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A multi-scale analysis of the different interactions between defects and hydrogen: a review on the contribution of the elastic fields

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Abstract - Hydrogen Embrittlement (HE) is one of the causes mainly evoked in premature rupture of industrial components exposed to an aggressive environment. Many studies have been conducted in order to understand the mechanisms involved during this degradation and the influence of the metallurgical states. Good knowledge of hydrogen interactions with crystal defects is a key element in the understanding of the different damage processes associated with HE in fcc materials. In this state of mind, we have undertaken a systematic study of these interactions in nickel alloys using coupled multi-scale approaches. These latter correspond to the association of atomistic calculations (EAM, DFT) with experimental tests: Electrochemical Permeation (EP), Secondary Ionization Mass Spectrometry (ToF-SIMS) analysis and Thermal Desorption Spectroscopy (TDS) in order to evaluate the hydrogen states in presence of different crystal defects. Among the major results, we focus our attention on the interaction between hydrogen and vacancies in nickel single crystals, the trapping and the segregation of hydrogen for several dislocation distributions (cells, PSB, GBs,...) and the contribution of the grain boundaries (GBs) as well as the precipitates to the hydrogen diffusion and trapping in nanocrystals, polycrystals and bi-crystals. In all the cases, we have questioned the impact of elastic fields associated with the defect to apparent solubility and diffusion of hydrogen. In the second part, we explore the potential impacts of hydrogen on elastic properties and their implication on the mechanisms of plasticity.

51 Introduction

52
53 It is now acted that the interactions of the environment with metals are strongly implied in the
54 embrittlement of materials and alloys of the engineering structures and can lead to premature
55 failures [1-5]. Among a large variety of processes which involves a stress/strain state and an
56 aggressive environment, we shall note that the impact of the internal and/or external hydrogen
57 can lead to severe loss of functional properties. A key element for the understanding of
58 hydrogen embrittlement is based on a good knowledge of the interactions between the solute
59 and the metallurgical state of the metal. In particular, hydrogen bonds favorably with defects
60 and affect the physical and chemical properties of metal [6]. Through the so-called trapping
61 phenomenon, the metallurgical state and structural defects can affect the apparent solubility
62 and the diffusion coefficient of the solute which, sometimes, can explain why literature data
63 on the subject exhibit some incoherence. As it has been widely established in literature, the
64 electrochemical permeation technique and the thermal desorption spectroscopy can be used to
65 extract and to classify the different hydrogen concentrations based on the difference in
66 binding forces between hydrogen and the trapping sites. The lower, medium and higher
67 binding energies correspond to the insertion in the interstitial sites C_L (0.1 to 0.2 eV), in the
68 reversible trapping sites C_{Tr} (around 0.3 eV) associated with elastic field near edge
69 dislocations network and/or semi-coherent precipitates the insertion in irreversible or deep
70 trapping sites, C_{Tr} (0.5 to 0.6 eV) associated with dislocation core and/or vacancy [9,10],
71 respectively. In each case, there is a purely mechanical contribution and a contribution of
72 chemical origin that is not always easy to distinguish, especially at the atomic scale. In this
73 work, we restrict our contribution to the question of the multiple interactions between a solute
74 and the elastic stress field at the different microstructural scales and their implications on the
75 apparent solubility and diffusivity of hydrogen. We begin our analysis by a brief presentation
76 of the different techniques used in our work. Then the thermodynamic framework is recalled
77 for an easy questioning of the couplings between mechanics and diffusion. Then, we give a
78 brief reminder of the different origins of the strain fields and their gradients to finally
79 illustrate our discussion on multiple cases recently investigated in our group.

81 82 1 – Brief review of the different techniques used

83
84 In this section, we recall briefly the different techniques used in our work to identify on the
85 one hand the various microstructural defects studied and, on the other hand, the experimental
86 and the numerical investigation methods that have been used to characterize the interaction of
87 hydrogen with these defects. Dislocation and vacancy organization in nickel single crystal, bi-
88 crystals and polycrystals have been investigated using a JEOL JEM 2011 transmission
89 electron microscope (TEM) operating at 200 kV. Foils for transmission electron microscopy
90 (TEM) were thinned in a double twin-jet electro-polisher using electrolytes with the
91 conditions described previously [12]. We focus our attention on differing dislocation features
92 issues to tensile and cyclic loading of (001) single crystal orientation, grain-boundaries with
93 four misorientations and (001) single crystal with different hydrogen charging conditions.
94 Dislocation densities were measured using the standard intersection method from TEM
95 micrographs collected by Digital Micrograph™ software [11,12]. The size of vacancies
96 cluster is obtained from classical bright field conditions. The vacancy concentrations have
97 been evaluated using differential scanning calorimetry (DSC) as previously describe [13].
98 DSC measurements were performed using a Q100 TA Instruments DSC apparatus. The
99 heating of the samples was carried out linearly from 273 to 723 K at a rate of 10 K min⁻¹. The
100 existence of an exothermic peak in the evolution of the heat flow as a function of temperature

101 is associated with the annihilation of vacancies, and the area of this peak corresponds to the
102 vacancy stored energy. The equilibrium vacancy concentration is obtained using the
103 formation energy of a vacancy deduced from our DFT calculations and exothermic peak (1.49
104 to 1.52 eV between 0 K to 1200 K [14, 15]). The grain-boundary character distribution is
105 investigated using crystallographic orientation mapping data extracted from electron
106 backscatter diffraction (EBSD) analyses as previously proposed (EBSD was carried out using
107 an EDAX/TSL OIM system coupled to a FEI Quanta 200 ESEM-FEG scanning electron
108 microscope) [16]. For polycrystalline structure, grain boundaries are categorized into two
109 families: the special GBs (Σ 29) corresponding mainly to the Σ^{3n} in nickel [16] (Σ 3, Σ 9 and
110 Σ 27), and random GBs ($>\Sigma$ 29). For bi-crystals, grain-boundaries with four misorientations
111 have been identified: Σ 11-50°30<110>{311}, Σ 11-129°30<110>{332}, Σ 3-
112 70°30<110>{111} and Σ 5-37°<100>{310} ($\Sigma_{x-\theta}$ <hkl>{uvw} with x the index of
113 Coincidence Site Lattice (CSL), θ the rotation angle, <hkl> the rotation axis and {uvw} the
114 grain boundary plane) [17,18].
115

