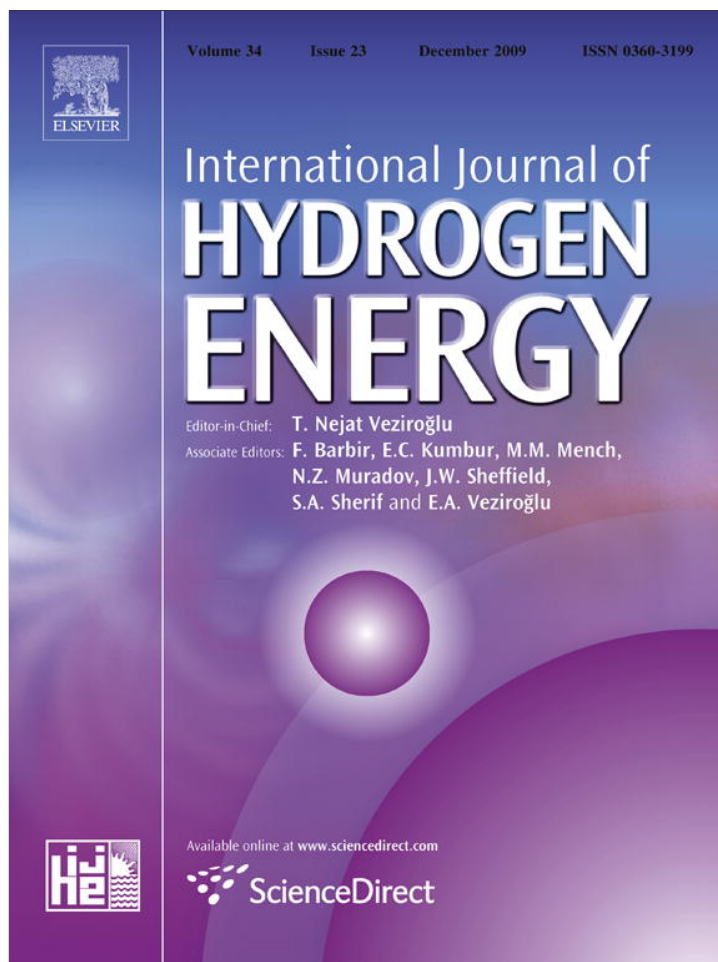


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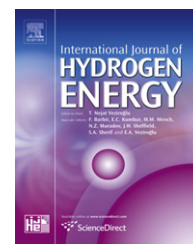


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# The hydrogen effect in the electronic structure and bonding of the B2 FeAl alloy with a Fe vacancy

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## ABSTRACT

A study of H absorption near a Fe vacancy in a B2 FeAl alloy is performed using density functional calculations. The H locates in an octahedral site (Al capped) where one of the Fe atoms in its base is replaced by a vacancy. The computed Fe–H equilibrium distance is 2.065 Å and the H becomes negatively charged. The overlap population analysis reveals metal–metal bond breaking being the intermetallic bond the more affected.

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## 1. Introduction

In the strongly corrosive environment of the molten carbonate fuel cells (MCFC) the protection of the wet-seal areas of the bipolar plates is accomplished by aluminum diffusion coatings. The coating layer is usually produced by depositing metallic aluminum onto a stainless steel surface with the ion vapor deposition technique followed by a diffusion annealing treatment in order to transform the as-deposited Al into a corrosion resistant FeAl-based intermetallic surface alloy [1].

Numerous intermetallic compounds crystallize in the cubic B2 structure. Some of these compounds have outstanding properties and are considered high-temperature structural materials of the future. One of the most promising candidates for high-temperature applications is FeAl because of its high mechanical strength and excellent corrosion resistance [2–4]. The commercial importance of iron aluminides for high-temperature structural applications has been well established. Iron aluminides contain two of the most

easily temperature available metals, namely Fe and Al. They offer low material cost, conservation of strategic materials and lower density than stainless steels. The importance of these iron aluminides is due to their excellent oxidation and sulphidation resistance. The oxidation resistance of Fe–Al alloys increases with increasing Al content. The critical amount of Al for external alumina oxide formation has been determined to be about 14 at% at 800 °C [4].

