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Diffusion and trapping of hydrogen due to elastic interaction with η -Ni₃Ti precipitates in Custom 465[®] stainless steel



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HIGHLIGHTS

• The local distribution of hydrogen around η -Ni₃Ti precipitates in C-465 steel is calculated.

- Local compressive and tensile hydrostatic stresses form around these precipitates.
- These give rise to repulsive and attractive interaction, respectively.
- The total effect of coherent precipitates is higher solubility & lower diffusivity.
- The elastic fields also guide the local diffusion of hydrogen in the matrix.

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ABSTRACT

Since it is difficult to determine the local distribution of hydrogen in alloys experimentally, it is desired to estimate it theoretically. Here, the effect of elastic stresses around η -Ni₃Ti precipitates in Custom 465[®] martensitic age-hardenable stainless steel on the distribution of hydrogen and its diffusivity in the matrix is evaluated. A comparison is made to recent experimental data. The calculations are based on the solution of the stresses associated with coherent precipitates in the framework of linear elasticity combined with expressions for hydrogen concentration and diffusion in the presence of stress. Local compressive and tensile hydrostatic stresses form around the η -Ni₃Ti precipitate, resulting in regions of reduced or increased hydrogen concentration, in agreement with the experimental results. The equilibrium concentration of hydrogen due to the elastic stresses decreases with increasing temperature, in conformance with experimentally measured temperature programmed desorption (TPD) data. This quantitatively confirms that the coherency stresses of the precipitate in the peak-aged condition increase the concentration of absorbed hydrogen and decrease its diffusivity.

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Introduction

Structural metals for hydrogen energy and other applications where the metal is exposed to hydrogen might be sensitive to hydrogen embrittlement (HE) [1-6]. As the strength of the steel increases, the amount of allowable diffusible hydrogen content decreases. At these low hydrogen levels, both the hydrogen content and distribution are important [1,2]. A relatively low average hydrogen content of a few ppm has been found sufficient to embrittle high-chromium martensitic steels for nuclear reactors [7].

Much work has been devoted to identify the sites occupied by hydrogen in metals [8-12]. Defects that have been identified as potential trap sites for hydrogen include vacancies, substitutional atoms, dislocations, interfaces and grain boundaries, crack tips, precipitates, inclusions, internal gas bubbles, elastic stress fields, etc. Some of the traps are considered reversible (shallow) traps, while others are considered irreversible (deep) traps, depending on the interaction energy between the hydrogen and the trap. The interaction mechanism may be either chemical attraction or elastic attraction. The trapping of hydrogen at the interface between ferrite and TiC particles, for example, has been attributed either to chemical bonding when the particles are incoherent, or to elastic stress field when the particles are (semi)coherent [13]. Using atom probe tomography (APT), deuterium atoms were detected on the surface of various nano-precipitates: TiC [14], (Ti,Mo)C [15], and vanadium carbides [16].

The attraction of dissolved hydrogen to sources of hydrostatic stress, like dislocations, precipitates, crack tips, internal gas bubbles, etc., may also be related to elastic interactions [17–24]. A tensile hydrostatic component (which leads to a local decrease of the chemical potential) gives rise to attractive interaction, while a compressive hydrostatic component gives rise to repulsive interaction [25]. Hydrogen in reversible traps with low binding energy could act as a source of hydrogen diffusing to the high-stressed site at a crack tip, thus increasing the susceptibility of the steel to HE [15,26,27]. The maximal hydrogen sensitivity of AERMET 100 steel, for example, was detected in the near-peak-aged condition [28,29]. Also, the trapped hydrogen concentration in peakaged Custom 465[®] steel has been found to be higher than in all other conditions [30,31].

Much work has been focused on the interaction of hydrogen with dislocations in steels [e.g., [32-43]] compared to its interaction with precipitates [e.g., [44-50]], although both affect the distribution and diffusivity of hydrogen in metals. In the present work, Carpenter Technology's Custom 465[®] (UNS S46500) [51-59] is chosen as a case study of hydrogen interaction with precipitates. Custom 465[®] is an advanced precipitation hardened (PH) martensitic stainless steel that exhibits a unique combination of high strength, high fracture toughness and good corrosion resistance. Those properties make this steel attractive for load-bearing structural applications such as landing gears. The high strength of this steel is attributed to the hexagonal η -Ni₃Ti precipitates in the soft bcc martensitic matrix. Recently, the total absorption, activation energy for hydrogen release from traps, and

diffusion coefficient of hydrogen in this steel were studied experimentally [30,56,57]. Three thermal conditions of the steel were studied: (1) SA: solution annealed, (2) H900: peakaged at 482 $^{\circ}$ C for 4 h, and (3) H1000: aged at 540 $^{\circ}$ C for 4 h (overaged). Some of the experimental results are summarized in Table 1.