116 To quantify the hydrogen concentration and the maximum solubility in nickel, we use
117 Thermal Desorption Spectroscopy (TDS, Jobin Yvon Horiba EMGA-621W hydrogen
118 analyzer) composed of an impulsion furnace system coupled with a thermal conductivity
119 detector [9, 15,16]. The procedure consists to measure the hydrogen concentration in the pre-
120 charged samples by fusion. The pre-charging conditions are defined in the Volmer domain of
121 cathodic electrochemical potential range in an alkaline solution of 0.1 M NaOH at room
122 temperature [15, 16]. According to thermodynamic and kinetic analysis the over potential
123 range explored correspond to a fugacity of 10^5 to $4 \cdot 10^7$ Pa at 300K [19]. Electrochemical
124 Permeation (EP) is the main technique used to detect the mechanisms of diffusion and
125 trapping of hydrogen in different microstructures in our laboratory [15, 16, 20]. This
126 technique is composed of two cells separated by a membrane with an exposed surface in
127 contact with an electrolytic solution. The charging side or entry side of the membrane is
128 galvanostatically polarized at a constant cathodic charging current density (predefined
129 according to the cathodic polarization curve and fugacity range defined previously) in 0.1 M
130 NaOH (pH ~ 13). The detection side or exit side of the membrane was maintained at a
131 constant anodic potential of ~630 mV/SSE in 0.1 M NaOH (pH ~ 13), and the hydrogen flux
132 (current density) at this side is recorded to study the transport of hydrogen through the
133 sample. A constant temperature is maintained between a range of 283 to 313K and both
134 solutions were continuously deaerated by argon gas at 1.4 bar (see the reference [19] and [20]
135 for more details). Using different conditions in term of temperature and cathodic charging
136 current density/potential (equivalent to a specific fugacity), a sequence of charging followed
137 by a sequence of desorption combines with TDS measurements at each step, allow to obtained
138 the apparent diffusion coefficient D_{app} , the average concentration of hydrogen on the sample,
139 the three different hydrogen concentrations namely interstitial C_L , reversible trapping C_{Tr} ,
140 irreversible or deep trapping sites, C_{Tir} and their respective energies [9,16]. In the specific
141 case of grain-boundaries, the hydrogen concentration profile maps were obtained from time-
142 of-flight SIMS measurements (TOF.SIMS5, ION-TOF GmbH, Germany) to elucidate the
143 local distortion around GB impact on hydrogen segregation in polycrystalline structures [21].
144

145 The thermodynamic and elastic properties of nickel with hydrogen and/or vacancies were
146 determined from *ab initio* calculations using the framework of the density functional theory
147 (DFT) implemented in the Quantum ESPRESSO package [22]. Details about our calculations
148 and convergence details can be found in our previous studies [14, 23-26]. First, we determine
149 the H and vacancy concentrations at thermodynamic equilibrium with a H_2 gas at the
150 temperature T and secondly the solubility and the jump rates of H in the bulk Ni lattice and in

151 the vicinity of a vacancy core are evaluated in relation with the lattice elastic distortion. For
 152 other defects, such as dislocations and grain boundaries, atomistic simulations based on the
 153 energy minimization method were performed using the LAMMPS code [27], to compute the
 154 structural and defect properties of nickel grain boundaries [17,18,29] and edge dislocation
 155 dipoles [30]. The EAM potential developed by Angelo *et al.* [28] for pure Ni and Ni-H
 156 systems has been used for this study. The hydrogen insertion sites that can be found in the GB
 157 region or dislocation edge dipole region were examined in terms of energy, excess volume
 158 and local stress state [17].
 159

161 2 - Thermodynamic framework

162
 163 The influence of the elastic stress/strain field on the chemical potential for solute is treated in
 164 the basis of a continuum approach with a thermodynamic framework [15,19, 31, 32].
 165 According to the elastic work associated with the incorporation of the solute from the infinity
 166 to the solid, the modification of the chemical potential in an isothermal state can be expressed
 167 as :

$$169 \mu_H(C_H, \bar{\sigma}) = \mu_0(C_{H0}, 0) + k_B T \ln \left(\frac{C_H}{1-C_H} \right) - \Omega_a \sigma_{ij} \varepsilon_{ij}^s + \left[\frac{1}{2} S_{ijkl} \sigma_{ij} \sigma_{kl} + \frac{1}{2} \left(\frac{\partial S_{ijkl}}{\partial C_H} \right) \sigma_{ij} \sigma_{kl} \right] \Omega_a$$

170 (1)

171
 172 with Ω_a is the atomic volume of the host matrix, μ_0 and C_{H0} the corresponding standard state
 173 chemical potential and the concentration, σ_{ij} the stress tensor, S_{ijkl} the compliance and ε_{ij}^s the
 174 strain tensor associated with the insertion of a solute in the crystal lattice, respectively. The
 175 first term of equation (1) is the H standard state with the absence of stress, the second one is
 176 the solute distribution entropy, the third term is the elastic strain energy associated with the
 177 insertion of a solute, and the fourth term is the mechanical energy in the system and its
 178 modification in relation with the impact of solute on the compliance tensor S_{ijkl} . In the
 179 absence of external stress, the stress state only depends on the elastic energy from the
 180 insertion of a solute in the crystal lattice (self-stress) or directly on elastic storage energy
 181 associated with the “defects” (precipitates, grain boundaries, vacancies, dislocations).
 182 Considering that the other contributions can be neglected, we can get a simplified form of the
 183 chemical potential:

$$184 \mu_H(C_H, \bar{\sigma}) = \mu_0(C_{H0}, 0) + k_B T \ln \left(\frac{C_H}{1-C_H} \right) - \Omega_a \sigma_{ij} \varepsilon_{ij}^s \quad (2)$$