It is well known that the concentration of certain point defects (vacancies, interstitials, impurities, etc.) affect the behavior of dislocations in crystals, and hence their mechanical properties. The vacancy is one of the simplest defects in crystal structure and so represents a benchmark for experimental and theoretical understanding. When a vacancy is formed, the surrounding material reacts both electronically and elastically [5].

Vacancy migration is the dominant mechanism behind atomic transport, i.e., self-diffusion, in most elemental crystals, and is of fundamental importance in processes like solid

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phase transformations, nucleation and defect migration [5,6]. Vacancies also play an important role for surface morphology, as shown very recently [7].

Interestingly, several researchers noted that constitutional vacancies form in aluminides. However, FeAl appears to be the only aluminide to exhibit such a high concentration of thermal vacancies. The highest vacancy concentration is found at the stoichiometric B2 compound with more than 3.5% at the melting point in FeAl [8,9].

Latham et al have reported that the Fe vacancy ( $V_{Fe}$ ) has low formation energy in all conditions, in good agreement with experimental observations. The fact that  $V_{Fe}$  and  $V_{Fe-FeAl}$  are defects with a low formation energy in Fe-rich FeAl provides support for the idea that vacancies play an important role in the mechanical properties of the material [10].

There are few studies related to the role of structural defects on the electronic structures and atomic bonding in FeAl alloys, which could help us to give a better understanding of their behavior and mechanical properties. In particular, as these materials are sensitive to quench-in vacancies, the interaction of hydrogen atom with vacancies has not been fully addressed and is of a particular interest [11].

Metals can absorb hydrogen atoms during manufacture and/or service. These dissolved hydrogen atom can greatly affect the mechanical properties of structural metals, often leading to material failure. In particular, hydrogen frequently decreases a metal's ductility (hydrogen embrittlement) [12]. The close relationship between hydrogen transport and embrittlement is indicated by the evidence of hydrogen absorption preceding degradation of mechanical properties in structural metals [13]. The hydrogen embrittlement (HE) occurs in both polycrystalline and single crystal samples of pure metals and alloys [14–19].

The effects of hydrogen on vacancy properties in metals have received a considerable attention in scientific and technologic fields [20,21]. Tensile experiments with hydrogen charged samples showed that the susceptibility of steel to hydrogen embrittlement increases with the amount of strong trap sites for solute hydrogen [22,23]. It was then suggested that those sites correspond to some point defects like vacancies [24]. However, no clear (quantitative) characterization has been provided on the defects states and their interactions with hydrogen.

Iron aluminides present several obstacles for their practical application: low plasticity at room temperatures, excess of thermal vacancies and environmental embrittlement. The point defects structural is dominated by substitutional antisite defects on both sublattices and thermal vacancies on Fe sublattice. The brittleness is caused by the reduction of water vapor (steam), with the formation of aluminum oxide and atomic hydrogen. After chemisorption, hydrogen penetrates into the metal lattice and induces the classical embrittlement at crack tips. The mechanism of the embrittlement in Fe–Al alloy is not fully understood.

Recently, we used theoretical calculations to model the interaction of impurities with defects such as vacancies [25,26], and stacking faults [27,28] in iron-based systems. We also studied the H–Pd interactions with dislocations [29] and the electronic structures of a Mg–Ni hydride [30].

The objectives of this paper it to study at a theoretical level the H–metal bond strength and metal–metal interaction in an

ideal B2 FeAl alloy containing an Fe vacancy. Our aim is to contribute to model complex mechanism starting with a vacancy because is a common defect.

## 2. Computational method

Gradient-corrected density functional theory (GC-DFT) calculations were performed on a supercell containing 108 atomic sites in a cubic lattice (B2-phase) to model bulk FeAl, with a  $4 \times 4 \times 4$  reciprocal space grid in the supercell Brillouin zone [31–33]. We used the Amsterdam Density Functional 2000 package (ADF-BAND2000) [34]. The molecular orbitals were represented as linear combinations of Slater functions. The gradient correction the Becke [35] approximation for the exchange energy functional and the B3LYP [36] approximation for the correlation functional were employed.