The highest increase in concentration of hydrogen in the interstitial sites and decrease in the effective diffusion coefficient measured at low occupancy of atomic hydrogen in reversible traps, $D_{\rm eff}^{\rm l}$, is evident in the H900 condition compared to the SA and H1000 conditions [30]. In the H900 condition, the ratio between hydrogen diffusivity at high occupancy of atomic hydrogen in reversible traps, $D_{\rm eff}^{\rm h}$, and $D_{\rm eff}^{\rm l}$ was 3.9, approximately twice the ratio for the SA and H1000 conditions, supporting the claim for stronger effects of trapping in the H900 condition.

It should be noted that E_{aT} is the sum of the binding energy of hydrogen trap, E_b, and the activation energy for hydrogen lattice diffusion from a reversible trap, E_{aD} . The latter was measured as 10 kJ mol⁻¹ for AERMET 100 steel [20]. A similar value of E_{aD} was reported for pure α -iron [60]. Hence, a similar value may be assumed for Custom 465® steel. Furthermore, the hydrogen diffusion coefficient in the SA condition of Custom 465[®] in the high trap occupancy state is lower by a factor of ~4000 than the diffusion coefficient of hydrogen in pure α -Fe (7.2 × 10⁻⁵ cm² s⁻¹ [61]), even though they both have a bcc structure. Hydrogen diffusivity may be hindered by two processes: trapping at various sites and tortuosity of the hydrogen diffusion path [62-70]. Tortuosity describes the increase of the diffusion paths due to the complexity of the microstructure and local elastic fields. The last effect is described in the generalized Fick's law that contains the gradient of the hydrostatic stress [71]. The three orders of magnitude lower diffusivity of hydrogen in Custom 465[®] steel in the SA condition compared to pure iron is most likely related to tortuosity of the diffusion paths and not to trapping. Trapping is more likely responsible to the factor of ~4 times lower diffusivity in the H900 and H1000 conditions of Custom

Table 1 – Trapping parameters extracted from electrochemical hydrogen permeation (EP) transients and temperature programmed desorption (TPD) spectra of Custom 465® in the SA, H900 and H1000 thermal conditions [30]. Hydrogen concentrations in interstitial sites, Ci, activation energies of hydrogen desorption (or detrapping), Eat, the effective diffusion coefficients measured at low occupancy of atomic hydrogen in reversible traps, $D^{
m l}_{
m eff}$, i.e. at 20-10% of the steady-state flux during the decay transient where the influence of trapping on the diffusion is most significant, and the effective diffusion coefficients measured at high occupancy of atomic hydrogen in reversible traps, D^h_{eff}, i.e. at the time of 100-90% of the steady-state flux early in the decay transient, which is most similar to lattice diffusion, are summarized.

	SA	H900	H1000
C _i , TPD (wtppm-H)	16 ± 0.2	60 ± 2.7	23.5 ± 1.7
E _{aT} , TPD (kJ∙mol ⁻¹)	61 ± 5	44 ± 10	49 ± 8
$\mathrm{D}_{\mathrm{eff}}^{\mathrm{l}}$, EP ($ imes$ 10 $^{-9}$ cm 2 s $^{-1}$)	8.8 ± 1.1	1.8 ± 0.2	2.7 ± 0.1
D_{eff}^{h} , EP (\times 10 $^{-9}$ cm 2 s $^{-1}$)	18.7 ± 2.5	7.1 ± 0.5	6.1 ± 0.5

 $465^{\ensuremath{\circledast}}$ compared to its SA condition [72]. This paper is focused on the latter observation.

