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A theoretical study of the effects of *sp*-elements on hydrogen in nickel-based alloys

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ABSTRACT

By using first-principles calculations, we present a theoretical study of the interactions between hydrogen (H) and *sp*-elements from the 3rd, 4th and 5th period (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) in nickel-based alloy. The interactions between H and *sp*-atom are evaluated by the calculated interaction energy. Judged by the interaction energy, H is repelled by all these elements (except S) in nickel-based alloy. The atomic and electronic structures are analyzed. Especially, the interaction energy is found to be closely related with the electronic structure and electronegativity. The larger the electronegativity of the *sp*-elements, the weaker the H-*sp* bond. The weaker H-*sp* bond results in the more positive interaction energy and the repulsion to H. Particularly, for the cases of S and Se, the long H—S and H—Se distances can largely relieve the strain effect induced by the insertion of the H atom, thus decrease the repulsion to H. The interaction energy for S is even reduced to a negative value, which means that H is attracted in the Ni—S—H system. Our work presents a fundamental understanding of the effects of the *sp*-elements on H in nickel-based alloys systematically.

1. Introduction

Hydrogen (H) behavior in alloys is a fundamental subject for the challenging phenomenon of H embrittlement [1,2] suffered by almost all alloys. On the other hand, alloys can also be used as the membranes for the purpose of H separation because of their high selectivity over other gases [3–5]. Since the alloying elements can directly modify H behavior in alloys by influencing H diffusion and accumulation, it is essential to understand the interactions between H and the alloying elements.

While it is difficult for routine experimental techniques to explore H behaviors in alloys directly, first-principles calculations can easily investigate H behaviors in alloys and their underlying physical mechanisms at the atomic and electronic levels [6–10]. The attractive and repulsive interactions between H and the alloy elements are studied in previous first-principles calculations [4,11–13]. The elastic mechanism [11] and the “reverse stability” rule [12] are proposed. Hu et al. [11] investigated the interactions between 3d transition metal (TM) atoms and H in Ti-based alloy and found that if the binding of the TM and matrix atoms is weaker than the binding between matrix atoms, the TM-H interactions obey the elastic mechanism: undersized 3d element attracts H and vice versa. Li et al. [12] studied the interactions between 3d/4d TM atoms and H in Pd-based alloy and concluded that if the binding of TM and matrix atoms is stronger than the binding between matrix atoms, these interactions follow the “reverse stability” rule: the 3d/4d element with a large binding energy in Pd matrix repels H and vice versa.

In our previous first-principles calculations [13], we studied the interactions between H and 3d TM alloying atom in Ni and found that these interactions are influenced greatly by the electron distribution and electronegativity and do not obey the elastic mechanism [11] or the “reverse stability” rule [12]. In this work, we further utilize first-principles calculations to study the interactions between H and *sp*-elements from the 3rd, 4th and 5th period (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) in nickel-based alloy, and rare earth elements are not included in this paper. Many of these *sp*-elements are common alloys elements or impurities, so the study of the effects of these *sp*-elements on H is very helpful to understand H behavior in Ni-based alloys.

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The stability of the *sp*-H interaction is considered in this work, and the kinetic effects to H by the sp-elements in Ni are not addressed in this paper and will be studied in our future work.

2. Computational details

Spin-polarized electronic state calculations are performed within the density functional theory [14,15] using Vienna ab initio simulation package (VASP) [16]. Electron-ion interactions are described by the projector-augmented plane-wave (PAW) method [17] and the wave functions are expanded in a plane-wave basis set with an cutoff energy of 400 eV. A generalized gradient approximation (GGA) [18] of the exchange correlation energy is employed. The Brillouin zone is sampled using a Monkhorst-Pack $5 \times 5 \times 5$ 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 1×10^{-5} eV/atom for the total energy.

We adopt a $3 \times 3 \times 3$ Ni supercell with 108 Ni atoms, and the calculated lattice parameter of pure Ni is 3.512 Å which is in good accordance with the experimental value when extrapolated from room temperature to 0 K (3.517 Å) [19]. In the Ni-*sp* supercell, we replace a Ni atom by a *sp*-atom. In the Ni-*sp*-H supercell, a H atom is placed in the octahedral interstitial site (O-site) nearest to the substitutional *sp*-atom. Our calculations find that the O-site is more energetically favorable for H atom than the tetrahedral interstitial site in all the Ni-*sp*-H supercells, so only the cases with H atom in O-site are taken into consideration in the work. O-site is much larger than T-site and can accommodate the H atom without inducing any lattice expansion, which is in agreement with the results in Ref. [13]. The zero point energy (ZPE) is also calculated for H atom.

According to Refs. [11–13], the interaction between H and *sp*-atom can be judged by the interaction energy, and a positive value means the rejection to H in the Ni-*sp*-H system, and a negative value stands for the attraction for H. The method of calculating the interaction energy is as follows:

$$\Delta E = [E(\mathrm{Ni}, sp, \mathrm{H}) + E(\mathrm{Ni})] - [E(\mathrm{Ni}, sp) + E(\mathrm{Ni}, H)]$$

where the four terms on the right are the total energies of the Ni-*sp*-H supercell, the pure Ni supercell, the Ni-*sp* supercell and the supercell with a H atom in the O-site, respectively.

