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Theory of hydrogen solubility in binary iron alloys based on *ab initio* calculation results

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Interaction of hydrogen atoms with three substitutional impurities ($X = $ Pd, Ti, Cr) in bcc iron base solid solution was modelled *ab initio* using the WIEN2k package. It was shown that in spite of attraction between H and X atoms, excess energy of the H atom in tetrahedral sites in the first sphere of coordination of the X atom has a significant positive value, while the lowest negative values are observed in the second (Pd, -0.087 eV; Ti, -0.091 eV) or the third (Cr, -0.032 eV) sphere. A new thermodynamic theory of hydrogen solubility in dilute bcc Fe–X alloys was developed on the basis of these results. The resulting equation was used to analyze existing experimental data on H solubility in a number of Fe–X alloys, and X–H interaction energies were determined for each case. The energies determined from high-temperature solubility data for Fe–Pd, Fe–Ti and Fe–Cr are somewhat greater than those obtained in *ab initio* calculations. The theory gives a new basis for analyzing hydrogen behaviour in iron-base solid solutions.

Keywords: hydrogen; bcc iron alloys; Fe–Pd; Fe–Ti, Fe–Cr

1. Introduction

It is well known that hydrogen (H) degrades the properties of iron and steels. Despite decades of experimental investigation, the exact mechanisms involved in the degradation process remain incompletely understood. Hydrogen is highly mobile in bcc iron. However, the diffusion of H in bcc Fe can be hindered by atoms of other impurities [1]. Such interaction could potentially be the reason for hydrogen trapping on impurity atoms [2,3].

Statistical thermodynamics of interstitial solid solutions of hydrogen in metals was first examined by Wagner [4] for palladium. McLellan [5] built up a theory of hydrogen solubility taking into account partial molar enthalpies and entropies of solution depending on the oscillation frequency of hydrogen atoms. Like Wagner, McLellan considered hydrogen to be located in octahedral interstitial sites, though assuming a possibility of occupying tetrahedral sites at higher temperatures. Later McLellan [6] developed a more general theory of hydrogen solubility in binary Fe–X alloys, where X is an arbitrary substitutional element. Short-range order of both substitutional and interstitial atoms was accounted for in [7] in terms of the quasichemical theory of M.A. Shtremel [8]. However, in the case of low hydrogen concentrations the result was close to Wagner's equation.

It should be noted that not all assumptions of these theories are proved. First-principles computational tools based on density functional theory (DFT) are ideally suited to study defect trapping in bcc Fe because of the high degree of accuracy. According to recently published *ab initio* results, preferential positions of hydrogen atoms are tetrahedral (T) rather than octahedral (O) interstices [9], and interaction between H and substitutional X atoms are more complex, namely, attraction occurs only for the second and third nearest T-sites, while a strong repulsion occurs at the first ones [10].

Since these results are extremely important for thermodynamics of hydrogen in iron alloys, we performed our own *ab initio* calculations of hydrogen interaction with substitutional impurities in order to re-assess the theory of hydrogen solubility in binary Fe–X alloys.

2. *Ab initio* calculation of H–X interaction

Ab initio calculations have been performed in the WIEN2k program code [11]. The program package WIEN2k allows one to calculate the electronic structure of solids using density functional theory (DFT). It is based on the full-potential (linearized) augmented plane-wave (LAPW) method, one among the most

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accurate schemes for band structure calculations. In this method electronic wave functions are expanded in spherical harmonics inside the nonoverlapping atomic spheres of radius R_{MT} and in plane waves in the remaining space. In systems with H impurity the periodicity of crystal lattice is lost. Such an irregularity can still be treated within the conventional band-structure scheme by considering a large unit cell (supercell) that contains the defect site and a number of surrounding host atoms. For H in bcc Fe we used 54 atoms supercells. We have chosen $R_{MT} = 2.0$ a.u. for Fe atoms and $R_{MT} = 0.7$ a.u. for hydrogen. For the exchange-correlation functional the generalized gradient approximation of Perdew, Burke and Ernzerhof [12] was employed. All calculations were spin-polarized. Plane-wave bases with a cutoff of 500 eV and supercell geometry were used. The ions were relaxed such that the maximum component of the force on each ion was less than 0.01 eV/Å while the total energies were converged to within 0.01 meV. We tested k-point sampling and kinetic energy cutoff convergence for collinear magnetic structure for all 54 atoms in supercell. As a result of convergence tests, plane wave expansion of the wave functions was truncated at $K_{max} = 5.0$ a.u.$^{-1}$ (a kinetic energy cutoff of 350 eV). Structural relaxations were performed until forces on each atom were below 0.01 eV/Å. Using a $3 \times 3 \times 3$ k-point mesh for the supercell we obtained for bcc Fe a lattice constant of 5.37 a.u. and a local magnetic moment of 2.17 μ_B, which agrees very well with experiment and previous DFT-GGA-FLAPW results [13].