In order to increase the computational efficiency, the innermost atomic shells of electrons are kept frozen for every atom except hydrogen, since the internal electrons do not contribute significantly to the bonding. We have used a triple-zeta basis set (this means three Slater-type functions for each atomic valence orbital occupied) with polarization functions to express the atomic orbitals of Fe and Al. The basis set of Fe consisted of 3p, 3d and 4s orbitals and for Al 3s and 3p. With this set we obtained a magnetic moment of  $2.26 \mu_B$  for BCC Fe, which compares very well with the experimental value of  $2.20 \mu_B$ .

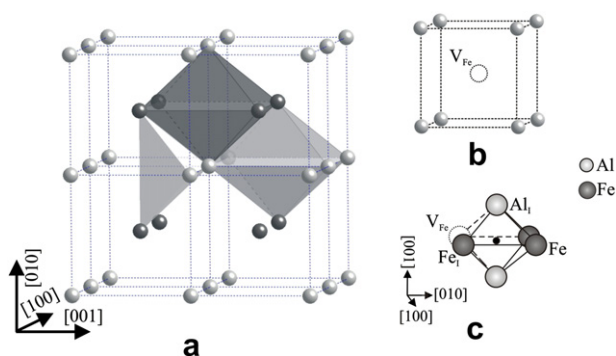
To understand the Fe–Al–H interactions we used the concept of density of states (DOS) and overlap population (OP). The DOS curve is a plot of the number of orbitals as a function of the energy. The integral of the DOS curve over an energy interval gives the number of one-electron states in that interval; the integral up to the Fermi level ( $E_F$ ) gives the total number of occupied molecular orbitals. If the DOS is weighed with the overlap population between two atoms the overlap population density of states (OPDOS) is obtained. The integration of the OPDOS curve up to  $E_F$  gives the total overlap population of the specified bond orbital and it is a measure of the bond strength. If an orbital at certain energy is strongly bonding between two atoms the overlap population is strongly positive and OPDOS curve will be large and positive around that energy. Similarly, an OPDOS negative around a certain energy corresponds to antibonding interactions.

The interaction energy was computed as the difference  $\Delta E$  between the Fe–Al–H composite system when the H atom is absorbed at its minima location geometry and when it is far away from the Fe–Al with an Fe vacancy alloy. It can be expressed as

$$\Delta E_{\text{Total}} = E(\text{FeAlH}) - (E(\text{FeAl}) + E(\text{H})) \quad (1)$$

where  $E$  is the electronic energy;  $E(\text{FeAl})$  corresponds to the pure alloy with an Fe vacancy. A negative value of  $\Delta E$  stands for a favorable process. The absorption energy was computed as:

$$\Delta E_{\text{Abs}} = E(\text{FeAlH}) - \left( E(\text{FeAl}) + \frac{1}{2}E(\text{H}_2) \right) \quad (2)$$



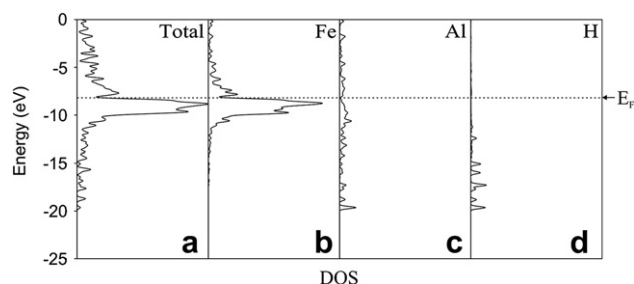
**Fig. 1** – Crystal structure of the B2 FeAl alloy (a). Schematic view of the Fe vacancy frame (b). Schematic view of the H location frame (c).

### 3. Crystal and defect structure

The B2 FeAl phase has ClCs structure with a lattice parameter  $a_0 = 2.90 \text{ \AA}$  [37,38]. The crystal structure is shown in Fig. 1a. The B2 FeAl structure has three types of interstitial sites, one tetrahedral (T) and two octahedral (O1, O2). All tetrahedral are equivalents with the same chemical environment around the site. The O2 is an octahedral formed by four iron atoms in its base capped with two aluminum atoms, while the O1 has four aluminum atoms in its base capped with two iron atoms.

We have introduced an Fe vacancy ( $V_{Fe}$ ) at the center of the supercell (unit cell) (see Fig. 1b). The Fe vacancies are the most stables while the Al vacancies cannot survive because they quickly transform into Fe antisites. The formation enthalpy of  $V_{Fe}$  is 0.99 eV, which agrees with the experimental data [8].