185
 186
 187 Considering the problem of hydrogen incorporation into a crystal lattice is reduced to a
 188 spherical inclusion in a homogeneous medium (centrosymmetric problem) with anisotropic
 189 elastic properties, the strain induced by the incorporation of solute is expressed as $\varepsilon_{ij}^s =$
 190 $\frac{1}{3} \varepsilon_H \delta_{ij} = \frac{\bar{V}_H}{3\Omega_a} \delta_{ij}$. The partial volume of hydrogen \bar{V}_H (m³/at.) is a measurement of the volume
 191 variation induced by hydrogen insertion into the interstitial site. According to experimental
 192 data and DFT-based atomistic calculations, \bar{V}_H for nickel is of the order of $2.1 \times 10^{-3} \pm 10^{-4}$
 193 nm³/at [24, 33, 34]. The first order impact in centrosymmetric case of the elastic field
 194 associated with defect is then reduced to:

$$196 \mu_H = \mu_0 + k_B T \ln \left[\frac{C_H}{1-C_H} \right] + \sigma_m \bar{V}_H \quad (3)$$

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with σ_m the hydrostatic stress associated with lattice strain induced by the defect. On the other hand, the evaluation of the self-stress including the hydrostatic strain associated with a variation in the composition ΔC_H and a component resulting from stress applied by the crystal lattice on the expansion volume, allows to a chemical potential which takes the following form:

$$\mu_H(C_H) = \mu_0 + k_B T \ln \left[\frac{C_H}{1-C_H} \right] - \frac{Y}{9} \bar{V}_H^2 \Delta C_H \quad (4)$$

Y is an elastic parameter equal to $-\frac{2E}{(1-\nu)}$ (E is the Young's modulus, ν is the Poisson's ratio) when considering isotropic elasticity and takes a more complex form when considering anisotropic elasticity. The latter case depends on the orientation and the components of the stiffness tensor (see the references [15,19] for more details). Consequently, the "apparent hydrostatic self-stress" can be expressed as: $\sigma_m = -\frac{Y}{9} \bar{V}_H \Delta C_H$. This approach can be extended to any other centrosymmetric "defects" (vacancy clusters, spherical precipitate, ...) as $\Delta \mu_H = \sigma_m \bar{V}_d$ and $\sigma_m = -\frac{Y}{9} \bar{V}_d \Delta C_d$ with C_d and \bar{V}_d are the concentration of these defects and their partial volume, respectively.

Based on continuum approach associated with equations (3) and (4), we can reconsider the set of equations which govern the diffusion and the solubility at stationary state first and secondly their impact on the apparent elastic properties (elastic properties of an equivalent homogeneous medium).

3 - Some orders of hydrostatic stress and their impact on apparent hydrogen solubility

For an open system equilibrated with an external system (hydrogen flux equal to zero) and in the Boltzmann approximation, the elastic model derived from the modification of the chemical potential of hydrogen due to the action of a hydrostatic stress allows to define the ratio of the local solubility of a solute under a hydrostatic stress field (C_H) to the solubility of the solute in a stress-free crystal (C_0) at the temperature T [14]:

$$\frac{C_H}{C_0} = \exp \left[\frac{\sigma_m \bar{V}_H}{k_B T} \right] \quad (5)$$

At room temperature, the theoretical impact of hydrostatic stress on the apparent solubility ratio is illustrated in figure 1. An increase of one decade of hydrogen solubility can be predicted for an hydrostatic stress of 5 GPa. The self-stress contribution on the solubility ratio can be neglected because the self-stress stays lower than 5 MPa for an hydrogen content of 7 wppm (experimental related solubility at room temperature and atmospheric pressure, 4.15×10^{-4} H/Ni) which allows to a solubility ratio equal to 1.003. Near a basic crystalline defects, the hydrostatic stress induced is in the GPa order range : on the order of 0.5 GPa for octahedral site near a vacancy [14], 1 GPa for interstitial site close to the edge dislocation core [35] and 30 to 50 GPa for some octahedral site in a grain boundary [17, 64, 65] (refer to publications for the calculation of stresses and their location). In all these cases, these values correspond to a maximum obtained for one site and cannot be directly extended at a long-range scale without integrate the concentration of defects or solute insertion sites.

243 A recent work, based on DFT calculations and isotropic models [14], have questioned the
244 implications of the elastic strain of the interstitial sites on the hydrogen solubility near
245 vacancy in nickel. It was highlighted that a compressive hydrostatic stress acting, on the first
246 neighboring sites except the octahedral and tetrahedral sites at a position to the center of a
247 vacancy of respectively 0.3948 nm for octahedral site and 0.3848 nm for tetrahedral site. For
248 both sites a local dilatation δ equal to 0.24% and 0.33% was identified and conduces to a
249 solubility ratio equal respectively to 1.4 and 1.6. This last effect stays moderate and can
250 partially compensate by electronic contribution (“chemical contribution”) [25]. However, for
251 a larger size centrosymmetric defects (cluster of vacancies or semi-coherent precipitates), as
252 sources of long-range residual stress/strain, the intrinsic properties of the solid can be
253 modified (for the diffusion and the elastic properties see the next section). Specifically, it was
254 related recently by TEM observations that the incorporation of hydrogen in nickel single
255 crystal induces the formation of vacancy clusters with a spherical volume of 4.2 nm³ (with
256 T=300 K, C_H=7 wppm and C_V=0.15 x C_H) [15, 26]. This size corresponds to a cluster of
257 around 1000 vacancies which can induce, with the isotropic approximation, a hydrostatic
258 stress in the order of 1.3 GPa ($\sigma_m = -\frac{\gamma}{9}\bar{V}_d \Delta C_d$) and consequently an increase of the
259 apparent solubility by a factor of 2.5.

260

261 For the precipitates, the excess of solubility is mainly related to the elastic strain
262 accommodation associated to strain incompatibility. This last one results to the difference
263 between interatomic distances associated with the precipitates and the matrix, and it is a
264 function of the degree of coherence δ of the precipitate/matrix and the volume fraction f_v of
265 precipitate. The order of magnitude of the excess of solubility is 6 for M_xC_y carbides and 300
266 for TiC precipitates in martensitic steel in agreement with experimental data [20, 36]. For
267 nickel base alloys, our recent experimental work with semi-coherent γ' precipitates in
268 Waspaloy and Inconel 718 alloys relates an apparent solubility ratio which can be reach 3.25
269 and 2.36, respectively [37]. Consequently, a large hydrogen content can be stored with the
270 addition of a semi-coherent precipitates. For the other configurations, the chemical and
271 electrical effect (bond change) is also have contribution on ground-state energy around
272 precipitate (short range interaction) in relation with trapping processes (see as example
273 reference [63]).