Binding energy of a H–X pair was defined by equation

$$
\begin{aligned}
E_b(H - X) = {} & E(Fe_{53}XH) - E(Fe_{54}H) \\
& - E(Fe_{53}X) + E(Fe_{54})
\end{aligned}
\tag{1}
$$

where $E(Fe_{54}H)$ is the total energy of a supercell containing $N = 54$ iron atoms and an H atom placed in tetrahedral interstitial site, $E(Fe_{53}X)$ and $E(Fe_{53}XH)$ are total energies of a cell with X impurity and H–X pair respectively, and $E(Fe_{54})$ is the energy of defect-free Fe cell needed to balance the number of Fe atoms.

Results of calculation are shown in Figure 1 and Table 1. One can see that binding energy E_b between an X atom and a hydrogen atom in a T-site located in the first sphere of coordination (SC) of the X atom has a significant positive value, while the lowest negative values were observed in the second (Pd, -0.087 eV; Ti, -0.091 eV) or the third (Cr, -0.032 eV) sphere. In the third and the fourth spheres of coordination the interaction is weaker, but may remain significant. These results coincide with the data of [10] for Ti, but
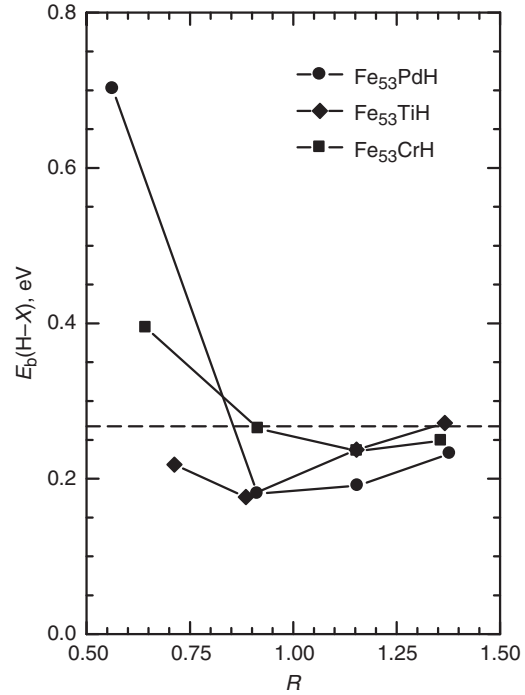

Figure 1. Energy of H atom at different distances R (in units of lattice parameter of pure iron) from an X atom in a relaxed Fe$_{53}X$H supercell. Horizontal line corresponds to H in pure iron.

differ from them for Cr; Pd was not analyzed in that work.

This shows that new effects found in *ab initio* calculations may require significant changes in thermodynamic description of hydrogen solutions in alloys, and the theory developed here thus provides a new basis for analyzing hydrogen behaviour in iron-base solid solutions.

3. Thermodynamic theory of hydrogen solubility

Results of *ab initio* modelling described in the previous section require developping a new thermodynamic theory of hydrogen solubility in iron alloys that would take into account two effects: (a) blocking of T-sites from occupation by hydrogen in the first SC of substitutional solute atoms (Pd, Ti, etc.), and (b) strong attraction between H and substiutional solute atoms in the second (and sometimes third) SC. In this section an attempt will be made to develop such a theory.