Commonly, the total absorbed hydrogen is measured and reported, employing methods such as TPD/thermal desorption spectroscopy (TDS) [73,74] or hydrogen analyzers. Even the use of more advanced techniques with higher locality, resolution and sensitivity, such as secondary ion mass spectrometry (SIMS) [75] and APT [14-16,76] has not resulted in experimental mapping of the local distribution of hydrogen around precipitates. The EP technique, on the other hand, only allows measuring the subsurface concentration of atomic hydrogen in interstitial lattice sites and the hydrogen concentration distribution across the thickness of the specimen [46,56,57,61,62,64,72]. Therefore, since it is difficult to determine the local distribution of hydrogen around precipitates experimentally, it is desired to estimate it theoretically. Many numerical simulations have assessed hydrogen trapping around defects and HE based on coupled hydrogen diffusion/solid mechanics approaches. For example, Carrasco et al. [77] simulated numerically the effect of reversible and irreversible hydrogen trapping on crack propagation in API 5CT P110 steel under cathodic overprotection, using a model based on a synthesis of fracture mechanics and continuum damage mechanics. Eliaz et al. [78] developed a coupled diffusion/fracture mechanics approach to describe the expansion of high-pressure hydrogen bubbles and propagation of cracks between them in the absence of external loads in an iron-base metallic glass. Jemblie et al. [79] presented a coupled diffusion and cohesive zone modelling approach for numerically assessing HE of steels. Yet, we are not aware of any numeric model that allows estimating the effect of elastic stresses around precipitates in steels on the distribution of hydrogen around the precipitates and its diffusivity in the matrix.

The aim of this study is thus to estimate theoretically the effect of local elastic stresses around coherent $\eta-Ni_3Ti$ precipitates in Custom 465[®] PH martensitic stainless steel on the steady-state distribution of hydrogen around individual precipitates and its diffusivity and solubility in the steel. The sum of the calculated local concentrations of hydrogen around precipitates is compared with the experimental bulk absorbed hydrogen concentration and hydrogen diffusivity in order to test the hypothesis that the elastic interaction is responsible for the enhanced hydrogen absorption in the peak-aged state of this steel.

Experimental

Samples from solution and aged conditions were prepared for transmission electron microscopy (TEM) by first mechanically polishing followed by ion-milling to electron transparency using a Gatan Precision Ion Polishing System (PIPS). JEOL JEM-2100F transmission electron microscope (TEM) equipped with an energy-dispersive X-ray spectrometer (EDS) system model JED 2300T was used to observe the microstructure.

Crystallographic analysis

TEM observations reveal rod-shaped $\eta-Ni_3Ti$ precipitates with aspect ratio 1:3 between the longitudinal and transverse

axes of the precipitate, with the long axis being parallel to the <111> directions of the matrix (Fig. 1a and Fig. 1b). Rod-shaped η -Ni₃Ti precipitates are also observed in Maraging steels [80,81]. The orientation relationship between the hexagonal precipitates (a = 0.5101 nm and c = 0.8307 nm) [80] and the bcc lath martensite (a = 2.878 nm [81]) was found to conform to Kurdjumov-Sachs relation [80–82], see Fig. 1:

$$(111)_{\rm m}/((11\overline{2}0)_{\rm Ni_3Ti}, (011)_{\rm m}/((0001)_{\rm Ni_3Ti}))$$
 (1)

In order to keep the Kurdjumov-Sachs relation between the hexagonal basal plane of η -Ni₃Ti and the irregular hexagonal (110) plane of the bcc matrix, the [1210] and [2110] directions of the η -Ni₃Ti are found to be rotated by 5.26° relative to the near-(111) directions of the matrix [83], as shown in Fig. 1e.

The misfit strain calculated in the coordinate axes $x = [\overline{1}11], y = [\overline{1}1\overline{2}], z = [110]$ is:

$$\eta - \text{Ni}_3 \text{Ti} / \text{matrix}: \tilde{e}_{xyz} = \begin{pmatrix} 0.02257 & -0.0904 & 0\\ -0.0904 & -0.0606 & 0\\ 0 & 0 & 0.0198 \end{pmatrix}$$
(2)

The misfit strain in the bcc coordinate system (x' = [100], y' = [010], z' = [001]) is found by the transformation equation of a second-rank tensor:

$$\eta - \text{Ni}_3 \text{Ti} / \text{matrix} : \tilde{\epsilon}_{\text{xyz'}}^{\text{T}} = \begin{pmatrix} 0.0499 & -0.0301 & -0.0064 \\ -0.0301 & 0.0499 & 0.0064 \\ -0.0064 & 0.0064 & 0.1181 \end{pmatrix}$$
(3)

Those strains would have occurred if the formation has taken placed in free space. In a rigid solid matrix, however, the precipitate is constrained to the shape of its original region and, hence, it is loaded to maximum stresses $-C_{ijkl} e_{kl}^{T}$. In a softer matrix, the precipitate is partially relaxed. As the precipitates approach their stress-free shape, the stresses in the precipitate decrease while the stresses in the matrix increase. Mechanical equilibrium is achieved when the tractions of the stress at the interface are equal in the precipitate side and the matrix side [84]. The displacements in the material in this equilibrium state are given in Eq. (5) for a homogenous system, namely, when the elastic constants of the matrix and precipitate are the same. For an ellipsoid-shaped precipitate, Eshelby found the equivalent precipitate method to calculate the strains in inhomogeneous systems [84].

