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Conference paper

First-principle study on the structural, electronic and mechanical properties of High Entropy Alloy TiZrFeRu for hydrogen storage applications

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ABSTRACT

High-entropy alloys are promising for hydrogen storage, especially in terms of their tunable hydrogen storage properties. Although several experimental studies, a fundamental and detailed atomistic comprehension of physical and electronic of the hydrogenation process is still lacking. This work investigated the structural, electronic and mechanical properties of TiZrFeRu high-entropy alloys (HEAs) using first-principle calculation. Indeed, we employed both density functional theory and density functional perturbation theory in the calculations with generalized gradient approximation and plane-waves pseudo-potential formalism. In addition, we used Virtual crystal approximation (VCA) to describe HEA as is well suited for predicting elastic properties. We have calculated relevant physical parameters, including lattice constants, elastic constants, elastic modulus, Poisson's ratio, Pugh's ratio, anisotropy factors and Vickers hardness..etc. Our calculated finding show that that TiZrFeRuH2 is mechanically stable and has a good ductility with a Pugh's ratio (B/G) greater than 1.75. Lastly, we investigated and discussed electronic bandstructure, the total and partial electronic density of state. The results indicate that this compound exhibit a metallic character concentrated in a zone between -5 and 5 eV. The value of the Poisson ration (0.35) confirm again that this compound is metallic (for metal materials the Poisson ratio is above 0.25).

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1. INTRODUCTION

The greenhouse effect is mainly caused by the emission of CO_2. Various green energies without CO_2 emissions (such as solar, wind and hydrogen) have been widely explored.

Among them, hydrogen (H_2) is the most abundant substance in terms of resource availability and thus considered a promising energy vector and a high-efficiency, emission-free fuel source. Due to its small and simple molecular size, the combustion of 1 kg of H_2 produces only water and about 120 MJ of energy, exceeding that of most conventional hydrocarbon fuels (Luo et al. 2024, Keith et al. 2024).

However, due to its low gas density the use of H_2 encounters many difficulties such as the storage in safe and efficient way especially on-board applications (Luo et al. 2024). In fact, Gaseous, liquid and solid-state storage systems are the three main hydrogen storage techniques available, chosen based on the corresponding storage size, application area and specific conditions. For mobile application, it seems that solid-state storage in the form of metal hydrides provides the most compact and safety technology with low cost and high storage capacity per volume and high absorption/desorption reversibility.

Among these metal hydrides, high entropy alloys (HEAs) emerge as a new road in order to improve of vehicular hydrogen storage (Keith et al. 2024). These alloys usually contain equal or more than five equimass or near equimass proportion element (Keith et al. 2024).

In recent years, more intention and various efforts have been made to develop HEAs for hydrogen storage (Luo et al. 2024, Keith et al. 2024, Edalati et al. 2020, Hu et al. 2021, Moore et al. 2022 and Zlotea et al. 2019). Indeed, Edalati et al. (Edalati et al. 2020) found that a novel HEA TiZrCrMnFeNi, capable (without activation treatment and in fast kinetics) of absorbing and desorbing 1.7 wt% hydrogen at 298 K.

Hu et al. (Hu et al. 2021) have studied TiZrVMoNb properties for hydrogen storage applications using DFT calculations. They found interesting results such as: the phase transformation (BCC to FCC) occurs at hydrogen content of 1.5 wt% and the hydrogen atoms prefer both octahedral and tetrahedral sites before and after phase transformation. They conclude by suggesting that this material can be very good candidate for hydrogen-solid-state-storage.

However, Moore et al. (Moore et al. 2022) have modelled the HEA TiZrNbHfTaH0.4- 2.0, using DFT and Special quasi-random structures (SQS). Indeed, they have examined the thermodynamics of vacancy formation, hydrogen accommodation and hydride decomposition. They have found interesting results confirming the experimental data and results of Zlotea et al. (Zlotea et al. 2019). Therefore, they proposed a model to predict the decomposition of the TiZrNbHfTaH system based on: i) hydrogen solution energies ii) vibrational entropy terms iii) the temperature dependence of configurational entropy.

Recently, Gong et al. (Gong et al. 2024) have investigated the absorption hydrogen aspect and mechanical properties of NbTiVZr HEA hydrides using electronic structure calculations. They have found that a phase transition occurs from BCC to FCC at 0.05 wt% of hydrogen content in HEA and the saturation of hydrogen storage capacity is predicted 2.94 wt%.

In this study, first-principles calculations within density functional theory (DFT) are employed to examine and the effect of the hydrogen absorption in high-entropy alloys hydride (HEAs). In fact, we study the structural, electronic and mechanical properties of TiZrFeRu using Virtual crystal approximation (VCA).