We will describe concentrations of substitutional solute X and iron in ternary solid solution Fe–X–H as

$$
\theta_X = \frac{N_X}{N} \text{ and } \theta_{Fe} = \frac{N_{Fe}}{N}
\tag{2}
$$

where N_X and N_{Fe} are numbers of X and Fe atoms, and $N = N_X + N_{Fe}$ is the total number of lattice

Table 1. Maximum binding energy E_b (in eV) of hydrogen atom and a substitutional impurity X.

X	Calculated *ab initio* (our results)	Calculated *ab initio* (results of [10])	Evaluated from H solubility data (Table 3 below)	Experimental values
Pd	−0.087	–	−0.204	–
Ti	−0.091	−0.08	−0.229	−0.19 [2]
Cr	−0.032	0.00	−0.042 . . . −0.083	−0.10 [14]

Table 2. Radii R_i (in lattice parameters) of SC of T-sites around a lattice site and numbers z_i of T-sites on each SC for bcc lattice.

SC number i	R_i	z_i
1	0.559	24
2	0.901	24
3	1.146	48
4	1.346	72
5	1.521	24

Table 3. Interaction energies ε determined from experimental data on hydrogen solubility in binary iron alloys by means of Equation (29).

Impurity X	ε, eV	Temperature range of experimental data (in kelvins) and source
Al	0.071	773 . . . 973 [16]
Si	0.140	673 . . . 1273 [17]
	0.062	573 . . . 973 [18]
Ge	0.074	573 . . . 973 [19]
Ti	0.229	973 . . . 1073 [20]
V	0.183	973 . . . 1073 [20]
Cr	0.083	673 . . . 1473 [21]
	0.069	673 . . . 1273 [17]
	0.042	773 . . . 1273 [22]
	0.083	673 . . . 973 [23]
Mo	0.059	573 . . . 1023 [24]
	0.013	573 . . . 1023 [25]
W	0.045	673 . . . 1323 [26]
	0.040	673 . . . 1073 [27]
Mn	0.161	673 . . . 1073 [17]
	0.102	973 . . . 1073 [20]
Ni	0.089	573 . . . 973 [21]
	0.121	673 . . . 1073 [17]
	0.081	573 . . . 923 [28]
	0.109	973 . . . 1073 [20]
Pd	0.204	723 . . . 923 [29]

atoms. Concentration of N_H hydrogen atoms located in T-sites will be described as

$$\theta_H = \frac{N_H}{N\nu} \quad (3)$$

where ν is the number of T-sites per one lattice atom ($\nu = 6$ for bcc). T-sites are located at different distances from the lattice site containing an X atom forming a sequence of spheres of coordination (Table 2).

According to the results of *ab initio* modelling every X atom neighbours with $z_1 = 24$ T-sites that hydrogen atoms cannot occupy due to strong repulsion between H and X. If θ_X is low, then overlapping of SC of X atoms may be neglected, so the total number of such positions in the solution is $N_X z_1$. Total number of T-sites on the second SC where an attraction appears between H and X is $N_X z_2$. In the rest $N\nu − N_X z_1 − N_X z_2$ of T-sites H atoms will not interact with X and will have the same energy as if surrounded by Fe atoms only. So all H atoms can be divided into two groups: N_H^I atoms strongly attracted by X and N_H^{II} atoms located beyond the 2nd SC of X atoms and not interacting with them.

By analogy with [7] let us introduce a parameter

$$p = \frac{N_H^I}{N\nu\theta_H} = \frac{N_H^I}{N_H} = \frac{\theta_H^I}{\theta_H} \quad (4)$$

to characterize short-range order in mutual position of H and X atoms, or the degree of trapping of hydrogen atoms by the atoms of X. If all H atoms are located

near X atoms, then $N_H = N_H^I$ and $p = p_{max} = 1$. In case of uniform distribution of hydrogen $N_H^I \approx N_X z_2 \theta_H$ and $p = p_{disordered} = \frac{N_X z_2}{N\nu}$. In Equation (4)

$$\theta_H^I = \frac{N_H^I}{N\nu} \quad (5)$$

Let E_0 be the energy of H atom in a T-site located far from X atoms. If the H atom finds itself in a T-site located in the second SC of an X atom, its energy will become $E_0 − \varepsilon$ where $\varepsilon = −E_b(H − X)$ is the binding energy of H and X. So the total potential energy of all H atoms is

$$E = N_H^I(E_0 − \varepsilon) + (N_H − N_H^I)E_0 = N_H E_0 − N_H^I \varepsilon \quad (6)$$