The equivalent transformation strain derived from the sets of elastic moduli of the matrix and precipitate (see next section) is:

$$\tilde{\varepsilon}_{xyz}^{\text{T,eq}} = \begin{pmatrix} 0.0868 & -0.0288 & -0.0026\\ -0.0288 & 0.0692 & 0.0093\\ -0.0026 & 0.0093 & 0.1613 \end{pmatrix}$$
(4)

These transformation strains were used in the following calculations.

Calculation method

The displacements u_i due to a homogeneous precipitate has been expressed as a Fourier series in [85,86]:

$$u_{i}(\mathbf{x}) = \sum_{\mathbf{k}} \left(C_{klmn} e_{mn}^{T} \theta k_{1} \mathcal{Q}_{ik} \right) \exp(i\mathbf{k} \cdot \mathbf{x})$$
(5)



Fig. 1 – (a) TEM image of precipitates in a sample aged at 560 °C for 4 h, acquired at a zone axis $[112]_m$. Dark field (DF) image acquired at the $(22\overline{4}0)$ reflection of one variant of η -Ni₃Ti precipitates [57]. (b) TEM electron diffraction pattern at zone axis $[112]_m$, demonstrating the Kurdjumov-Sachs crystallographic relation between the precipitate and matrix [57] and that the precipitate's long axis is parallel to the $[1\overline{1}1]_m$ direction. (c) A schematic rod-shaped precipitate in the [111] preferred orientation on the (101) plane. (d) The irregular hexagonal structure of atoms in the {110} planes observed in three bcc unit cells. (e) Schematic illustration of the orientation relation between the hcp precipitate η -Ni₃Ti and the bcc martensite matrix. Close-packed planes are mutually parallel. The close-packed direction $[11\overline{2}0]_{hcp}$ is parallel to the close-packed direction [111]_{bcc}, causing shear and normal strains in the perpendicular direction.



Fig. 2 – (a) A map of the hydrostatic stress around a precipitate with c/a = 0.33 on the $(1\overline{10})$ plane. *a* is the short radius and c is the long radius. X and Y are the black axes defined in Fig. 1e. The stress levels are given in units of GPa. The tensile stresses are marked by black digits; the compressive stresses are marked in red. (b) Profiles of the elastic interaction energy between the precipitate and hydrogen atoms at the tensile (black line) and the compressive (red line) regions across the hydrostatic stress map. *d* is the distance measured from the matrix/precipitate interface to the hydrogen atom. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Summation is taken over the reciprocal space vectors **k**. Ω is the Fourier transform of the Green function, defined by $\Omega_{ij}^{-1}(\mathbf{k}) = C_{ijmn}k_mk_n$, and C_{klmn} are the elastic constants. The Einstein summation convention is assumed. ε_{mn}^{T} are the transformation strains given in Eq. (4). $\theta(\mathbf{r})$ is the shape function of the precipitate, defined as unity in the precipitate and zero in the matrix. We approximate the shape of the precipitate (Fig. 1a) by an ellipsoid with aspect ratio 1:3 (Figs. 1c and 2a). The elastic strains are derived from Eq. (4) by the compatibility equation, and the stresses are related to the strains by Hooke's law. All the sums were calculated by an algorithm of Fast Fourier Transformation (FFT) with 256³ terms.

The elastic constants representing the bcc matrix were taken as the constants of pure iron [87]: $C_{11} = 232$ GPa, $C_{12} = 136$ GPa, $C_{44} = 117$ GPa. The properties of η -Ni₃Ti are taken from [88]: $C_{11} = 344$ GPa, $C_{12} = 122$ GPa, $C_{13} = 94$ GPa, $C_{33} = 345$ GPa, $C_{44} = 87$ GPa.

