theoretical studies on the adsorption of ZrCo hydrogen storage alloys in an impurity-containing atmosphere and the effects of Ti doping on the properties of ZrCo alloys. Therefore, we choose the substitution structure for ZrCo with titanium.

Research on improving the hydrogen disproportionation effect has confirmed that Ti-doped ZrCo alloys can greatly improve the anhydrogen-induced disproportionation performance to reduce the hydrogen release temperature and improve the cycle life [21]. Significant research progress has been made on the gas poisoning of hydrogen storage alloys. However, there have been a few theoretical studies on the adsorption of ZrCo hydrogen storage alloys in an impurity-containing atmosphere and the effects of Ti doping on the properties of ZrCo alloys. Therefore, this study investigated the effects of impurity gases represented by CO on the adsorption behavior of Ti-doped ZrCo alloy surface for Ti-doped ZrCo alloys with excellent application potential in the field of tritium operations.
2. Computational Model and Methods

The first-principles calculation method based on the theory of quantum mechanics is a powerful tool to accurately obtain the electronic structure by directly solving the Schrödinger equation without relying on any empirical or semiepipirical parameters [22]. In this work, the total energy of the electronic structure was calculated using the Cambridge serial total energy package (CASTEP) [23] program based on the density functional theory (DFT). The ultrasoft pseudopotential (Ultrasoft) has been employed on the plane wave basis to describe the interaction potential between the ions and valence electrons, as it offers obvious advantages for solving the single electron Schrödinger (Kohn-Sham) equation and describing the interaction potential between electrons [24]. In addition, the exchange correlation function Perdew Burke Ernzerhof (GGA PBE) in the generalized gradient approximation has been used to describe the interactions between electrons. Through the optimization of the Broyden Fletcher Goldfarb Shanno (BFGS) algorithm, cell geometry with good stability can be obtained.

Before lattice optimization calculations, a convergence test for truncation energy value was carried out, and the test results are shown in Figure 1. We observed that the total energy of the system was stable after 360 eV. When the energy reached 400 eV, the total energy reached the lowest value, and the system was in a stable state. When the cut-off energy was increased again, the energy change of the system was less than 0.001 eV. Therefore, to balance the calculation accuracy and calculation speed, the truncation energy was selected as 400 eV. The 8 × 8 × 8 and 8 × 6 × 2 k-points were set for the ZrCo bulk and ZrCo surface. The structures were considered relaxed when the convergence criterion was smaller than 5 × 10^{-6} eV/atom, the forces between atoms were smaller than 0.01 eV/Å, the internal stress of the crystal was smaller than 0.02 GPa, and the maximum atomic displacement was smaller than 5 × 10^{-4} Å. Table 1 shows the relevant parameters involved in the calculations. Although DFT may incorrectly predict the adsorption site preference for CO on metals, due to underestimation of the energy of the CO orbital, it is still capable of describing the relative reactivity of various metal surfaces toward CO chemisorption [25]. Since one of the main concerns of this work was to study whether Ti doping is beneficial in resisting the adsorption of CO, any correction to the DFT-GGA results has not been applied in our paper [22].

![Figure 1. The cut-off energy of the plane wave convergence test.](image-url)
Table 1. Computational parameters for density functional theory (DFT) simulations.

<table>
<thead>
<tr>
<th>Cut-Off Energy (eV)</th>
<th>k-Points</th>
<th>Total Energy ($\times 10^{-6}$ eV/atom)</th>
<th>Lattice Stress (GPa)</th>
<th>Interaction between Atoms (eV/Å)</th>
<th>Maximum Atomic Displacement ($\times 10^{-4}$ Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>Fine</td>
<td>5</td>
<td>0.02</td>
<td>0.01</td>
<td>5</td>
</tr>
</tbody>
</table>

ZrCo is a hydrogen storage alloy with a typical CsCl type body centered cubic structure [26], a lattice constant of 3.196 Å, and where the spatial position of the Co atom is (0, 0, 0), the spatial position of the Zr atom is (0.5, 0.5, 0.5). By adjusting the proportion of Zr elements to 80% and Ti elements to 20%, element replacement could be realized to form a Zr$_{0.8}$Ti$_{0.2}$Co alloy (molar ratio) and establish a 2 × 2 × 2 supercell consisting of 16 atoms. First, the optimal structure of the unit cells in the ZrCo and Zr$_{0.8}$Ti$_{0.2}$Co alloys could be optimized according to the P6$_{3}$/m space group with the lowest symmetry and then cut to obtain ZrCo (110) and Zr$_{0.8}$Ti$_{0.2}$Co (110) surface structures. To ensure that there were no obvious interactions between the surfaces, the height of the vacuum layer was 10 Å. We calculated the surface energy. According to our calculations, the surface energy was 1.63 J m$^{-2}$ when using a four-layer slab. The surface energy was merely reduced by 0.94% when the slab thickness was from four to six layers, which suggests that the four ZrCo layers were good enough. In the calculations, the atomic co-ordinates were kept fixed, except for the surface layer, and the other atoms were allowed to relax. Additionally, the coverage of molecules was 6.9 molecules/nm$^2$. The model of ZrCo is shown in Figure 2.