If one assumes a solid solution without short-range order, where H atoms are uniformly distributed among all T-sites, as a reference state, then the thermodynamic probability of atomic configurations for the dissolved hydrogen in a solution with certain value of order parameter p is

$$W = \frac{(N\nu - N_X z_1)!}{N_H! \cdot (N\nu - N_X z_1 - N_H)!} \cdot \frac{W_1(p) \cdot W_2(p)}{W_1(p_{\text{disordered}}) \cdot W_2(p_{\text{disordered}})} \tag{7}$$

where the first factor is the number of ways to place N_H hydrogen atoms on permitted T-sites, while in the second factor

$$W_1 = \frac{(N\nu - N_Y(z_1 + z_2))!}{(N\nu - N_Y(z_1 + z_2) - N_H^{II})! \cdot N_H^{II}!} \tag{8}$$

is the number of variants of placing N_H^{II} hydrogen atoms on possible positions where no X-H interaction is present, and

$$W_2 = \frac{(N_Y z_2)!}{N_H^I!(N_Y z_2 - N_H^I)!} \tag{9}$$

is the number of variants of placing N_H^I hydrogen atoms on $N_Y z_2$ T-sites where such interaction occurs.

In the case of chaotic distribution of hydrogen atoms $N_{H(\text{disordered})}^I = N_X z_2 \theta_H$ and $N_{H(\text{disordered})}^{II} = N_H - N_X z_2 \theta_H$. Equations (6)–(9) permit to calculate the free energy function for hydrogen atoms subsystem:

$$F = E - kT \ln W \tag{10}$$

Using Stirling formula and the condition

$$\frac{\partial F}{\partial N_H^I} = 0 \tag{11}$$

one obtains the equation

$$\frac{\varepsilon}{kT} = \ln \frac{(N_X z_2 - N_H^I)(N_H - N_H^I)}{N_H^I(N\nu - N_X(z_1 + z_2) - (N_H - N_H^I))} \tag{12}$$

reflecting the 'quasichemical' equilibrium condition [8]. After simple transformations Equation (12) may be presented in the form

$$\frac{\varepsilon}{kT} = \ln \frac{(\theta_X m_2 - \theta_H^I)(\theta_H - \theta_H^I)}{\theta_H^I(1 - \theta_X m - (\theta_H - \theta_H^I))} \tag{13}$$

where $m_2 = \frac{z_2}{\nu}$ and $m = \frac{z_1 + z_2}{\nu}$. Exponentiating (13), one obtains

$$\exp\left(-\frac{\varepsilon}{kT}\right) = \frac{\theta_H^I(1 - \theta_X m - (\theta_H - \theta_H^I))}{(\theta_X m_2 - \theta_H^I)(\theta_H - \theta_H^I)}. \tag{14}$$

This relation may be transformed into a quadratic equation in θ_H^I (or N_H^I):

$$(\theta_H^I)^2 \left(\exp\left(-\frac{\varepsilon}{kT}\right) - 1\right)$$
$$+ \theta_H^I \left((-\theta_X m_2 - \theta_H)\exp\left(-\frac{\varepsilon}{kT}\right) + \theta_X m + \theta_H - 1\right)$$
$$+ \theta_H \theta_X m_2 \exp\left(-\frac{\varepsilon}{kT}\right) = 0 \tag{15}$$

Its solution is

$$\theta_H^I = \frac{N_H^I}{N\nu} = -\frac{1 - (m - m_2)\theta_X + (1 - m\theta_X - \theta_H)h}{2h}$$
$$+ \frac{\sqrt{(1 - (m - m_2)\theta_X + (1 - m\theta_X - \theta_H)h)^2 + 4\theta_X \theta_H mh}}{2h} \tag{16}$$

where $h = \exp\left(-\frac{\varepsilon}{kT}\right) - 1$.