The interaction energy E_{int} between the precipitate and hydrogen atoms is calculated as the total work done by a hydrogen atom to arrive from infinite distance to the site r against the local stress σ_{ii}^{p} due to the precipitate [84]:

$$E_{\rm int}^{\rm el}(\mathbf{r}) = -\sigma_{\rm ij}^{\rm p} \varepsilon_{\rm ij}^{\rm H} V^{\rm H}$$
(6)

where V^{H} is the molar volume of a hydrogen atom, ϵ_{ij}^{H} is the misfit strain tensor due to hydrogen atoms, $\sigma_{ij}^{\text{p}}(\mathbf{r})$ are the local stress tensor components set up by the precipitate at the site of the hydrogen atom, \mathbf{r} . Assuming that a single hydrogen atom gives rise to a pure dilation in the matrix $\epsilon_{ij}^{\text{H}} = \epsilon^{\text{H}} \delta_{ij}$, the interaction energy is:

$$E_{\rm int}^{\rm el}(\mathbf{r}) = -\sigma_{ij}^{\rm P} \varepsilon^{\rm H} \delta_{ij} V^{\rm H} = -\sigma_{ii}^{\rm P} \Delta V^{\rm H}$$

$$(7)$$

where δ_{ij} is the Kronecker delta, σ_{ii}^{p} is the local hydrostatic stress due to the precipitate, and ΔV^{H} is the volume change of

the solid solution (i.e. the lath martensite phase) as a result of hydrogen absorption (or, the partial molar volume of hydrogen in iron). Reported $\Delta V^{\rm H}$ values for hydrogen in iron and steel are typically within the range of 1.6–2.1 cm³·mol⁻¹ [19,21,89,90]. According to Fukai [91], in many cases this value is in the range of 1.69 ± 0.12 cm³·mol⁻¹, in octahedral sites in bcc and hcp lattices it is 1.26 ± 0.12 cm³·mol⁻¹, and in Fe–Ni–Mn alloys at high hydrogen concentrations (x > 0.7) it is distinctly smaller (0.18–0.42 cm³·mol⁻¹). According to Frappart et al. [22], the partial molar volume of hydrogen in pure iron is somewhat higher in the microplastic and plastic domains compared to unstrained lattice, and is even higher in the elastic regime due to a higher vacancy concentration.

Another approach to represent the strains associated with hydrogen atoms in bcc iron was suggested by Wang et al. [92] who showed by density functional theory (DFT) calculations that the misfit stains are tetragonal and are expressed by:

$$\tilde{\epsilon}^{\rm H} = \begin{pmatrix} 0.015 & 0 & 0 \\ 0 & 0.059 & 0 \\ 0 & 0 & 0.059 \end{pmatrix}$$
(8)

Thus, the interaction energy is:

$$E_{\rm int}^{\rm el}(\mathbf{r}) = -\sigma_{\rm ij}^{\rm p} \varepsilon_{\rm ij}^{\rm H} V^{\rm H} = -\left(\sigma_{11}^{\rm p} \varepsilon_{11}^{\rm H} + \sigma_{22}^{\rm p} \varepsilon_{22}^{\rm H} + \sigma_{33}^{\rm p} \varepsilon_{33}^{\rm H}\right) V^{\rm H}$$
(9)

Model results

Elastic fields and energy of interaction with hydrogen

The hydrostatic stress distribution in the selected (110) plane of the steel due to the η -Ni₃Ti precipitate in mechanical equilibrium with the matrix is shown in Fig. 2a. An actual image of the precipitates is shown in Fig. 1a. The range of

significant stresses in the matrix is of the order of the dimensions of the precipitate; these stresses sharply decay. In linear elasticity, a scaling principle holds, namely, if the size of the precipitate increases by a factor of K, then the range of stresses increases by the same factor. The equivalent transformation strains, Eq. (4), are expansion in the three axes (with shear strains that have secondary effect). These strains give rise to compressive radial stresses in the matrix and to tensile tangential stresses. In some regions in the matrix, the normal stresses sum up to tensile hydrostatic stress, while in other regions they sum up to compressive hydrostatic stress. The regions of compressive stresses are expected to either repel the hydrogen toward the other two regions of tensile stresses that behave as weak reversible traps for hydrogen atoms or distort their path, thus contributing to tortuosity. The elastic interaction energy profiles between the precipitate and hydrogen atoms at each region is described in Fig. 2b. At long distances, all the curves converge to zero, implying that there is no elastic effect. At short distances, on the other hand, there is an effect on the distribution of hydrogen. Assuming a constant molar volume change of 1.6 cm³ mol⁻¹, the attractive interaction energy of the tensile stresses raise up to -14.7 kJ mol⁻¹, while the repulsive interaction energy increases up to 8 kJ mol⁻¹. This value is similar in magnitude to previous calculations of the elastic interaction with hydrogen for trapping at nano-precipitates [13]. The values of E_{aT} in Table 1 are averages of the experimentally measured energies of the different traps in the material, showing a decrease in the activation energy for hydrogen detrapping from the SA condition to the peak-aged condition (H900). This implies that the precipitates in the aged conditions form shallow (reversible) traps.

