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A computational study of hydrogen embrittlement phenomena in an iron nickel based alloy

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The interaction between H atoms and a $Fe_{50}Ni_{50}$ alloy containing vacancies was studied. The energy of the system was calculated by the atom superposition and electron delocalization molecular orbital (ASED-MO) method. The electronic structure was studied using the concept of density of states (DOS) and crystal orbital overlap population (COOP) curves. The minimum energy position for the H atom in the vacancy region was found at 1.32 Å from the vacancy centre. The changes in the electronic structure of Fe and Ni atoms near the vacancies were analyzed. The interactions mainly involve Fe and Ni metal 4s and 4p atomic orbitals, the most important being the contribution of Fe orbitals. Fe–Fe, Fe–Ni and Ni–Ni bonds weakened as new Fe–H ones were formed. The effect of H atoms is limited to its first neighbours. The detrimental effect of H atoms on the metallic bonds can be related to the mechanism for H embrittlement.

Key words: *vacancy; alloy; hydrogen; embrittlement*

1. Introduction

The presence of hydrogen atoms in a solid metal absorbed in a metal matrix and accumulated in defect regions can result in the reduction of its ductility by decreasing the energy of cohesion and consequently in the increase of the probability of brittle fracture. Dissolved hydrogen atoms in metals tend to concentrate in defects of the crystal structure such as vacancies. Vacancy contributions to hydrogen embrittlement and hydrogen-induced degradation of mechanical properties are very important in steel and Fe based alloys. Hydrogen may degrade the mechanical performance of metallic materials and lead to operational failure [1–4]. A review of H embrittlement in steels was

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reported by Oriani [5]. The author describes there important properties and effects of H in iron and steel that are relevant to understanding the embrittlement phenomena.

Liang and Sofronis investigated the hydrogen embrittlement in nickel-based alloys. In general, hydrogen was found to decrease both the macroscopic stress and strain at which void initiation starts, and reduce the energies expended on bulk deformation and interfacial separation [6]. The mechanical behaviour of very high purity nickel based alloys, charged with hydrogen and deformed in tension was investigated by Cornet et al. [7].

Molecular dynamics simulation was applied to study hydrogen embrittlement in Ni–Cr–Fe alloys. The results of this study were discussed in terms of the influence of the simulation method on the grain boundary fracture of the alloys in function of the boundary type, boundary structure and hydrogen content [8].

Hydrogen entrapment in lattice defects in nickel was studied by Angelo et al. The authors concluded that the embrittlement process is most likely associated with the trapping of hydrogen on/at grain boundaries and in Lomer–Cottrell locks [9]. H embrittlement is not completely understood at the microscopic level. A better understanding of the environmental factors affecting hydrogen embrittlement is critical for the development of alloys as engineering materials for industrial use. Experimental approaches are quite limited owing to the extremely low solubility of hydrogen. In this context, a computational approach would seem to be a suitable way to address the problem.

In this paper, we used the atom superposition and electron delocalization molecular orbital (ASED-MO) method and the YAeHMOP software to study the hydrogen absorption near a γ-FeNi based alloy containing vacancies and the effect of the impurity in the electronic structure of the solid. Ni–H and Fe–H bonding were also analyzed.

2. Computational method

The calculations were performed using the ASED-MO method [10–13]. The modification of the extended Hückel molecular orbital method (EHMO) was implemented with the YAeHMOP software [14]. Double zeta expansions of metal d orbitals were employed. The ASED-MO method is a semi-empirical method which makes a reasonable prediction of molecular and electronic structure. The EHMO method in its original form is not able to optimize geometries correctly, as it lacks repulsive electrostatic interactions. This deficiency can be overcome by introducing a two-body electrostatic correction term [15]. ASED theory is based on a physical model of molecular and solid electronic charge density distribution functions [13–16].