If alloys with low concentrations of hydrogen and substitutional solute are considered, on can put $\sqrt{1 + a} \approx 1 + \frac{1}{2}a$, where

$$a = \frac{4\theta_X \theta_H m_2}{(1 - (m - m_2)\theta_X + (1 - m\theta_X - \theta_H)h)^2}$$

so (16) transforms into the following approximate equation describing equilibrium values of θ_H^I and p:

$$\theta_H^I \approx \frac{\theta_X m_2}{1 - (m - m_2)\theta_X + (1 - m\theta_X)h} \cdot \theta_H \tag{17a}$$

$$p \approx \frac{\theta_X m_2}{1 - (m - m_2)\theta_X + (1 - m\theta_X)h} \tag{17b}$$

In the case of very strong attraction between H and X atoms $\varepsilon \to \infty$ and $h \to -1$, so one finds from (17b) that $p \to 1$. If there is no interaction between H and X then $\varepsilon = 0$; $h = 0$ and $p = \frac{\theta_X m_2}{1 - (m - m_2)\theta_X}$. Parameter p is defined by Equation (4) so that in the variant of disordered distribution of hydrogen atoms $p \neq 0$. The value of p deviates from $\theta_Y m_2$ because T-sites nearest to X atoms are forbidden to be occupied by hydrogen. Finally, if $\varepsilon \to -\infty$, which means strong repulsion between two impurities, $p \to 0$.

Applying condition (11) to formula (10) enables one to calculate the equilibrium value of free energy. The result is rather combersome, but in order to calculate hydrogen distribution one needs to know only the chemical potential of hydrogen atoms

$$\mu_H = \left(\frac{\partial F}{\partial N_H}\right)_{T, \theta_X, p} \tag{18}$$

After differentiating F with respect to the number of hydrogen atoms N_H one finds

$$\mu_H = E_0 + kT\ln\frac{(N_H - N_H^I)(N\nu - N_X(z_1 + z_2) - N_H(1 - \frac{N_X z_2}{N\nu}))}{(N\nu - N_X(z_1 + z_2) - (N_H - N_H^I))(N\nu - N_X z_1 - N_H)(1 - \frac{N_X z_2}{N\nu})}$$
$$- \frac{N_X z_2}{N\nu}kT\ln\frac{(N\nu - N_X(z_1 + z_2) - N_H(1 - \frac{N_X z_2}{N\nu}))}{(N_X z_2 - N_H\frac{N_X z_2}{N\nu})(1 - \frac{N_X z_2}{N\nu})}. \quad (19)$$

If we restrict ourselves to the case of small hydrogen concentrations ($\theta_H \ll \theta_X$), then

$$\mu_H \approx E_0 + kT\ln\frac{\theta_H}{1 - \theta_X m} + kT\ln(1 - p)$$
$$- \theta_X m_2 kT\ln\frac{1 - \theta_X m_1}{1 - \theta_X} \quad (20)$$

where $m_1 = \frac{z_1}{\nu}$. The last addend is actually proportional to θ_X^2 and so can be neglected. Then substituting p from Equation (17b) we find

$$\mu_H \approx E_0 + kT\ln\theta_H$$
$$- kT\ln\left(1 - m\theta_X + m_2\theta_X \exp\left(\frac{\varepsilon}{kT}\right)\right) \quad (21)$$

Since it was assumed that the character of hydrogen distribution does not affect the kinetic energy of its atoms, one should add to Equation (21) an addend taking account of kinetic energy, and replace E_0 with μ_H^0, the chemical potential of hydrogen atom in the standard state of infinitely dilute solution. Per one mole of solution it is equal to

$$\mu_H = \mu_H^0 + RT\ln\theta_H$$
$$- RT\ln\left(1 - m\theta_X + m_2\theta_X \exp\left(\frac{\varepsilon}{kT}\right)\right) \quad (22)$$