274

275 Strain incompatibilities between some microstructural components can be also a source of
276 residual stresses which potentially modify the local solubility of hydrogen. When considering
277 heterogeneous distributions of dislocations, long-range internal stresses can develop and
278 induce hydrostatic stresses with an amplitude in the order of 0.2 GPa near dislocations walls
279 which allows to an excess of solubility ratio equal to 1.3 [30,38]. The direct relation between
280 long-range internal stresses and the dislocation density suggests a direct proportionality
281 between the excess of the solubility and the dislocation density. However, the experimental
282 data relate only an increase of the apparent solubility of 8% for quenched and tempered
283 martensitic steels [36] and 4% for a density of 2.5x10¹⁴ m⁻² for nickel single crystal deformed
284 in simple tension along the <100> axis [8]. This result highlights the difficulty to extend a
285 local effect to a global measurement, i.e., the impact of the transition scales which integrates
286 the length scale of the elastic strain (from 100 nm to 1 μ m for heterogeneous distribution of
287 dislocations). In the other part, the incompatibility of deformation between grains will also
288 result in substantial hydrostatic stresses (in the order of 0.6 GPa [39]) which can lead to an
289 increase of the local solubility to a factor 1.4.

290 An inclusion state and/or two phases microstructure can induce large stress concentrations
291 near interfaces following a fabrication process and/or under mechanical loading. For instance,

292 in the case of α/β titanium alloys or duplex austeno-ferritic stainless steels, the hydrostatic
 293 pressures can reach 1.6 GPa [40,41], for a nodular cast iron is of the order of 0.8 GPa [42], for
 294 hydrides is of the order of 0.6 GPa [40, 43] and for oxides and/or sulphides of Manganese is
 295 of the order of 0.2 GPa [44]. Consequently, the solubility ratio in these different situations can
 296 be reach a maximum value around 2.3.

297 To conclude, all "macroscopic defects" or particular geometries (cavity, crack, reduction of
 298 section, ...) will be the reason for stress concentration that can lead to hydrostatic pressures of
 299 several GPa. These hydrostatic pressures directly affect the partial molar volume of hydrogen
 300 of metals and alloys, thus providing a non-negligible elastic energy which can promote
 301 hydrogen solubility.

304 **4 - The impact of self-stress and point defect stress on the apparent diffusion coefficient**

306 The hydrogen flux and the apparent diffusion coefficient can be derived from chemical
 307 potential using first and second Fick's laws. According to equations (3) and (4), the hydrogen
 308 diffusion properties result to a chemical potential formalization that includes local
 309 concentration and hydrostatic stress arise to self-stress and stress induced by point defects.
 310 Based on the thermodynamics of irreversible processes, the phenomenological description of
 311 the solute diffusion is described by assuming a linear relationship between the flux and the
 312 driving forces, which are the concentration and the stress gradient in this present case. The
 313 relationship is expressed by an equation related to the gradient of the chemical potential, $\nabla\mu$
 314 [45,46]:

$$316 \quad \bar{J} = -\bar{L} \cdot \nabla\mu \quad \text{with} \quad \bar{L} = \frac{\bar{D} \cdot C_H}{k_B T} \quad (6)$$

318 \bar{D} is the diffusion tensor, k_B is the Boltzmann constant and T is the temperature. The
 319 combination of equations (3) and (6), gives a relationship between the hydrogen flux and the
 320 apparent diffusion coefficient for a stress state [15,19]:

$$322 \quad \bar{J} = -\bar{L} \cdot \nabla\mu = \bar{L} \cdot \frac{\partial\mu}{\partial C_H} \nabla C_H = -D \left[1 + \frac{Y(\bar{n})}{9} \bar{V}_H^2 \frac{C_H}{k_B T} \right] \nabla C_H = -\bar{D}_{app} \nabla C_H \quad (7)$$

324 Consequently the apparent diffusion coefficient $D_{app}(\bar{n})$ in the direction \bar{n} is given as :

$$325 \quad D_{app}(\bar{n}) = D[1 + \beta C_H] \quad \text{and} \quad \beta = \left[\frac{Y(\bar{n}) \bar{V}_H^2}{9 k_B T} \right] \quad (8)$$

326 This last equation clearly highlights an explicit effect of the solute concentration to the
 327 diffusion. Additionally, considering the elastic anisotropy, the variation of $Y(\bar{n})$ as a function
 328 of the crystallographic orientation $\bar{n} = [hkl]$, allows a direct impact on the apparent diffusion
 329 coefficient [15]. Figure 2a illustrates these both effects in the case of the hydrogen self-stress
 330 in nickel single crystal. The order of the self-stress implication stays lower than 0.1 for 35
 331 wppm (0.025 for 7 wppm) but highlights clearly the potential implication of the hydrogen
 332 concentration and the possibility to obtain an anisotropic diffusion behavior in relation with
 333 elastic anisotropy.

334 Experimental data of this anisotropy was initially reported by Brass *et al.* for two
 335 crystallographic orientations ($\langle 001 \rangle$ and $\langle 110 \rangle$) [47]. More recently, a significant effect of
 336 crystallographic orientation on hydrogen diffusivity was observed by Li *et al* for several