To study the interaction of H we mapped the energy surfaces with 0.01 Å steps in the central region of the cell with cuts perpendicular to the (001) planes. Fig. 1c shows the chemical environment for H interaction. After determining



**Fig. 2** – Total DOS curves for the B2 FeAl- $V_{Fe}$  alloy after H absorption (a); projected DOS in an Al atom (b), in a Fe atom (c), and in the H atom (d).

the more stable position for the impurity atom, we studied the electronic interaction between this interstitial and the metallic atoms.

### 4. Results and discussion

The electronic structure of pure FeAl alloy has been previously reported by several researchers and by us [39–44]. The introduction of an Fe vacancy does not change the DOS plots in Fig. 2. A depression of the 3d DOS is observed at the Fermi level ( $E_F$ ). The d band width is maintained at 3.6 eV which corresponds to the extension of the Fe states while Al based states contribute much less showing several small peaks between -20 eV and  $E_F$ .

The detailed composition for the orbital population gives for Fe  $d^{8.24} s^{0.39} p^{0.15}$ . The Al orbital population is  $s^{1.04} d^{1.25} d^{0.00}$  (see Table 1).

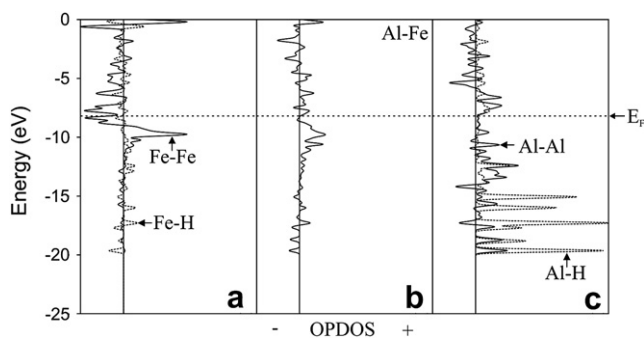
Regarding the bonding, in the perfect alloy the Fe–Fe bond near the  $E_F$  presents some antibonding contribution, while the Fe–Al and the Al–Al OPDOS curves are almost all bonding.

**Table 1** – Electron orbital occupation, overlap population, charges and distances for the B2 FeAl perfect alloy and the B2 FeAl- $V_{Fe}$  alloy before and after H absorption.

Structure	Electron orbital occupation			Bond type	OP	$\Delta OP\%$ <sup>a</sup>	Distances (Å)
	s	p	d				
FeAl							
Fe <sub>i</sub>	0.39	0.15	8.24	Fe <sub>i</sub> –Fe	0.073		2.904
Al <sub>i</sub>	1.04	1.15	0.00	Al <sub>i</sub> –Al	0.224		2.904
				Al <sub>i</sub> –Fe <sub>i</sub>	0.168		2.515
FeAl- $V_{Fe}$							
Fe <sub>i</sub>	0.39	0.16	8.39	Fe <sub>i</sub> –Fe	0.073	0	2.904
Al <sub>i</sub>	1.04	1.16	0.00	Al <sub>i</sub> –Al	0.224	0	2.904
				Al <sub>i</sub> –Fe <sub>i</sub>	0.187	11.3	2.515
FeAl- $V_{Fe}$ +H							
Fe <sub>i</sub>	0.36	0.10	8.26	Fe <sub>i</sub> –Fe	0.048	-34.2	2.904
Al <sub>i</sub>	0.94	1.13	0.00	Al <sub>i</sub> –Al	0.227	1.3	2.904
				Al <sub>i</sub> –Fe <sub>i</sub>	0.092	-45.2	2.515
H	1.15	0.00	0.00	Fe <sub>i</sub> –H	0.022		2.065
				Al <sub>i</sub> –H	0.477		1.450

<sup>a</sup>  $\Delta OP\%$ : Overlap Population percentage change computed referring to B2 FeAl pure.





**Fig. 3 – Overlap population curves of the B2 FeAl- $V_{Fe}$  alloy after H absorption: Al-Al and Al-H (dotted line) (a), Al-Fe (b) and Fe-Fe and Fe-H (dotted line) (c) bonds.**

After introducing the vacancy there is an 11.3% increase in the Al-Fe OP value (see Table 1).