2. COMPUTATIONAL DETAILS

All calculations are performed using ABINIT code based on density functional theory (DFT) (Gonze et al. 2002). We used the generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) functional to describe exchange and correlation energy. Also, we used: conserved norm pseudopotential; 6 × 6 × 6 k-point grid in reciprocal space and 700 eV for energy cutoff. We have studied carefully the convergence of our computations to ensure the accuracy as we have done in our previous work (Bouhadda et al 2023).

We have used "virtual crystal approximation" (VCA) to describe and characterize the disordered solid solution of TiZrFeRu HEA.

Briefly, VCA replace the reel potential by a virtual one via the averaging the ionic potentials of atoms that alternate at the same position in the crystal structure. More detail can be found in (Wang et al. 2021).

3. RESULTS AND DISCUSSION

3.1 Crystal structure

We constructed and optimized the crystal structure of $TiZrFeRuH_2$ based on the structure of $TiFeH_2$. Indeed, $TiFeH_2$ crystallizes in the orthorhombic structure as shown below (Fig. 1) with the following lattice parameters:

a = 4.278, b = 2.905 and c = 4.558 A°

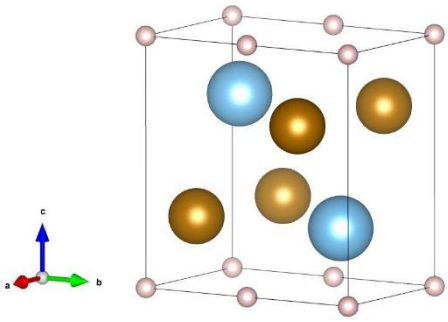

Fig. 1. Crystal structure of $TiZrFeRuH_2$

After a geometric optimization and relaxation of the interatomic forces to have equilibrium atomic positions, the calculated lattice parameters for $TiZrFeRuH_2$ are:

a = 3.902, b = 3.382 and c = 4.571 Angstrom. This crystallographic structure is stable in the orthorhombic structure.

3.2 Electronic properties of $TiZrFeRuH_2$ hydrides

We present in the following figure the total electronic density of state (DOS) of $TiZrFeRuH_2$ (Fig.2). It is clear that the DOS shows the behaviour of a metallic structure concentrated in a zone between -5 and 5 eV.

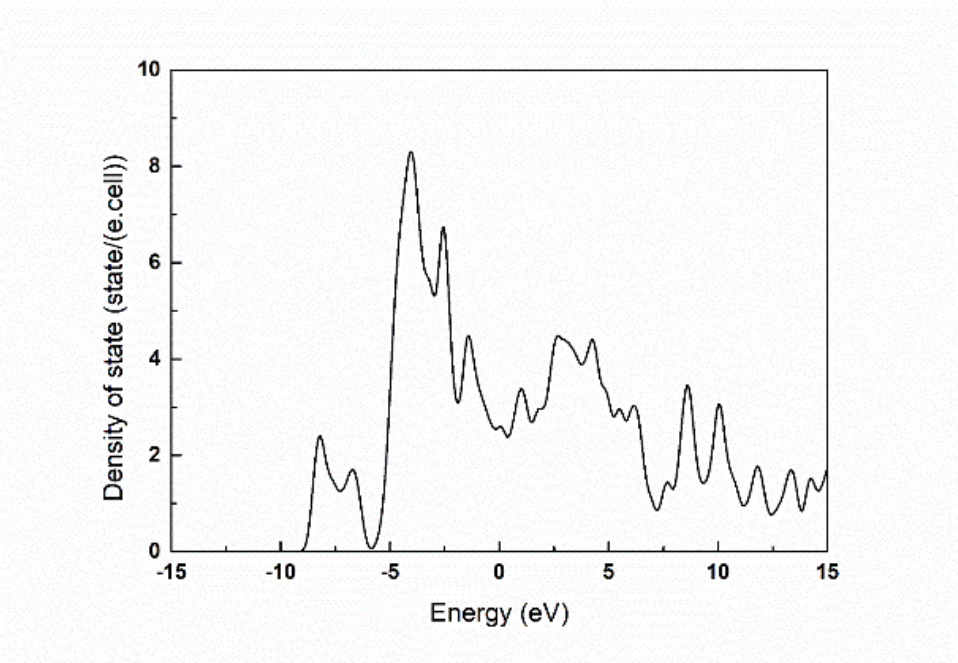

Fig. 2. Total electronic density of state of $TiZrFeRuH_2$.

Next, we represent in the below figure the structure of the electronic band structure of $TiZrFeRuH_2$ (Fig.3) along the special points in the reciprocal space Gamma, Z, T, Y, S, X, U and R respectively. The horizontal dashed line is the Fermi level (Fig.3).

The illustration once again shows the metallic nature of the compound. It should be noted that this behaviour is similar to the behaviour of the binary compound $TiFeH_2$.