337 crystallographic orientations: $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 219 \rangle$ and $\langle 111 \rangle$ with a hydrogen concentration of
338 7 wppm [15]. According to the theoretical approach hydrogen diffusion is the fastest along
339 the $\langle 111 \rangle$ orientation and the slowest along the $\langle 100 \rangle$ orientation. As reported by Li *et al.*, the
340 experimental data, the apparent diffusion coefficients could be ranked as follows: $D_{\langle 111 \rangle} >$
341 $D_{\langle 110 \rangle} > D_{\langle 219 \rangle} > D_{\langle 100 \rangle}$ for a same hydrogen content of 7 wppm [15] ($D_{\langle 111 \rangle} = 17.5 \times 10^{-14} \text{ m}^2/\text{s}$,
342 $D_{\langle 110 \rangle} = 11.2 \times 10^{-14} \text{ m}^2/\text{s}$, $D_{\langle 219 \rangle} = 9.3 \times 10^{-14} \text{ m}^2/\text{s}$ and $D_{\langle 100 \rangle} = 7.1 \times 10^{-14} \text{ m}^2/\text{s}$). The impact of
343 crystallographic orientation on apparent diffusion coefficient is clearly higher than the one
344 predicted by Eq. 8 ($\Delta D/D = D_{\langle 111 \rangle}/D - 1$ for the orientation $\langle 111 \rangle$ is equal to 4 with
345 $D = 3.5 \times 10^{-14} \text{ m}^2/\text{s}$ [25, 48, 49] instead of the modeling prediction: eq. (8) with a value around
346 0.02 for 7 wppm, see figure 2a). Moreover, the impact of the hydrogen content on the
347 apparent diffusion coefficient has been experimentally questioned for the orientation $\langle 001 \rangle$ in
348 nickel single crystal [15,19]. A linear relation between D_{app} and C_H is related by the authors
349 which allows an experimental value of β equal to 0.29 instead of the one predict by the model
350 equal to 0.01 (eq. 8 and figure 2a). The discrepancy between the model and experimental data
351 motivates to reconsider the origin of the impact of solute content on the apparent diffusion
352 coefficient. Based on the fact that hydrogen content promotes the formation of vacancies and
353 vacancy clusters [15,16,26,33,50], we have recently proposed that D_{app} is affected more by the
354 elastic stress field induced by vacancy clusters than the solute itself [15].
355

356 From a thermodynamic point of view, DFT calculations have demonstrated that hydrogen
357 decreases the formation energy of vacancies in nickel [24,51,52]. This result is also supported
358 by experimental data reported by Fukai *et al.* [33,50], Oudriss *et al.* [16], Li *et al.* [15] and
359 Hachet *et al.* [26] obtained in Ni single and poly-crystals. Hydrogen incorporated into nickel
360 matrix induces a quite linear increase in vacancy concentration ($C_{vac} = k \times C_H$). A lower value
361 of k for polycrystalline nickel ($k=0.15$) than $\langle 001 \rangle$ oriented nickel single crystal ($k=1$)
362 indicates a significant contribution of the grain boundary to vacancy concentration. Moreover,
363 recent TEM observations relate the formation of vacancy clusters with an average spherical
364 volume of 4.2 nm^3 for 7 wppm of hydrogen in nickel single crystal [26]. Following these
365 observations, equations (2), (4) and (8) are reconsidered to take into account the elastic
366 stress/strain fields arisen from vacancy clusters. According to Li *et al.*'s [15], the apparent
367 diffusion coefficient is determined as a function of the number of vacancies into a cluster n_v
368 and the partial molar volume of vacancy \bar{V}_{vac} :
369

$$370 \quad \bar{D}_{app}(\bar{n}) = D[1 + \beta C_H] \quad \text{with} \quad \beta = k \left[\frac{Y(\bar{n})(n_{vac} \bar{V}_{vac})^2}{9k_B T} \right] \quad (9)$$

371
372 As illustrated in figure 2b, the impact of a cluster of vacancies on D_{app} is more significant than
373 the solute itself and reproduce our experimental data (hydrogen diffusion anisotropy and
374 diffusion dependence on solute content) for a cluster of 40 vacancies and a partial molar
375 volume of vacancy \bar{V}_{vac} equal to $2.25 \times 10^{-6} \text{ m}^3/\text{mol}$ [15,24]. If we obtain a same order for the
376 different physical parameters for the continuum thermodynamic model and the experiment,
377 this approach remains limited because we do not consider self-interstitial and we have
378 assumed that elastic coefficients are constant and that solute content doesn't modify the
379 electronic contributions to the energy of the system.

380 To bypass this difficulty and separate chemical and mechanical contributions, we have
381 recently computed the components of the elasto-diffusion tensor d_{ijkl} [53] from first principles
382 calculations of the elastic dipole tensors P_{ij} of hydrogen in the interstitial sites of perfect
383 lattice nickel and at the saddle point along the migration path [54]. We have considered
384 vacancies and vacancy clusters, but also the solute itself and self-interstitial, as sources of

385 residual strain in the solid. This last work allows to formalize the impact of stress/strain field
 386 of any centrosymmetric defects on the hydrogen diffusion.

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5 - Some contributions of self-stress on the hydrogen segregation at grain-boundaries

390 The contribution of self-stress on hydrogen diffusion and segregation processes on non-
 391 defective lattice has been discussed in the previous sections. More recently, the question of
 392 stress/strain energy contribution on the segregation energy of hydrogen on the defective
 393 lattice is an interesting challenge [17-19,55]. The grain boundaries offer the opportunity to
 394 have a large variety of situations associated with the local distortion of lattice. Following this
 395 approach, we have studied grain boundaries differentiated by their energy and excess volume
 396 [17-19,29] to explore the diversity of GBs in nickel reported by Olsmted *et al.* [56]. Atomistic
 397 simulations based on the energy minimization method were performed using the LAMMPS
 398 code to compute the structural configurations of GBs and segregation energy of hydrogen
 399 [17-19]. Based on the fact that the insertion of an atom in lattice site creates a hydrostatic
 400 dilatation (hydrostatic strain) and a distortion of the volume (deviatoric strain), we have
 401 managed the evaluation of both at atomistic scale. The calculation of the elastic dipole tensor
 402 P_{ij} according to defect force method [17, 27, 62] and the hydrogen atomic volume V_H at the
 403 segregation site in different GBs offer the opportunity to question the impact of elastic energy
 404 associated with hydrogen insertion on adsorption energy (or insertion energy) E_H^{Ins} and
 405 segregation energy E_H^{Seg} . Thus, the atomic stress σ_{ij} and the elastic strain energy E_{el} by unit
 406 volume induced from the insertion of the hydrogen interstitial are related to the lattice-defect
 407 elastic tensor [17]:

408

$$409 \sigma_{ij} = \frac{P_{ij}}{V_H} = \sigma_m \delta_{ij} + \sigma_{ij}^d \quad \text{and} \quad E_{el} = E_{el}^d + E_{el}^m = \frac{1}{2B} (\sigma_m)^2 + \frac{1}{2G} (\sigma_d)^2 \quad (10)$$

