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Effect of hydrogen pair in an iron-nickel alloy embrittlement

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Abstract

Computational calculations have been performed to study the location of two hydrogens in a vacancy zone of a $Fe_{50}Ni_{50}$ cell. H debilitates the original metal-metal bonds by forming strong interactions with local Fe atoms. H-metal exchange contributes to the absorption process. The interactions mainly involve $4s$ and $4p$ metal atomic orbitals. The bond strength of Fe-Fe, Fe-Ni, and Ni-Ni, nearest neighbors to H, decreases to about 60%, 33%, and 20%, respectively, with the Fe-Fe bond as the most affected. The net H-H interaction is almost null; H_2 molecule is not formed in the vacancy zone of the $Fe_{50}Ni_{50}$ cell.

Keywords: Iron; Nickel; Alloy; Hydrogen; Computer modeling; Simulation

Background

Hydrogen embrittlement is a form of environmentally assisted failure which is caused by the action of hydrogen often in combination with residual or applied stress resulting in the reduction of the load bearing capacity of a component. The materials used for industrial processes are generally Fe- and Ni-based alloys that offer high corrosion and creep resistance, but the structure of the alloy is not totally immune to this type of embrittlement. Generally a small quantity of hydrogen is sufficient to cause failures because it has the ability to magnify its effect by migrating to regions of high triaxial stress. The problem of hydrogen embrittlement has been of great concern in various industries. For instance, in power plants, several major components such as steam generator tubes, boilers, steam/water pipe lines, and water box of condensers and other auxiliary components like bolts, nuts, screw fasteners, and supporting assemblies are commonly fabricated from plain carbon steels as well as from low and high alloy steels. These components often fail catastrophically due to hydrogen embrittlement [1]. Due to the engineering importance of this problem, a great deal of research has been directed at determining the conditions under which H embrittlement occurs,
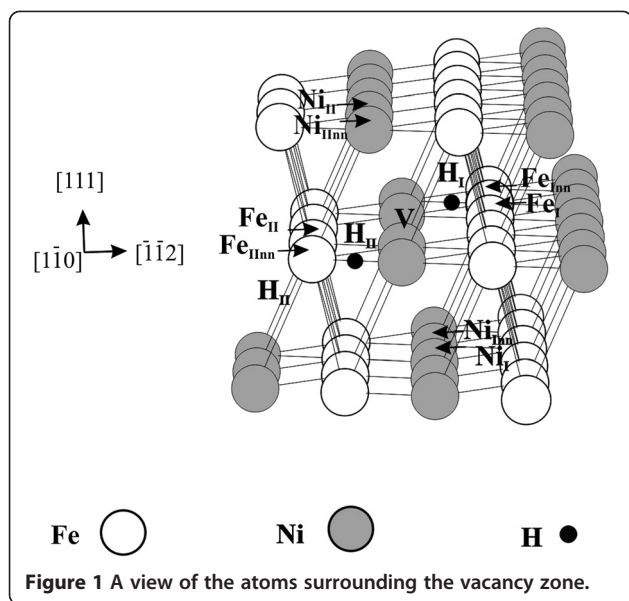
quantifying the effects and finding different classifications and theories to explain the phenomena.

One effect of hydrogen on fracture is that it causes a decrease in atomic bond strength, e.g., decohesion. H is predicted to weaken metallic bonding and to form metal-H interactions. In the past, the atom superposition and electron delocalization molecular orbital (ASED-MO) theory was used to study the H-Fe interaction in the iron structure. Results indicate that several H atoms can be associated in the Fe void due to a strong indirect interaction mediated by the Fe matrix. The relative stability of this situation was compared with the H-H bond in a vacuum [2].

Energy of metal-metal and metal-hydrogen bonds in hydrogen-free and hydrogen-charged face-centered cubic (FCC) iron, nickel, and iron-nickel alloys was calculated. Short-range decomposition of Fe-Ni solid solution and difference in Fe-H and Ni-H bonds are responsible for the splitting of γ reflections in X-ray diffraction patterns, which is at variance with common interpretation in terms of a hydrogen-caused γ^* phase. X-ray diffraction measurements confirm the absence of miscibility gap in the FeNi-H solid solution and its occurrence in Ni-H. Results of calculations are consistent with the absence of H-H pairs in pure nickel [3].