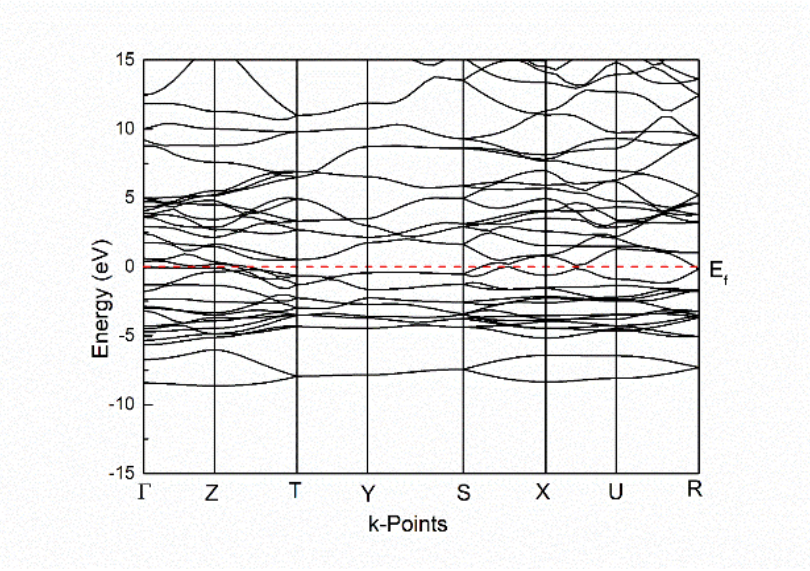

Fig. 3. Bandstructure of $TiZrFeRuH_2$.

3.3 Mechanical properties of $TiZrFeRuH_2$

In the following, we report the mechanical properties of $TiZrFeRuH_2$. Thus, the elastic constants C_{ij} (i,j=1.6) are:

Table 1. The theoretical elastic constants (GPa) of the TiZrFeRuH2

C11	C22	C33	C44	C55	C66	C12	C13	C23
333.92	370.56	314.86	37.28	164.69	54.41	180.09	225.09	168.167

We notice that the elastic constants meet the stability criteria of BORN. Then, the compound is mechanically stable.

Obviously, the values of C_{11}, C_{22} and C_{33} for $TiZrFeRuH_2$ are significantly higher than those of other elastic parameters, indicating strong uniaxial stress compressive strength in the [100], [010] directions. and [001], respectively.

We used these elastic constants to determine the elastic moduli such as B, G, Lame (λ), Young (E), the Poisson's ratio (ν), the elastic anisotropy A_U and Debye temperature T_d of TiZrFeRuH2. These parameters are listed in Table 2. Bulk modulus B and shear modulus G can be estimated using Voigt. - Reuss-Hill approach (VRH):

Table 2. Macroscopic moduli (Bulk B, shear G, Lame, young) and Poisson and Hardness (H) of $TiZrFeRuH_2$ estimated using Voigt, Reuss and Hill approaches

Elastic moduli	Voigt approach	Reuss approach	Hill approach
B (Bulk modulus) GPa	240.67	240.12	240.39
G (Shear modulus) GPa	81.01	61.30	71.15
Lame λ GPa	186.66	199.25	192.96
Young E (modulus) GPa	218.51	169.48	194.29
Poisson ν (ratio)	0.35	0.38	0.36
H Hardness	5.99	3.59	4.72

A_U : 1.61, T_d : 444.597 K

Here, the Bulk modulus B measures the resistance to volume change with invariable proportions, and the shear modulus G measures the resistance to shear deformation. Young E's modulus can be used to estimate the stiffness of materials.

The ductility of materials, which correlates with their reversible deformation in compression and their ability to fracture, is another important mechanical property. The ratio of bulk to shear modulus B/G is widely used to predict brittle-ductile behavior. Pugh proposed that ductile materials have a B/G ratio greater than 1.75. As our result, the B/G ratio for $TiZrFeRuH_2$ is well above the critical value of 1.75, suggesting that the hydride has good ductility. The value of the Poisson ration (0.35) confirm again that this compound is metallic (for metal materials the Poisson ratio is above 0.25).

4. CONCLUSION

In this paper, some hydrogen storage properties of HEA $TiZrFeRuH_2$ have been studied based on the first-principles calculations. The following conclusions were drawn:

1- The total electronic density of state (DOS) exhibited a metallic character of this compound.

2- The elastic constants are calculated and show that TiZrFeRuH2 is mechanically stable as the Born criteria was satisfied.

3- These constants indicate the existence of a strong uniaxial stress compressive strength in the [100], [010] directions. and [001], respectively.

4- The ratio of bulk to shear modulus B/G for is greater than 1.75, suggesting that the hydride has good ductility.

5- The value of the Poisson ration (0.35) confirm again that this compound is metallic.

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