410

411 where σ_m and σ_d are respectively the hydrostatic stress and the deviatoric stress defined as
 412 Von Mises equivalent stress. B and G are the bulk and shear modulus respectively. E_{el}^m and
 413 E_{el}^d represent the dilatational and distortion energies. The insertion energy (or the adsorption
 414 energy) of a hydrogen atom in the nickel lattice E_H^{Ins} and the segregation energy relative to
 415 the octahedral site E_H^{Seg} are given by:

416

$$417 E_H^{Ins} = E_{Ni+H}^{Tot} - E_{Ni}^{Tot} - \frac{1}{2} E_{H_2} \quad \text{and} \quad E_H^{Seg} = (E_{GB+H}^{Tot} - E_{GB}^{Tot}) - (E_{Ni+H}^{Oct} - E_{Ni}^{Tot})$$

418 (11)

419

420 where E_{Ni+H}^{Tot} is the total energy of nickel lattice with a hydrogen atom, E_{Ni}^{Tot} is the total
 421 energy of nickel lattice without hydrogen atom and E_{H_2} is the chemical potential of the
 422 molecular hydrogen. E_{GB+H}^{Tot} is the total energy of GB with a hydrogen atom, E_{GB}^{Tot} is the total
 423 energy of GB and E_{Ni+H}^{Oct} is the total energy of the nickel lattice with a hydrogen atom at the
 424 octahedral site. E_H^{Ins} expresses the local modification of energy instead of E_H^{Seg} which relates
 425 the global evolution of the energy of the GB. The evolution of the hydrogen energy E_H^{Ins} as a
 426 function of the strain energy E_{el} from the insertion of a hydrogen atom is illustrated in figure
 427 3a. Two distinct linear regimes are observed with a transition around a strain energy density
 428 about 2 GPa. The total strain energy is dominated by the hydrostatic stress for the first linear
 429 regime ($E_H^{Ins} > -0.5$ eV and $V_H < 6.6 \text{ \AA}^3$) while the other linear regime ($E_H^{Ins} < -0.5$ eV and V_H
 430 $> 6.6 \text{ \AA}^3$) is due to the contribution of the deviatoric stress. The hydrostatic stress is

431 significant for a low volume ($V_H < 6.6 \text{ \AA}^3$) such as an octahedral site in perfect fcc lattice. At
432 these cubic form or similar sites, the deviatoric stress is low due to the small distortion.
433 However, for high volume sites, the hydrostatic stress decreases and, at the same time, the
434 distortion component of the stress is more significant than the hydrostatic volume change
435 [17]. We examine now the correlation between the segregation energy E_H^{Seg} and the strain
436 energy E_{H_2} from the insertion of a hydrogen atom (figure 3b). For the first regime defined
437 previously (predominance of hydrostatic strain energy and low volume V_H), a linear relation
438 is obtained which clearly highlights the impact of hydrostatic stress on segregation process in
439 accordance with previous works [17,55]. However, for the second regime ($E_{el} < 2 \text{ GPa}$, $V_H >$
440 6.6 \AA^3), we observe some dispersion in our data. This last result illustrates a possible impact
441 of the long range elastic contribution as it has been recently demonstrated [18,19]. Future
442 prospects on the subject certainly will highlight the importance to distinguish the contribution
443 of the short and from the long range strain field on solute segregation. Recently, the hydrogen
444 concentration profile maps were obtained from TOF-SIMS measurements [21]. This work
445 highlights for some specific grain-boundaries that a local distortion around GB impacts the
446 hydrogen segregation and consequently supports the idea that long range strain field can be
447 significant on this process.

448
449

450 **6 - Self-stress and point defect stress impact on the elastic properties**

451

452 The hydrogen-enhanced localized plasticity (HELP) model is the one of the most significant
453 interpretation of slip localization in the hydrogen embrittlement context [57-59]. The model is
454 based on the reduction of the energy barrier to dislocation motion through an elastic shielding
455 effect induced by hydrogen or any other point defects [57,26]. According to the modification
456 of the elastic properties of the matrix, this screening effect has been introduced into the
457 classical results obtained with the elastic theory of dislocations on the base of a dimensionless
458 “screening coefficient” of the pair interactions [58,59]. Despite the fact that this fundamental
459 approach allows to partially explain some experimental observations [60], a clarification on
460 the influence of hydrogen on the elastic properties has been only proposed recently [26]. A
461 decrease of the Young's modulus of the $\langle 001 \rangle$ oriented nickel single crystal with hydrogen
462 concentration has been reported [26]. Additionally, a linear relationship between $E_{\langle 001 \rangle}$ and
463 C_H is observed: $E_{\langle 001 \rangle}(C_H)/E_{\langle 001 \rangle}(0) = 1 - A \times C_H$ with a slope A equal to 0.036 [26]. By using
464 the equation of the chemical potential (eq. 3), the diffusion equation of hydrogen and the
465 hypothesis of a hydrogen distribution in equilibrium with the local stress gradients, we can
466 express the elastic strain due to the incorporation of hydrogen or centrosymmetric defect as
467 follows [57,58, 26]:

468

$$469 \quad \varepsilon_{ij} = S_{ijkl}^* = \left[S_{ijkl} + \frac{C_d \bar{V}_d^2}{9k_B T} \right] \sigma_{ij} \quad \text{and} \quad \frac{E_{\langle 001 \rangle}^*}{E_{\langle 001 \rangle}} = \frac{S_{1111}}{S_{1111}^*} = \frac{1}{1 + \left[\frac{C_d \bar{V}_d^2}{9k_B T} \right] E_{\langle 001 \rangle}} \quad (12)$$

470

471 On the concentration range considered of this present work, the last equation can be reduced
472 as :

473

$$474 \quad \frac{E_{\langle 001 \rangle}^*}{E_{\langle 001 \rangle}} = 1 - \left[\frac{E_{\langle 001 \rangle} \bar{V}_d^2}{9k_B T} \right] C_d \quad (13)$$

475

476 Considering only the potential impact of the hydrogen, the vacancies and the cluster of
477 vacancies in the present discussion, we rewrite this equation to include the relation between