In nickel-base alloys, hydrogen decreases the macroscopic stress and strain at which void initiation commences

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Figure 1 A view of the atoms surrounding the vacancy zone.

and reduces the energies expended on bulk deformation and interfacial separation [4].

On the other hand, hydrogen atoms in metals tend to concentrate in defects of the crystal structure [5]. Vacancy-hydrogen complex contributes to hydrogen embrittlement and induces degradation of mechanical properties [6]. Theoretical calculations demonstrate that vacancies can combine with hydrogen impurities in bulk aluminum and play a crucial role in the embrittlement. A large number of H atoms (up to 12) can be trapped at a single vacancy, which overcompensates the energy cost to form a defect. In the presence of trapped H atoms, three nearest-neighbor single vacancies act as embryos for microvoids and cracks and result in ductile rupture along the plane [7]. In bcc iron, up to nine H atoms were located in a vacancy zone with favorable binding energy [8].
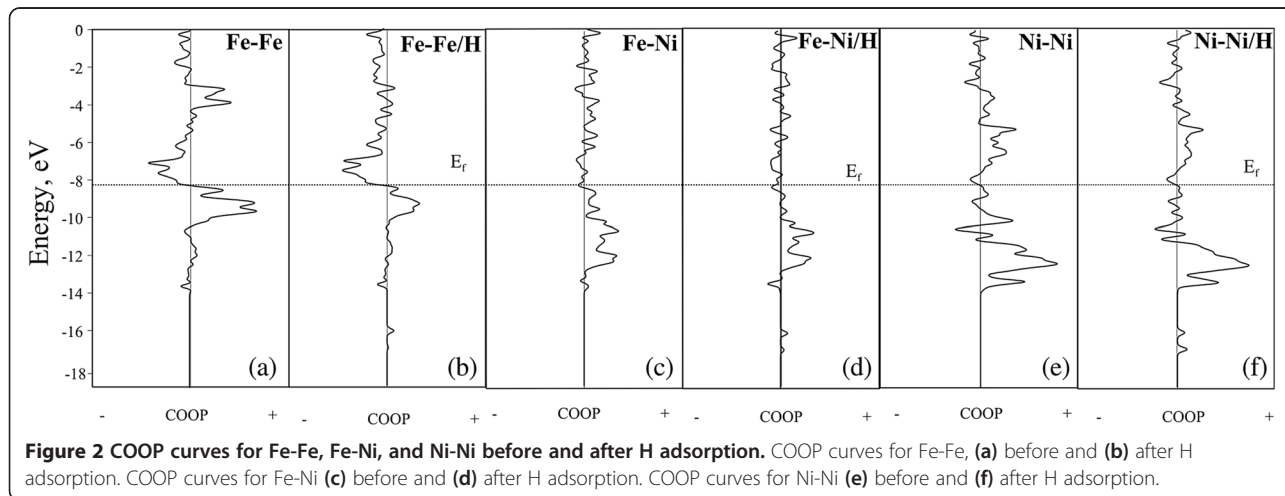
The reasons that cause the embrittlement of industrial materials are still a matter of debate in the scientific community. According to our knowledge, the literature shows a lot of references about theoretical studies on H embrittlement in pure metals but little information about H behavior in bimetallic alloys. It is crucial to understand H chemisorption in industrial alloys in order to determine the mechanism of heterogeneous catalysis at the atomic level. A better understanding of these phenomena is critical for H embrittlement control and for the future development of alloys as engineering materials for industrial use. The extremely low solubility and high mobility of hydrogen made this experimental study very difficult. In this context, computational approach would be a suitable tool to address the problem.

In this paper, ASED-MO method and the Yet Another extended Hückel Molecular Orbital Package (YAeHMOP) program are used to study the absorption of a pair of hydrogen atoms in vacancy zone of a γ-FeNi alloy and the hydrogen effect in the electronic structure of the solid. The metal-H and H-H bonding is also analyzed.

Methods

Computational method and the FeNi vacancy model

Calculations were performed using the YAeHMOP [9]. The extended Hückel (EH)-based methods supply useful information about a different aspect of the electronic structure and the chemical reactivity [10,11]. The theory is based on a physical model of molecular and solid electronic charge density distribution functions [12-14]. The EH method has been successfully employed for experimental information analysis and their correlation with atomic data. It is a methodology that reveals the basic interactions that are responsible for chemical bonding, and it makes possible the relationship between systems with similar geometrical and compositional distributions. Another advantage of the method is that it allows

Figure 2 COOP curves for Fe-Fe, Fe-Ni, and Ni-Ni before and after H adsorption. COOP curves for Fe-Fe, (a) before and (b) after H adsorption. COOP curves for Fe-Ni (c) before and (d) after H adsorption. COOP curves for Ni-Ni (e) before and (f) after H adsorption.

working with systems that include hundred transition metals per unit cell. The literature shows a lot of references about the application of this method in catalysis and adsorption phenomena on surfaces [15,16]. Our group has recently used this methodology in similar and other systems of industrial interest [17-19].