The adiabatic total energy values were computed as the difference between the electronic energy (E) of the system when the impurity atom is at a finite distance within the bulk and the same energy when that atom is far away from the solid surface. The hydrogen absorption energy can be expressed as:

$$\Delta E_{\text{total}} = E\left(\text{Fe}_{50}\text{Ni}_{50}-\text{H}\right) - E\left(\text{Fe}_{50}\text{Ni}_{50}\right) - E\left(H\right) + E_{\text{repulsion}} \tag{1}$$

The repulsive energy was computed taking into account all atom–atom interactions. To understand the interactions, we used the concept of density of states (DOS) and crystal orbital overlap population (COOP) curves. The DOS curve is a plot of the number of orbitals per unit volume per unit energy. The COOP curve is a plot of the overlap population weighted DOS vs. energy. The integration of the COOP curve up to the Fermi level (E_f) gives the total overlap population of the bond specified and it is a measure of the bond strength.

3. The FeNi vacancy cluster model

In order to simulate a FeNi alloy containing vacancies, it is necessary to consider the interaction between the extended nature of a solid and the local character of the defect. This requirement can be satisfied with a cluster of a reasonable size. A conventional FCC cell of chemically ordered FeNi is simulated [17]. A cluster consisting of 179, Fe and Ni, metal atoms (50:50) distributed in five close packed FCC (111) planes is used to represent the alloy containing the defect and its environment. The selected geometry for each plane is an equilateral triangle with the interplanar distance of 2.074 Å. The reference plane is the central one which contains the vacancy.

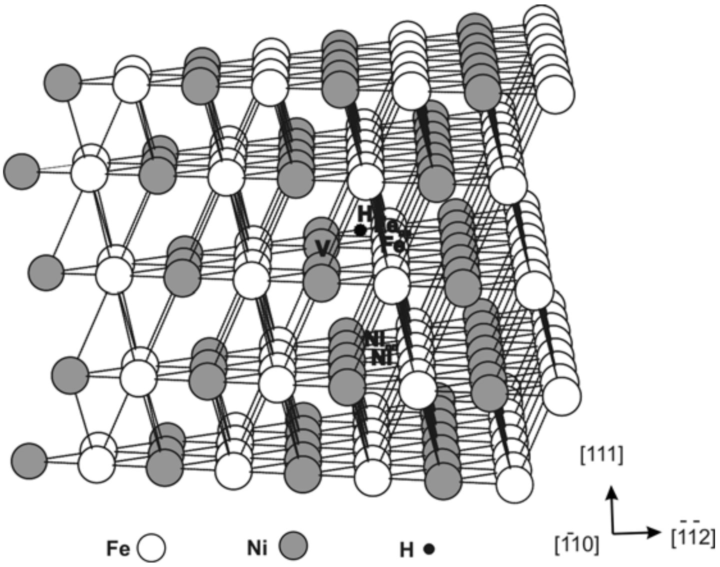

Fig. 1. The $\text{Fe}_{50}\text{Ni}_{50}$–H cluster containing the vacancy (V)
Metallic bonds close to the H atom are indicated

The cluster used in the calculations is shown in Fig. 1. All calculations were performed at the central section of the cluster in order to avoid border effects. The analysis of the results was made based on the energy contour corresponding to FeNi–H interaction mainly at the vacancy zone, covering all the (111) plane at steps of 0.05 Å. The predictions were made from the energy contour corresponding to FeNi–H interaction occurring mostly near the vacancy site: numerical computations were made by discretizing the (111) plane in a rectangular mesh having the step size of 0.05 Å. After determining the most stable position for the H atom inside the cluster, the electronic structure of the FeNi–H system was computed.

3. Results and discussion

The energy analysis is made from the energy contour plots corresponding to FeNi–H interaction in the vacancy region (see Fig. 2). The energy of the system has a relative minimum value of –5.98 eV at the H–vacancy distance of 1.32Å. We can notice the presence of a minimum energy zone when the vacancy is present. The positions of lower energy for the H atom result to be the zone close to the vacancy (V), according to the knowledge that vacancies act as traps for impurities.