3. Results and discussion

The calculated interaction energies with and without the ZPE correction are shown in Fig. 1, and it is clear that the ZPE correction has little effect on the interaction energy. For the *sp*-elements from the 3rd period in Fig. 1, the interaction energy increases from Al to P and then decreases in the case of S, and the S-H interaction energy has the minimum value of −0.17 eV in all these *sp*-elements. For the *sp*-elements from the 4th period, the interaction energy increases from Ga to As and then decreases in the case of Se. For the *sp*-elements from the 5th period, the interaction energy increases across the period and does not decrease, and the Te-H interaction energy has the maximum value of 0.30 eV in all these *sp*-elements. In a word, for each period of *sp*-elements (except for S in the 3rd period and Se in the 4th period), the interaction energy increases monotonously. Only the interaction energy for S is negative, and the interaction energies for the other cases are all positive, indicating that H is attracted only in the Ni—S—H systems.

Fig. 1 also shows the electronegativities of the *sp*-elements, and the electronegativities of H and Ni are 2.20 and 1.91 Pauling, respectively. For each period of *sp*-elements, the electronegativity increases monotonically. Particularly, the electronegativities of S and Se are much larger than those of the other *sp*-elements with the values of 2.58 and 2.55, respectively. The change trend of the electronegativity for each period of *sp*-elements (except for S and Se) is in good accordance with that of the interaction energy. As a result, it can be inferred that the electronegativity should be closely associated with the interaction energy, which will be discussed in more detail below. In our previous work on the interactions between H and 3d TM elements [13], we have already demonstrated the relationship between the electronegativity and the interaction energy.

Fig. 2(a) displays the shortest Ni-*sp* bond length in the Ni-*sp* supercell, $d_{\mathrm{Nisp}}^{\mathrm{Ni}-sp}$, relative to the Ni—Ni bond length in pure Ni supercell, $d_{\mathrm{Ni}}^{\mathrm{Ni-Ni}}$. Fig. 2(b) shows the binding energy of the *sp*-atom in Ni-*sp* supercell. According to Ref. [13], the binding energy of a Ni atom in Ni matrix is −5.13 eV. As shown in Fig. 2(b), the bindings of the sp-atoms in Ni matrix are all weaker than that of a Ni atom

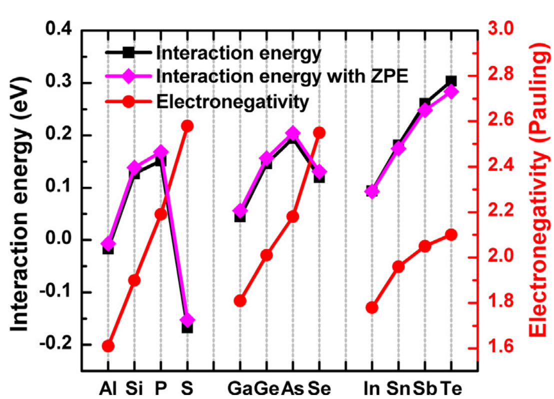

Fig. 1. Interaction energies between *sp* and H atoms with and without the ZPE correction in Ni and the electronegativities of the *sp*-elements.

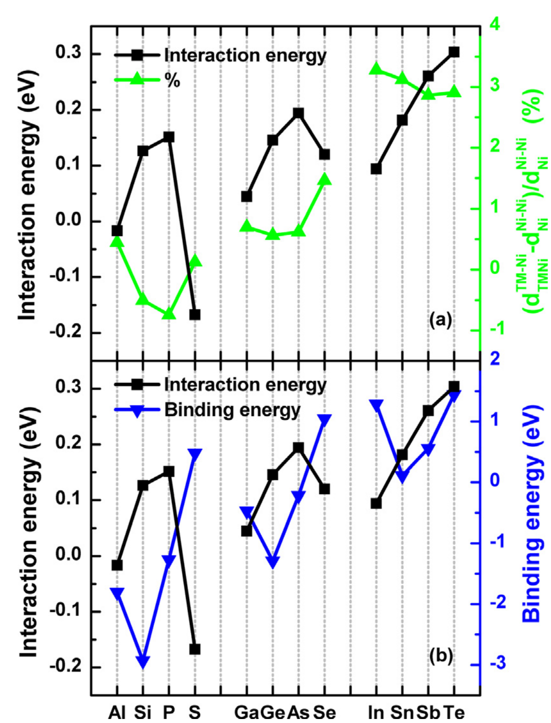

Fig. 2. Interaction energy between *sp* and H atoms and (a) bond length between the *sp*-atom and its nearest Ni atom in the Ni-*sp* supercell, $d_{\mathrm{Nisp}}^{\mathrm{Ni}-sp}$, relative to the Ni—Ni bond length in pure Ni supercell, $d_{\mathrm{Ni}}^{\mathrm{Ni-Ni}}$, (b) the binding energy of the *sp*-atom in Ni-*sp* supercell.