Adiabatic total energy values were computed as the difference between the electronic energy (E) of the system when the H atom is at a finite distance within the bulk and the same energy when that atom is far away from the solid. It can be expressed as

$$\Delta E_{\text{total}} = E(\text{Fe}_{50}\text{Ni}_{50}-\text{H}n)-E(\text{Fe}_{50}\text{Ni}_{50}-\text{H}n-1)-E(\text{H}) + E_{\text{repulsion}},$$
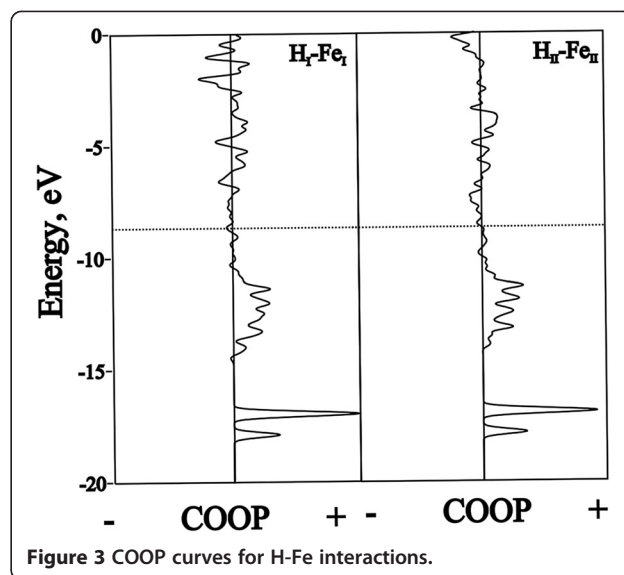
where n is the number of hydrogens.

The concept of crystal orbital overlap population (COOP) curves was used in order to understand the chemical interactions. The COOP curve is a plot of the overlap population's weighted density of states 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 is a measure of the bond strength.

In order to simulate the FeNi alloy containing a vacancy, it is necessary to consider the interaction between the extended nature of the solid and the local character of the defect. This requirement can be satisfied with a cell of reasonable size. A conventional FCC cell [20], constituted by 104 (Fe and Ni) metal atoms (50:50) distributed in five close-packed FCC (111) planes, was used to represent the defect and its environment. The selected geometry for each plane was a triangle having an initial distance between planes of 2.07 Å. The reference plane was the central one, which contains the vacancy. During the calculations, the cell containing the hydrogens was optimized at steps of 0.02 Å and convergence in energy of 0.01 eV. The isolated $\text{Fe}_{50}\text{Ni}_{50}$ system was studied, and it contained one and two H atoms, respectively. After determining the most stable position for the H atoms inside the cell, the electronic structure of the FeNi-HH system was computed.

Table 1 The indicated major metal-metal overlap population values before and after hydrogen adsorption

	With H	Free of H
$\text{Fe}_\text{I}-\text{Fe}_\text{Inn}$	0.01	0.24
$\text{Fe}_\text{II}-\text{Fe}_\text{IInn}$	0.11	0.25
$\text{Ni}_\text{I}-\text{Ni}_\text{Inn}$	0.26	0.33
$\text{Ni}_\text{II}-\text{Ni}_\text{IInn}$	0.27	0.33
$\text{Fe}_\text{I}-\text{Ni}_\text{I}$	0.15	0.22
$\text{Fe}_\text{II}-\text{Ni}_\text{II}$	0.14	0.22

Figure 3 COOP curves for H-Fe interactions.