478 vacancies concentration and hydrogen content ($C_{V_{ac}}=k \times C_H$) and the definition of C_d and V_d
 479 for the vacancy clusters assuming an additive contribution of monovacancies in an isotropic
 480 spherical cluster ($C_d= C_{V_{ac}}/n_{V_{ac}}$ and $\bar{V}_d = n_{V_{ac}} \times \bar{V}_{V_{ac}}$) introduced by Hachet *et al.* [26] :

$$482 \frac{E_{<001>}^*}{E_{<001>}} = 1 - \left[\frac{kE_{<001>} n_{V_{ac}} \bar{V}_{V_{ac}}^2}{9k_B T} \right] C_H \quad (14)$$

483
 484 Thus, the experimental slope A can be questioned with theoretical approach for which A is
 485 equal to $\frac{E_{<001>} \bar{V}_H^2}{9k_B T}$ and $\frac{kE_{<001>} n_{V_{ac}} \bar{V}_{V_{ac}}^2}{9k_B T}$ for hydrogen and vacancy clusters, respectively. This
 486 analytical model has been improved in figure 4a for different situations. The slope A is
 487 respectively equal to 0.015% for the incorporation of hydrogen, 0.04% for vacancies and
 488 0.036 for a cluster of vacancies with 100 vacancies. This last situation is in agreement with
 489 experimental observations with a slope of 0.036 (blue dot in figure 4a). Our DFT calculations
 490 support the low values obtained for hydrogen and vacancy cases [26]. The size of the vacancy
 491 clusters stays lower than the one observed by TEM [26]. Despite this fact, the prediction of
 492 the analytical model supports the idea that elastic shielding is more dependent of the
 493 superabundant vacancies than of a direct effect of the solute. The clustering of vacancies and
 494 the formation of self-interstitials in the conditions previously described are unknown and need
 495 further investigation.

496 Recently, we have explored the consequence of the modification of the elastic properties with
 497 the addition of hydrogen on edge dislocation dipoles of dislocations (elementary
 498 configuration of PSB) using molecular simulation within EAM potential [30,61]. This
 499 configuration is fundamental to explain the formation and equilibrium of dislocation pattern
 500 obtained under cyclic loading (dipolar walls, persistent slip band, ...). We incorporate
 501 successively different hydrogen content, vacancies and cluster of vacancies in the elastic
 502 fields of each edge dislocations (in a Cottrell's atmosphere defined for a hydrostatic pressure
 503 P larger or equal to 10 GPa), then we evaluated the critical passing stress for different dipole
 504 configurations. In two last situations, we consider that defects do not trap hydrogen.

505 The contribution of hydrogen and defects on the solid solution strengthening is discussed with
 506 the Labusch's theory describing the strengthening due to concentrated, weak obstacles and
 507 diluted, strong obstacles distributions. The figure 4b relates the evolution of the increase shear
 508 stress due to hydrogen and defects. The insertion of hydrogen to create Cottrell atmosphere
 509 leads to an increase of the critical passing stress need to break an edge dislocation dipole in
 510 accordance with the Labusch's theory. In opposite, the presence of vacancies and vacancy
 511 clusters reduces the effect of the solute alone and supports a softening of process. This new
 512 result offers the opportunity to revisit the impact of hydrogen on cyclic behavior and it is nice
 513 illustration of shielding process induces by point defects [30, 61].

514

515

516

517 **Conclusions et prospects**

518

519 A fundamental aspect to elucidate the mechanisms of HE is based on a good knowledge of the
 520 interactions between the solute and different defects of the metal. With a review of our recent
 521 works, we highlight the importance of the elastic energy associated with the solute and the
 522 defects to explain some processes implicated on HE. The confrontation of experiment and
 523 modelling approaches at different scales offers the opportunity to clearly demonstrate a large
 524 contribution of elastic field on the hydrogen solubility, diffusion, segregation and on the
 525 modifications of the elastic properties. Moreover, we illustrate that deviatoric stress
 526 contribution cannot be neglected in some case in opposite to a common consideration in the

527 literature. The possible contribution of chemical component and the separation of this one to
528 other contributions of the energy stays an interesting challenge.

529

530

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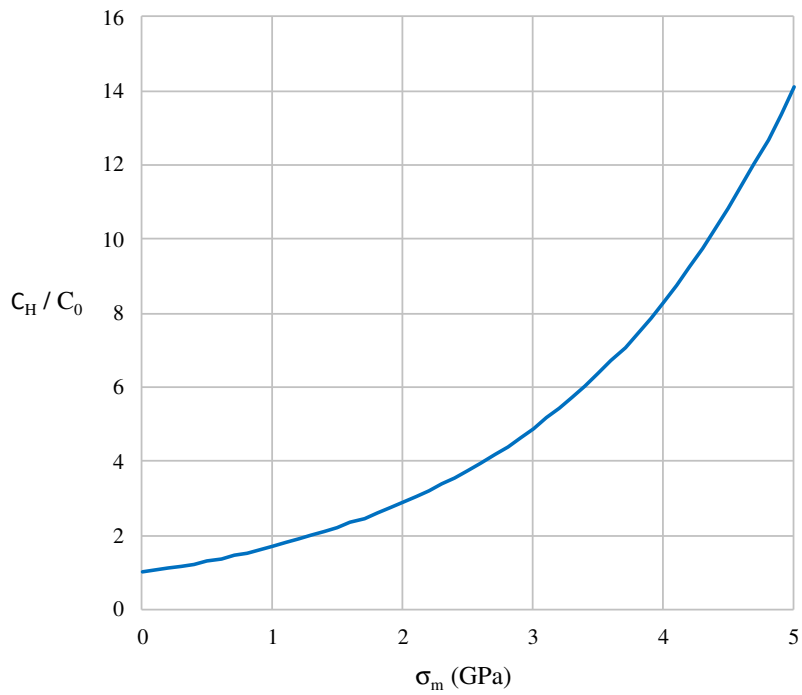


Figure 1 : Evolution of normalized hydrogen content with the hydrostatic stress at T=300K according to Eq. 5.