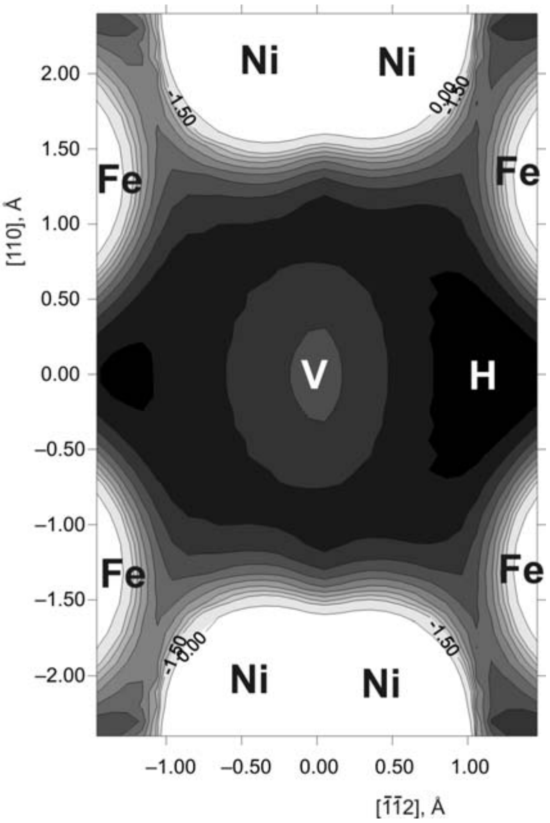

Fig. 2. Contour lines corresponding to the energy (eV) for the FeNi–H system at the vacancy region

An interaction diagram was analyzed (see Fig. 3). Comparing, the total DOS curve for the isolated FeNi system with the total DOS curve for FeNi–H system, the last one presents a small peak appearing below the d metal band corresponding to H based states. A small contribution of H to the DOS is due to its low concentration. The value of the Fermi energy changes slightly with respect to the isolated alloy.

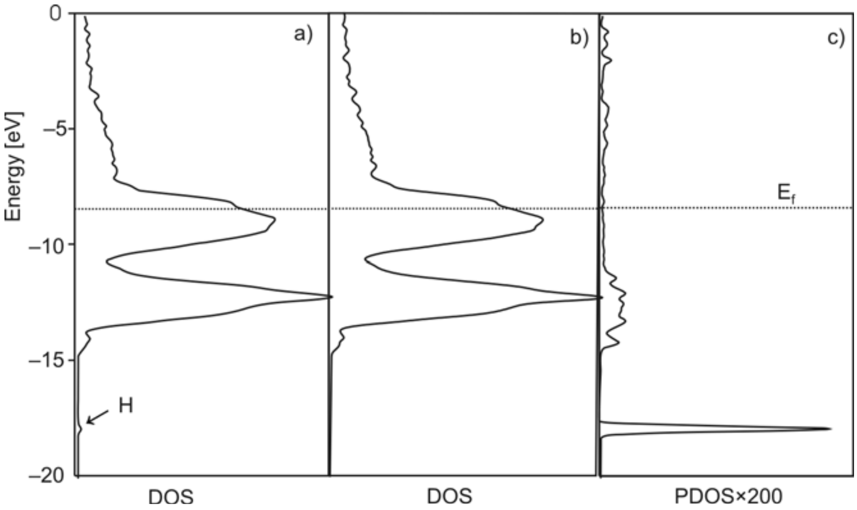

Fig. 3. Total DOS for the FeNi–H cluster (a), total DOS for the FeNi cluster (b) and projected DOS for the H atom (c)

The hydrogen atom affects the states of its surrounding Fe and Ni atoms, causing a change in their electronic densities. As a consequence, the orbital population (OP) between the metallic atoms nearest neighbouring to the hydrogen decreases (Table 1).

Table 1. Atomic orbital occupations and net charges for the H atom and their neighbouring Fe and Ni atoms[a]

Atom	s	p	d	Charge	Bond	Distance [Å]	OP	
H	1.195			–0.195	H–Fe	1.623		0.165
					H–Ni	2.830		
							H	free of H
Fe*	0.511	0.055	4.928	2.506	Fe–Fe$_{nn}$	2.540	0.096	0.239
Fe$_{nn}$	0.510	0.051	4.913	2.526				
Ni*	0.827	0.954	9.433	–1.213	Ni–Ni$_{nn}$	2.540	0.264	0.329
Ni$_{nn}$	0.822	0.949	9.442	–1.214				
					Fe–Ni	2.540	0.148	0.222

[a] The major overlaps population values for these atoms are indicated. An asterisk means a metallic atom (Fe or Ni), first neighbour to H, nn – a nearest neighbour.