Results and discussion

The H positions of lower energy correspond to the zone close to the vacancy (V; see Figure 1). The absorption is a favorable process; for such absorption, the total energy difference is negative. The minimum vacancy-hydrogen distances are 1.32 Å (V-H_I) and 1.23 Å (V-H_II), respectively. When two hydrogen atoms are present, the H-vacancy distance is little bigger (0.09 Å) compared with the system containing one hydrogen atom and is in agreement with getting less repulsion between the hydrogens. On the other hand, the energy of two H atoms within one vacancy is very close to the energy of one H atom with a vacancy. The energy difference is only 0.03 eV. This result indicates that there is a possible competition between the formation of another V-H pair and the formation of a V-H_2 complex. In general, the

Table 2 Atomic orbital occupations for hydrogen atoms and their neighboring iron and nickel atoms

Atom	s	p	d	Bond	Distance (Å)	OP
H_I	1.19			$\text{H}_\text{I}-\text{Fe}_\text{I}$	1.62	0.17
				$\text{H}_\text{I}-\text{Ni}_\text{I}$	2.83	
H_II	1.19			$\text{H}_\text{II}-\text{Fe}_\text{I}$	1.69	0.15
				$\text{H}_\text{II}-\text{Ni}_\text{II}$	2.81	
Fe_I	0.51	0.06	4.92			
Fe_Inn	0.51	0.05	4.91			
Fe_II	0.50	0.07	4.84			
Fe_IInn	0.50	0.05	4.95			
Ni_I	0.83	0.95	9.43			
Ni_Inn	0.82	0.95	9.44			
Ni_II	0.82	0.95	9.43			
$\text{Ni}_\text{II nn}$	0.83	0.94	9.53			

The major hydrogen-metal OP values are indicated.

vacancy concentration in the material is smaller than the H atom concentration, and a large proportion of the vacancies may be associated to one or two H atoms, with strong binding energies. The competition between hybridization and coulombic repulsion makes V-H_2 the major complex.

The hydrogens affect the states of its surrounding metal atoms causing a change in their electronic densities. The metal-metal bond strength changes in order to form the new metal-hydrogen interactions. A comparison between the metal-metal bond, before and after H location, is shown in Figure 2.

The Fe-Fe bond is the most affected after hydrogen location, and the strength of the Fe-Fe local bond diminishes to about 60%. The Fe-Ni and Ni-Ni overlap populations (OPs) decrease to about 33% and 20%, respectively, when the H atoms are present (see Table 1). The Ni-H interaction is not developed in the $Fe_{50}Ni_{50}$ cell. On the other hand, the Fe-H bonds are formed, and the bonding is achieved at the expense of the metallic nearest neighbors. The Fe-H COOP curves are plotted in Figure 3. As we can see, the interactions are bonding and mainly involve Fe $4s$ and Fe $4p$ atomic orbitals whose population decreases to about 15% and 40%, respectively, with respect to the cluster without hydrogen impurities (see Table 2). Ni $4s$ and Ni $4p$ atomic orbitals are also affected, but the populations decrease only to about 5% and 4%, respectively, when the hydrogen atoms are located in the vacancy zone. As predicted by electronegativity differences, there is an electron transfer to the H atoms from its nearest Fe and Ni neighbors. The most important electron transfer corresponds to Fe nearest neighbors. The H-metal exchange contributes to the hydrogen absorption process.

At this point, it is important to check the formation of a molecular hydrogen bubble in order to analyze the possible crack that is beginning to weaken the metal. This embrittlement class is responsible for failures in hydrogen-related process plants, a phenomenon known as 'Hydrogen attack'. The COOP curve corresponding to the H-H interaction presents bonding and antibonding peaks below E_f. We can observe that at the H-H distance of 2.55 Å, the H-H interaction is almost null, and it is because the H-H distance (at the minimum energy location) is longer than any bonding distance. According to the literature, a typical H_2 chemical bond is formed at the interatomic distance of 0.74 Å. Also, the H_2 molecule is not present in the γ-$Fe_{50}Ni_{50}$ cell.

Conclusions

The interaction between two hydrogen atoms and a γ-$Fe_{50}Ni_{50}$ alloy containing a vacancy was studied. The most stable position for the H absorption atoms was found in the region near the vacancy. V-H_2 is the most stable complex in the γ-FeNi cell. The Fe-H bonds were formed, and their bindings were achieved at the expense of their Fe-Fe,

Fe-Ni, and Ni-Ni first neighbors. The interactions mainly involve $4s$ and $4p$ metal atomic orbitals. The Fe-Fe bond is the most affected; the strength of the Fe-Fe local bond diminishes to about 60% after hydrogen location. The H_2 molecule is not formed in the studied γ-FeNi cell.

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