![Figure 2](image-url)

**Figure 2.** Crystal structures of the (a) conventional model and (b) surface adsorption model.

3. Results and Discussion

3.1. Adsorption Energy, Final Adsorption Distance, and C-O Bond Length

To study the adsorption characteristics of the ZrCo and Zr$_{0.8}$Ti$_{0.2}$Co alloys under a CO atmosphere, the adsorption models of CO on the (110) surface of ZrCo and Zr$_{0.8}$Ti$_{0.2}$Co were established. Figure 3 shows and the adsorption model of the ZrCo and Zr$_{0.8}$Ti$_{0.2}$Co alloys. As shown in the figure, the CO molecule adsorbed at the bridge site between the atoms, and the CO molecule adsorbed vertically to the surface of the alloy.
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![Figure 3. Crystal structures: (a) clean model (b) CO adsorption model.](image)

The physical adsorption energy of CO on the alloy surface was calculated as follows:

\[
E_{\text{ads}} = E_{\text{sur} + \text{CO}} - E_{\text{sur}} + E_{\text{CO}}
\]

(1)

where \(E_{\text{sur}}\) is the total energy of the alloy surface unit cell before adsorption, \(E_{\text{sur} + \text{CO}}\) is the total energy of the supercell after CO adsorption on the alloy surface, and \(E_{\text{CO}}\) is the energy of CO molecule. When \(\Delta E_{\text{ads}}\) is negative, the larger the absolute value of adsorption energy, the stronger effect between adsorbates and adsorbents.

The initial distance between the main adsorption atoms of the CO molecule and the substrate was set to 2 Å. After structure optimization, the adsorption distance between substrate and CO molecule altered because of the adsorption effect. Additionally, the final adsorption distance refers to the nearest distance between an atom in the molecule and substrate. The smaller the final adsorption distance, the stronger the adsorption effect between the CO molecule and the substrate. The bond length of the adsorbed CO molecule was also calculated. The calculation results are shown in Table 2.

### Table 2. Adsorption energy, final adsorption distance, and C-O bond length.

<table>
<thead>
<tr>
<th>Model</th>
<th>(\Delta E_{\text{ads}}/\text{eV})</th>
<th>Distance/Å</th>
<th>Bond Length/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO on ZrCo (110)</td>
<td>-1.031</td>
<td>1.863</td>
<td>1.169</td>
</tr>
<tr>
<td>CO on Zr(<em>{0.8})Ti(</em>{0.2})Co (110)</td>
<td>-1.662</td>
<td>1.744</td>
<td>1.173</td>
</tr>
</tbody>
</table>

According to the total energy results of the different systems, the adsorption energy \(E_{\text{ads}}\) of ZrCo (110) was \(-1.031\) eV, and the adsorption energy \(E_{\text{ads}}\) of Zr\(_{0.8}\)Ti\(_{0.2}\)Co (110) was \(-1.662\) eV. The adsorption energy value reflected the ease of adsorption of CO on the different alloy structure surfaces. We found that the adsorption energy on the Zr\(_{0.8}\)Ti\(_{0.2}\)Co (110) surface was greater than on ZrCo (110), and the final adsorption distance on the Zr\(_{0.8}\)Ti\(_{0.2}\)Co (110) surface was smaller than on ZrCo (110), which indicated that the Zr\(_{0.8}\)Ti\(_{0.2}\)Co alloy was more susceptible to CO poisoning in an atmosphere where CO was the main impurity gas, which was consistent with the experimental results of Zhang et al. [13]. This was the same as the result for Ti-doped graphene sheets [27].
Comparing the value of bond length, it revealed that doping a Ti atom could elongate the C-O bond length of a CO molecule. We found that the C-O bond length was 1.169 Å on the ZrCo (110). The bond length increased to 1.173 Å on the Zr_{0.8}Ti_{0.2}Co (110). Therefore, although doping Ti could certainly enhance the adsorption of a CO molecule, it would slightly weaken the bond strength of the CO molecule.

3.2. Crystal Structure

Before calculating the electronic structure properties of the alloy crystal, the crystal structure had to be optimized, and the unit cell parameters after crystal structure optimization are shown in Table 3. The optimized equilibrium lattice constant of the ZrCo alloy was 3.181 Å, and the unit cell volume was 32.19 Å³, which was consistent with the experimental results [28], indicating that the set parameters were reasonable and reliable. After element replacement, the volume of the system changed due to the changes in the atomic radii of the replacement elements. Because Ti had a smaller atomic radius than Zr, the equilibrium lattice constant became smaller, and the unit cell volume shrank after the replacement of the Ti elements.