These metal–metal bonds are then weakened. The Fe–Fe bond is the most affected after H location, its strength diminishes to about 60%. The Fe–Ni and Ni–Ni OPs decrease to about 33% and 20%, respectively, when an H atom is present. The Fe–H bond is formed and the bonding is achieved at the expense of the metallic nearest neighbours. Our results show how decohesion of metallic bonds contributes to the embrittlement process.

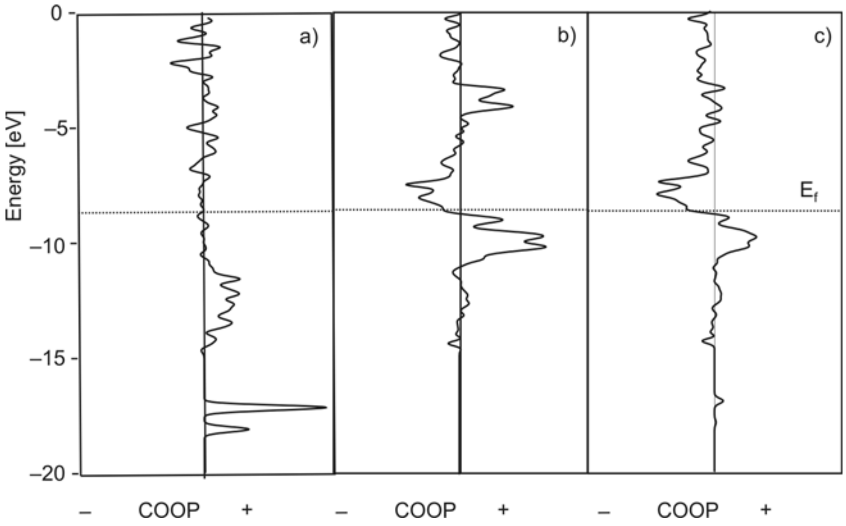

Fig. 4. COOP curves for the Fe–H interaction (a), Fe-Fe$_{nn}$ before H location (b) and Fe-Fe$_{nn}$ after H location(c)

The Fe–H COOP curve is plotted in Fig. 4a. The interaction is bonding, the Fe–H interaction mainly involves Fe 4s and Fe 4p atomic orbitals. The contribution of Fe 3d orbitals is much less important. The contribution of Fe 4s and Fe 4p populations decreases to about 15% and 40%, respectively, with respect to the cluster without H impurity. The Fe 3d population diminishes to about 7% when the hydrogen is present. In Figure 4b, c one can see the Fe–Fe interaction before and after H location. On the other hand, the Ni–H interaction is almost null, it mainly involves Ni 4s and Ni 4p atomic orbitals but the populations decrease only to about 5% and 4%, respectively, when the H atom is located in the vacancy zone.

The contribution of Ni 3d orbitals is lower than 1%. The Fe–H interaction presents an OP value of 0.165 at the distance of 1.623 Å. The Ni–H bond is much longer than the Fe–H one, thus the Ni–H bond is almost negligible. As predicted by the electronegativity differences, there is an electron transfer to the H atom from its nearest Fe neighbours. Atomic orbital occupations and net charges for the H atom and their neighbouring Fe and Ni atoms are summarized in Table 1.

4. Conclusions

The interaction between a hydrogen atom and a γ-FeNi structure having vacancies was studied. The most stable positions for the H absorption atom in the region near the vacancy were found. The Fe–H is formed and their bondings are achieved at the expense of their Fe–Fe, Fe–Ni and Ni–Ni first neighbour bonds. The interactions mainly involve Fe 4s and Fe 4p metal atomic orbitals. The greatest decrease in the metal overlap population is approximately 60%. The detrimental effect of the H atom on the metallic bonds can be associated with hydrogen embrittlement by the decohesion mechanism.

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