Journal of Nuclear Materials 465 (2015) 254–259

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

# First-principles calculations of the interaction between hydrogen and 3d alloying atom in nickel

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ARTICLE INFO

*Article history:*
Received 29 December 2014
Received in revised form
25 May 2015
Accepted 1 June 2015
Available online 3 June 2015

*Keywords:*
Hydrogen
Transition metal
Nickel
First-principles

ABSTRACT

Knowledge of the behavior of hydrogen (H) in Ni-based alloy is essential for the prediction of Tritium behavior in Molten Salt Reactor. First-principles calculations were performed to investigate the interaction between H and 3d transition metal (TM) alloying atom in Ni-based alloy. H prefers the octahedral interstitial site to the tetrahedral interstitial site energetically. Most of the 3d TM elements (except Zn) attract H. The attraction to H in the Ni–TM–H system can be mainly attributed to the differences in electronegativity. With the large electronegativity, H and Ni gain electrons from the other TM elements, resulting in the enhanced Ni–H bonds which are the source of the attraction to H in the Ni–TM–H system. The obviously covalent-like Cr–H and Co–H bindings are also beneficial to the attraction to H. On the other hand, the repulsion to H in the Ni–Zn–H system is due to the stable electronic configuration of Zn. We mainly utilize the results calculated in 32-atom supercell which corresponds to the case of a relatively high concentration of hydrogen. Our results are in good agreement with the experimental ones.



## 1. Introduction

Molten Salt Reactor (MSR) is the only liquid-fueled reactor in the six most promising Generation IV concepts [1,2]. Hastelloy N, a Ni-based alloy, is the structural material for MSR with the excellent corrosion resistance against molten salts. Tritium (T), a radioactive isotope of hydrogen (H) and a precious resource for fusion reactor [3,4], can be generated in MSR mainly by neutron reactions with Li which is an important constituent of molten salt [5,6]. T release to the environment from MSR would occur because it can flow readily through the metal (i.e. Hastelloy N) walls of the various systems [7]. However, T must be prevented from escaping into the environment. Knowledge of the behavior of H in Ni-based alloy is essential for the prediction of T behavior in MSR, and can be used to guide the T control and management processes [8].

Furthermore, H in metal or alloy has obtained extensive research for many years. Hydrogen embrittlement [9,10] is a challenging phenomenon in almost all alloys, which can seriously influence the mechanical properties of these materials. On the other hand, hydrogen is a promising future energy source [11], and hydrogen storage alloys [12] will play an important role in the "hydrogen economy" [13]. In both cases, the interaction between H and alloying atom is an essential and fundamental subject, and it is of great importance to understand this interaction.

First-principles calculations are powerful tools to investigate H in metal or alloy at the atomic and electronic levels which determine the physical mechanisms fundamentally [14,15]. H on the Ni surface [16,17] and in Ni grain boundary [18,19], H diffusion in Ni [20], and the effect of H on vacancy in Ni [21–23] have been investigated by First-principles calculations. Nevertheless, almost all of these studies focus on H in pure Ni without any alloying atoms. The interaction between H and alloying atoms is more important from the view of practical application, and the alloying additives can modify H behavior in alloys.

Although first-principles calculations on the interactions between H and alloying atoms in Ni-based alloys are lacking, these interactions in Ti-based and Pb-based alloys have been investigated systematically [24,25]. Hu and his co-workers [24] investigated the interactions between 3d transition metal (TM) alloying atoms and H in Ti, and Li et al. [25] studied the interactions between 3d and 4d

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http://dx.doi.org/10.1016/j.jnucmat.2015.06.001
0022-3115/

TM alloying atoms and H in Pb. From these References, it can be concluded that the H–TM interaction can be attributed to two effects: the elastic mechanism and the "reverse stability" rule. If the binding of the TM and host atoms (e.g. Ti [24]) is weaker than the binding between host atoms, the TM–H interaction is dominated by the elastic mechanism: undersized TM atoms attract H atom and vice versa. If the binding of TM and host atoms (e.g. Pd [25]) is stronger than the binding between host atoms, the TM–H interaction is controlled by the "reverse stability" rule: the larger the binding energy of the TM atom in the matrix, the stronger the repulsion between TM and H atoms.

In this paper, we investigate the interaction between 3d TM alloying atoms and H in Ni systematically by means of first-principles calculations. In real material like Hastelloy N alloy, the existing forms of alloying atoms are complex. In this work, we simply model the 3d atoms as single solutes in a pure Ni matrix as performed in the previous studies [24,25].

## 2. Computational details

Spin-polarized electronic state calculations are performed within the density functional theory [26,27] using Vienna ab-initio simulation package (VASP) [28]. Electron-ion interactions are described by the projector-augmented plane-wave (PAW) method [29] and the wave functions are expanded in a plane-wave basis set with an cutoff energy of 400 eV. A generalized gradient approximation (GGA) [30] of the exchange correlation energy is employed. The Brillouin zone is sampled using a Monkhorst-Pack $7 \times 7 \times 7$ k-point mesh. The positions of the atoms in the Ni supercell are relaxed with tolerances of 0.01 eV/Å for the atomic force and $1 \times 10^{-5}$ eV/atom for the total energy.