Solving of H_2 gas in metallic alloys occurs by reaction

$$\frac{1}{2}(H_2)_{gas} = [H]_{Me} \quad (23)$$

where $[H]_{Me}$ designates the hydrogen dissolved in metal. Equilibrium of this reaction corresponds to the equality of chemical potentials:

$$\frac{1}{2}\mu_{H_2} = \mu_H \quad (24)$$

For the gaseous hydrogen $\frac{1}{2}\mu_{H_2} = \frac{1}{2}\mu_{H_2}^0 + \frac{1}{2}RT\ln f_{H_2}$ where f_{H_2} is fugacity and $\mu_{H_2}^0$ is standard state chemical potential. Using Equation (22), one finds

$$\ln\theta_H = \frac{\frac{1}{2}\mu_{H_2}^0 - \mu_H^0}{RT} + \ln\left(1 - m\theta_X + m_2\theta_X \exp\left(\frac{\varepsilon}{kT}\right)\right)$$
$$+ \frac{1}{2}\ln f_{H_2} \quad (25)$$

When the pressure is not too high, it coincides with fugacity, so Equation (25) reflects the Sieverts law for the Fe-X–H alloy. In the case $\theta_X = 0$ it must turn into the equation of hydrogen solubility in α-Fe [15]:

$$\ln\theta_H = -7.84 - \frac{3270}{T} + \frac{1}{2}\ln p_{H_2} \quad (26)$$

which permits to find the value of the first addend in (25):

$$\frac{\frac{1}{2}\mu_{H_2}^0 - \mu_H^0}{RT} = -7.84 - \frac{3270}{T} \quad (27)$$

Therefore,

$$\ln\theta_H = -7.84 - \frac{3270}{T} + \ln\left(1 - m\theta_X + m_2\theta_X \exp\left(\frac{\varepsilon}{kT}\right)\right)$$
$$+ \frac{1}{2}\ln p_{H_2} \quad (28)$$

We used this equation to describe experimental data for 11 alloy systems available in the literature. Different investigators used different techniques and materials of different purity, then their measured H solubility in unalloyed iron may have varied. So we actually considered the first two terms in Equation (28) as free parameters:

$$\ln\theta_H = A - \frac{B}{T} + \ln\left(1 - m\theta_X + m_2\theta_X \exp\left(\frac{\varepsilon}{kT}\right)\right) \quad (29)$$

The last term is omitted since most available measurements were made at 1 atm. The values of A, B and ε were then determined by least-squares fit of experimental θ_H values. In accordance with results of *ab initio* modelling and Table 2 we took $m_2 = 4$ and $m = 8$. Energies ε evaluated in this way are given in Table 3.

4. Discussion and conclusions

According to the values of ε given in Table 3, three elements most strongly interacting with hydrogen in α-Fe solid solution are Pd, Ti and V ($\varepsilon \approx 0.2$ eV); somewhat weaker are Mn and Si ($\varepsilon \approx 0.1$ eV), and then Ni, Cr, Al, Ge, W and Mo ($\varepsilon \approx 0.1 \ldots 0.04$ eV). In general, values of ε derived from different sets of experimental data show significant scatter, probably

due to difference in methods and materials used by different authors. Another feature is that ε values obtained from high-temperature solubility data are greater than those calculated *ab initio* (see Table 3). To some extent this may be a result of inexact values of m and m_2. For example, if we consider attraction not only in the second, but also in the third SC in Fe–Pd and Fe–Ti systems (see Figure 1), i.e. if we put $m_2 = 12$ and $m = 16$, then ε values decrease to 0.110 and 0.144 eV, respectively. The theory can thus be improved by incorporating *ab initio* interaction energy values for each coordination sphere to achieve better correlation with thermodynamic data. However, this will make it less general, since the solubility equation that will substitute Equation (29) will differ from element to element, and it will be impossible to use the theory for systems where no *ab initio* information is available.

In general the results of our work confirm the conclusion of [10] that substitutional impurity atoms block the positions of the 1st sphere of coordination of tetrahedral interstitial sites from filling with hydrogen, while attraction occurs in the second and third spheres; this attraction is the strongest for Pd, Ti and V. These conclusions permitted to develop a new variant of statistical thermodynamics of hydrogen solid solutions in binary iron alloys. The general equation was applied to existing experimental data on hydrogen solubility in a number of alloys systems and energies of hydrogen–substitutional impurity interaction were evaluated, which correspond qualitatively to *ab initio* results.

Acknowledgements

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