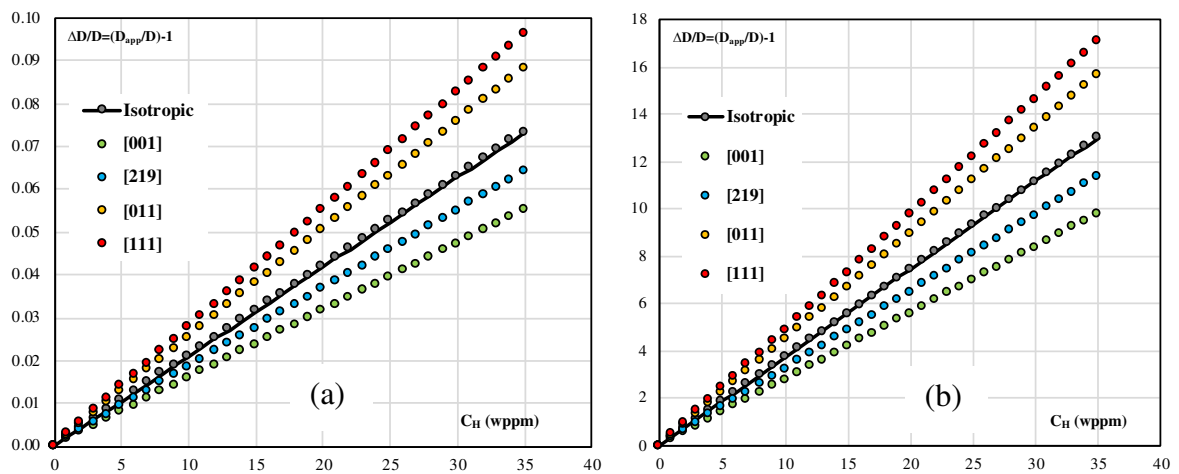


Figure 2 : Relative variation of the diffusion coefficient with the hydrogen content for different crystallographic orientations: solute impact (a) and vacancy clusters (b) [19].

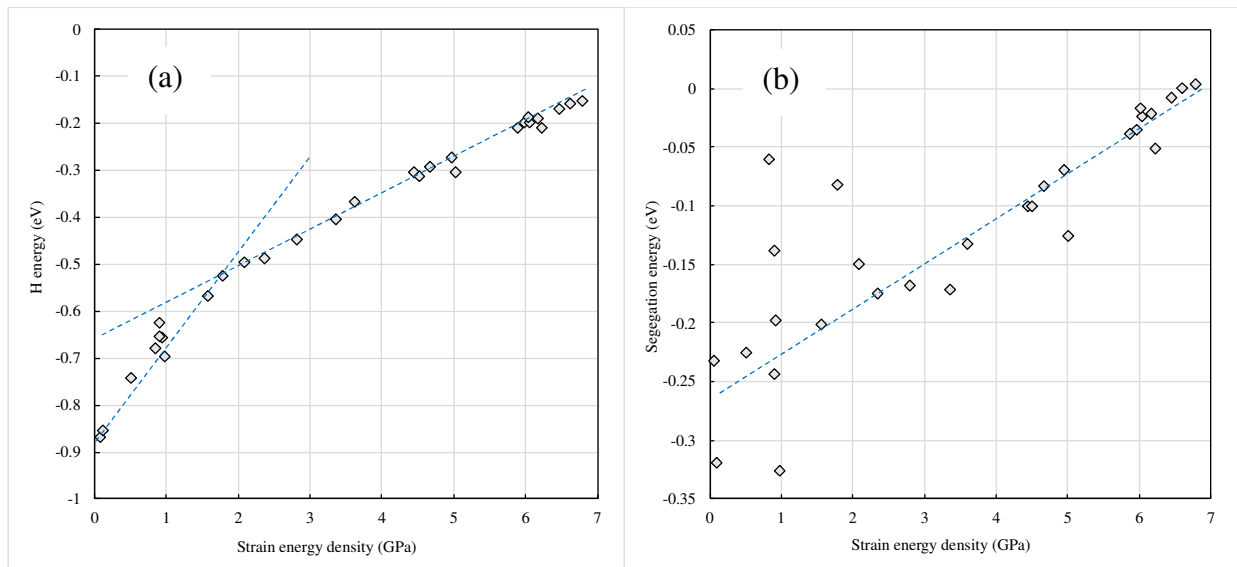


Figure 3 : Hydrogen atom energy (a) and segregation energy (b) as a function of strain energy density in the case of grain boundary in Ni [18,19].

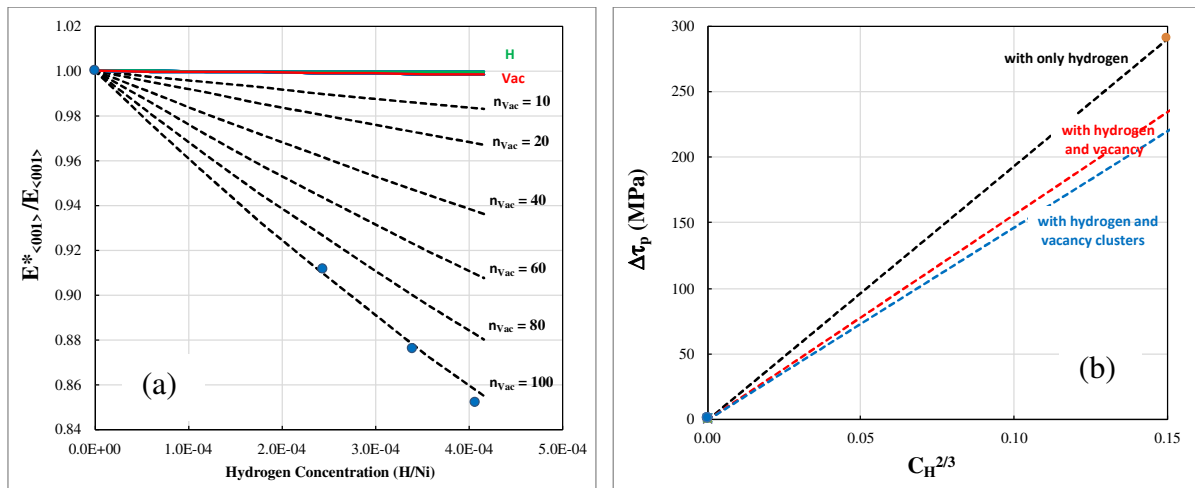


Figure 4 : Decrease of the Ni Young modulus with hydrogen content (blue dots correspond to experimental data) (a) [26]. Increase of the shear stress due to hydrogen content without and with the addition of vacancies and vacancy clusters (b) [30,61].