A $2 \times 2 \times 2$ Ni supercell containing 32 Ni atoms is used for first-principles calculations. The calculated lattice parameter of pure Ni is 3.513 Å, which is in good accordance with the experimental value when extrapolated from room temperature to 0 K (3.517 Å) [20]. In the Ni–TM supercell, a Ni atom is replaced by a TM atom. In the Ni–TM–H supercell, a H atom is placed in the octahedral or tetrahedral interstitial site (O-site or T-site) nearest to the substitutional TM atom.

The TM–H interaction can be described with the interaction energy according to Refs.[24] and [25]. And the interaction energy, $\Delta E$, is calculated as follows:

$$\Delta E = [E(Ni, TM, H) + E(Ni)] - [E(Ni, TM) + E(Ni, H)] \quad (1)$$

where $E(Ni,TM,H)$, $E(Ni)$, $E(Ni,TM)$ and $E(Ni,H)$ refer to the calculated total energies of the Ni–TM–H supercell, the pure Ni supercell, the Ni–TM supercell and the supercell with a hydrogen atom in the interstitial site (O-site or T-site), respectively. A positive value of $\Delta E$ means the rejection to H in the Ni–TM–H system, and a negative value refers to the attraction to H. Energies of H vibrations are taken into account by computation of the zero point energy (ZPE). Temperature dependent entropic contributions are not taken into account. To a first-order approximation, only the H vibrations are calculated and the network vibrations are neglected [23]. As will be shown later, the results with the ZPE correction are compared with those without the ZPE correction.

The case in this manuscript refers to dilute concentration of the alloying elements. The effects of concentrations of the alloying elements will be addressed in our future works.

## 3. Results and discussion

### 3.1. Interaction energy

To identify which interstitial site H atom is preferred to occupy, the total energy of the Ni–TM–H supercell with a H atom in O-site or T-site is calculated and displayed in Fig. 1. The ZPE correction does not influence the change trend of calculated total energies. As can be seen in Fig. 1, it is clear that O-site is more energetically favorable for H than T-site in all of the Ni–TM–H supercells. Since T-site is much smaller than O-site, T-site is not large enough to accommodate the H atom without resulting in any lattice expansion. Further, as shown in Fig. 2, the Ni–TM bond lengths for Sc, Ti and Zn are obviously longer than that of the Ni–Ni bond due to the large atomic radius of these three elements. As a result, T-site is not stable for H in the cases of Sc, Ti and Zn, and the total energies of these cases are not plotted in Fig. 1. Thus, only the O-site is taken into account in the following sections. As shown in Fig. 2, the Ni–TM bond lengths for Cu and Mn are also longer than that of the Ni–Ni bond, but are shorter than those for Sc, Ti and Zn. Thus the volume effects for Cu and Mn are not so obvious as those for Sc, Ti and Zn, which makes T-site still stable for H atom in the cases of Cu and Mn.

The interaction energy between 3d TM and H in 32-atom supercell is demonstrated in Fig. 3. The interaction energies with and without the ZPE correction have the same change trend. A negative value denotes the attraction to H in the Ni–TM–H system. The curve of the interaction energy increases from Sc to V, and then decreases from V to Mn. After that, the curve oscillates slightly from Fe to Cu, and then suddenly increases in Zn. The interaction energy only for Zn is positive, with the value of about 0.09 eV, and those for the other TM atoms are all negative, indicating that H is repelled only by Zn in the Ni–TM–H system in 32-atom supercell.

In order to justify the use of the 32-atom supercell, the interaction energy in 108-atom supercell is also calculated and shown in

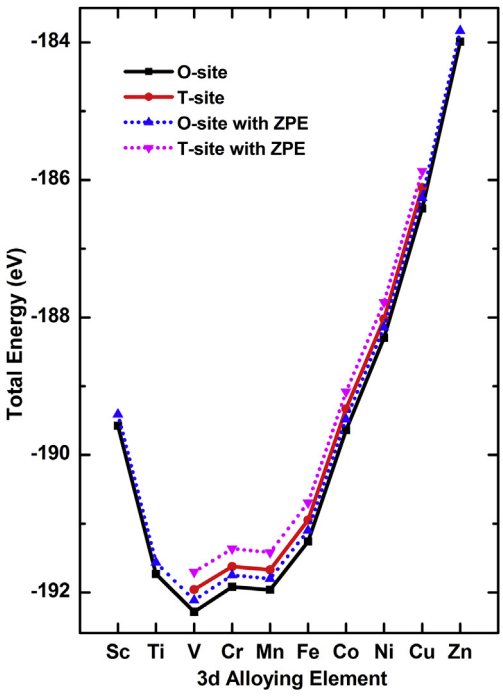


**Fig. 1.** Calculated total energy of the Ni–TM–H supercell with a H atom in the O-site or T-site with and without the ZPE correction.