The introduction of an Fe vacancy makes all metal–metal interactions stronger than in the perfect case. This effect has been discussed in detail by Juan and Hoffmann [45]. Comparing to the corresponding perfect alloy the bonding vacancy states are also less bonding and the antibonding states are less antibonding. For the bulk most all-antibonding states are filled. As an antibonding level is in fact more antibonding than the corresponding bonding level is bonding, the loss of antibonding character dominates close to the vacancy (see Table 1) causing an increase in the metal–metal OP. Schneibel et al. report that iron aluminides may be strengthened by grounded-in thermal vacancies as well as by solid solution alloying additions [46]. However, Kupka determined recently that vacancies are not the main reason of FeAl alloy hardening [47].

The hydrogen absorption in the FeAl alloy with a vacancy is a favorable process. The H atom usually occupies interstitial sites in pure metals and alloys. As shown in Fig. 1 there are three interstitials, one tetrahedral and two non-equivalent octahedral sites. Fu and Paintier absorbed H at the tetrahedral site, however, not full geometry optimization was performed [48]. Fu and Wang found the H located at tetrahedral sites with a Fe–H distance of 1.55 Å, which is close to the geometrical center of the tetrahedral interstitial site (1.623 Å) [49]. The tetrahedral locations for H in a perfect alloy are  $-1.75$  eV more stable than O1 but  $+0.93$  eV less stable than at the O2 site. Hydrogen locates nearby the vacancy in an O2 site where one of the Fe atoms in the base is replaced by a vacancy (see Fig. 1c).

The computed Fe–H equilibrium distance is 2.065 Å at O2, which is longer than that obtained for FeAl alloys when H is located at tetrahedral sites [5]. The Al–H distance is 1.45 Å, which is longer to that obtained in perfect B2 FeAl alloys [10].

Our computed absorption energy for H near a vacancy is 2.36 eV, which is very close to the value reported by Fu et al. [50]. In the case of the ideal B2 structure, the H absorption energy as an interstitial is 1.90 eV. The same computed value in pure BCC Fe is 1.76 eV [51] and for FCC Al is 0.47 eV [52].

The electronic structure is modified after H absorption. The H became negatively charged ( $-0.15e^-$ ) and the H 1s level is splitted in several peaks and shifted down in the d band (see Fig. 2). The Al–H interactions present several peaks between  $-12$  and  $-20$  eV.

The overlap population values reveal a metal–metal bond breaking, being the Al–Fe bond the most affected, after absorption the Fe–Al bond OP decreases 45.2%. The H bonds mainly with Al and the reported Fe–H OP is much longer than that corresponding in FePd alloys [53] and [45]. The  $\Delta(OP)$  in Table 1 shows that the Al–Al bond is weakened only 1.3% after H absorption, while the Fe–Fe bond is weakened 34.2%.

The OP peaks for Fe–Al interaction in Fig. 3 show a decrease in the metal–metal bonding character. The Al–H and Fe–H bonding interactions can be observed in Fig. 3b and 3c, with several peaks between  $-10$  and  $-20$  eV. The Fe–Al OP curve presents an important decrease in area (OP) when compared with the pure metal alloys. The Al–H interaction is higher than Fe–H one (see Fig. 3a and 3c).

## 5. Conclusions

H locates nearby the Fe vacancy in an octahedral site (O2) and becomes negatively charged in B2 FeAl alloy with the defect. The computed Fe–H equilibrium distance is 2.065 Å and the Al–H distance is 1.450 Å. Fe vacancies provide a favorable site for hydrogen segregation, being 0.46 eV more stable than the ideal B2 structure.

After H absorption, the Fe–Al OP decreases 45.2%, which can be interpreted as a decrease of the bond strength. The projected DOS for H presents several peaks showing the interaction with Al. The Al–H interaction is stronger than Fe–H as can be seen from OP curves.

Although important, vacancies are not the main reason of the FeAl alloy hardening [47]. The fully understanding of environment embrittlement should contain H–Fe di-vacancies or triple defects, antisite alloy and interaction in grain boundaries and dislocations.

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