**Table 3.** Structural optimization data of ZrCo and Zr_{0.8}Ti_{0.2}Co alloys.

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice Constant (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrCo</td>
<td>3.181</td>
<td>32.19</td>
</tr>
<tr>
<td>Zr_{0.8}Ti_{0.2}Co</td>
<td>3.147</td>
<td>31.17</td>
</tr>
</tbody>
</table>

By analyzing the conventional model, the stable crystal structure and formation energy of the alloy were calculated. The cohesive energy of a crystal can reflect the stability of a crystal structure, and it can be calculated as follows:

\[ E_{coh}(Zr_aTi_bCo_c) = \frac{1}{a+b+c}(E_{tot}(Zr_aTi_bCo_c) - aE_{Zr} - bE_{Ti} - cE_{Co}) \]  

(2)

where \( E_{coh}(Zr_aX_bCo_c) \) represents the cohesive energy of the system, \( E_{tot} \) represents the total energy of the system, and \( E_{Zr}, E_{Co}, \) and \( E_{Ti} \) represent the free atomic energies of single Zr, Co, and Ti atoms, respectively.

The cohesive energies of the ZrCo and Zr_{0.8}Ti_{0.2}Co alloys are shown in Table 4. According to the table, the cohesive energy values of the various crystals were negative, and the cohesive energy of the system after Ti doping was very close to that of the ZrCo alloy, indicating that the Zr_{0.8}Ti_{0.2}Co alloy structure was very stable. These results were consistent with the results of Wang [29].

**Table 4.** Calculated cohesive energy of ZrCo and Zr_{0.8}Ti_{0.2}Co alloy.

<table>
<thead>
<tr>
<th>System</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrCo</td>
<td>−7.418</td>
</tr>
<tr>
<td>Zr_{0.8}Ti_{0.2}Co</td>
<td>−7.376</td>
</tr>
</tbody>
</table>

3.3. Density of States

The density of states (DOS) is an indicator of the possible electron states between the unit energy and the number of quantum states and is a key parameter for studying atomic bonding and material properties [6]. To understand the effects of Ti replacement on the ZrCo alloy, we calculated the density of states of the ZrCo and Zr_{0.8}Ti_{0.2}Co alloys, as shown in Figure 4.
Figure 4. PDOS of C and Zr atom with CO adsorbed on (a) ZrCo (110) and (b) Zr_{0.8}Ti_{0.2}Co (110).

The figure shows the PDOS of C and a Zr and a Ti atom with CO adsorbed on ZrCo (110) and Zr_{0.8}Ti_{0.2}Co (110). There was a strong orbital hybridization between the s orbital of C and the s orbital of Zr and Ti in the range of $-25$ to $23$ eV and $-10$ to $8$ eV. From the $-25$ to $23$ eV and $-10$ to $8$ eV energy range, the hybridization was mainly contributed to from the s orbital of C and the p orbital of Zr and Ti. There were obvious resonance peaks between the p orbital of C and the p orbital of Zr and Ti in the range of $-25$ to $23$ eV, $-10$ to $8$ eV, and $-7$ to $5$eV. For the ZrCo (110), there were almost no hybrid orbitals between C and Zr. This also showed that Ti doping enhanced the adsorption effect of CO, which indicated that the Zr_{0.8}Ti_{0.2}Co alloy was more susceptible to CO poisoning in an atmosphere where CO was the main impurity gas. This was in line with the previous results [30].

3.4. Charge Density Difference

In addition, the charge density difference was calculated. The charge densities of the ZrCo and Zr_{0.8}Ti_{0.2}Co alloys are shown in Figure 5. As shown in Figure 5, the charge density distribution of CO on the surfaces of ZrCo and Zr_{0.8}Ti_{0.2}Co (110) was relatively similar. In the Zr_{0.8}Ti_{0.2}Co alloy, the charge density around the Zr atoms was higher because 20% of the Zr atoms were replaced by Ti atoms, which indicated that the Ti atom had stronger charge interactions with the surrounding atoms. Furthermore, it exhibited a stronger interaction with the C atom, making it more likely to attract CO molecules to adsorb on its surface, which was not conducive to its antitoxicity performance.
1. The adsorption energy for CO gas on the surface of the Zr\(_{0.8}\)Ti\(_{0.2}\)Co alloy (110) after Ti doping was higher than that of the ZrCo alloy (110) surface, which indicated that the Zr\(_{0.8}\)Ti\(_{0.2}\)Co alloy would be more susceptible to CO impurity gas poisoning.

2. In the Zr\(_{0.8}\)Ti\(_{0.2}\)Co alloy (110) after Ti doping, there was orbital hybridization between the s and p orbital of C atom and the s and p orbital of Zr and Ti atom, which resulted in easier adsorption by CO.

3. Moreover, the charge transfer analysis showed that the bonding of the C atom with Zr and Ti atoms in the Ti-doped system was stronger than that of C and Zr atom bonding in the pure system. After Ti doping, the charge density around the Zr and Ti atoms was higher, which indicated that the Ti atom had stronger charge interactions with the surrounding atoms and was not conducive to its antitoxicity performance.

The details mentioned in the study provide fundamental insights into the poisoning mechanism of CO on the Ti-doped ZrCo (110) surface and should be useful in the design of hydrogen storage material based on ZrCo.

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