The effect of the elastic stress field on the concentration and diffusion of hydrogen

The experimental data of the hydrogen concentration in different thermal conditions (Table 1) shows that hydrogen solubility in the SA condition is the lowest, in the H1000 overage condition it is slightly higher, while in the peak-aged H900 condition it is significantly higher. Both aging treatments were conducted after solution annealing at 982 °C for 1 h [56], after which the density of the remaining dislocations is small. Therefore, the precipitates should have the major influence on the hydrogen solubility. Experimentally [57], at H900 and H1000 the morphology of n-Ni3Ti precipitates is maintained rod-shaped. Nevertheless, the size of the precipitate is different, the length being ~5 times larger at H1000 and the diameter being ~3 times larger. Therefore, the main difference between the H900 and H1000 conditions is the degree of coherence of the precipitates. Hence, we assume that the increase in solubility in the H900 condition is the result of the elastic interaction of hydrogen with the coherency stresses.

Under the combined effect of traps and elastic fields, the local hydrogen concentration can be expressed as the product of two exponential terms – one representing the interaction with a single, specific trapping site for which the binding energy is $E_{\rm b}$, the second representing the elastic interaction with the local stress surrounding the trapping site. Here, we use the expression suggested before for the interaction of hydrogen

with the stress field around a crack tip [18,20] and adopt it to describe the distribution of hydrogen concentration in the stress field caused by a coherent precipitate:

$$C(\mathbf{r}) = C_{\rm L} \frac{N_{\rm R}}{N_{\rm L}} \left[\exp\left(\frac{E_{\rm b}}{RT}\right) \right] \left[\exp\left(\frac{E_{\rm int}^{\rm el}(\mathbf{r})}{RT}\right) \right]$$
(10)

where C_L (mol·cm⁻³) is the hydrogen solubility at equilibrium in a perfect lattice, governed by the heat of solution of an ideal dilute solution, N_R (mol·cm⁻³) is the number of reversible trap sites per unit volume, N_L (mol·cm⁻³) is the number of interstitial lattice sites per unit volume, and E_{int}^{el} (kJ·mol⁻¹) is the energy of elastic interaction with the local stress field. It is possible to describe the structure of the alloy as composed of repeated unit cells. Each unit cell contains a Ni₃Ti precipitate surrounded by its decaying coherency elastic stress in the bcc matrix (Fig. 2a). In this view, the binding energy expresses the overall chemical attraction of hydrogen atoms to the precipitate, which is considered not a function of the position in the unit cell. On the other hand, the elastic interaction energy varies in the unit cell according to the local stresses.

The hydrogen concentration in the SA condition depends neither on the trap binding energy nor on the elastic interaction term. Therefore, hydrogen concentration in this case is uniform:

$$\overline{C}_{SA} = C_L \frac{N_R}{N_L}$$
(11)

We assume that the experimentally observed enhanced concentration of hydrogen in the H1000 condition is due to chemical binding of hydrogen to the precipitates. Hence, the first exponential term in Eq. (10) represents the increase of the hydrogen concentration in the presence of trapping precipitates from the value extracted from Eq. (11), to:

$$\overline{C}_{H1000} = C_{L} \frac{N_{R}}{N_{L}} \left[exp\left(\frac{E_{b}}{RT}\right) \right]$$
(12)

The coherent precipitates in the H900 condition generate long-range elastic stress fields, which give rise to a distribution of hydrogen in the vicinity of each precipitate. This can be expressed, based on Eqs. (10) and (12), as:

$$C_{\rm H900}(\mathbf{r}) = \overline{C}_{\rm H1000} \left[\exp\left(\frac{E_{\rm int}^{\rm el}(\mathbf{r})}{RT}\right) \right] = 23.5 \exp\left(\frac{E_{\rm int}^{\rm el}(\mathbf{r})}{RT}\right) \quad [\rm H-ppm]$$
(13)

 \overline{C}_{H1000} is taken from Table 1. In order to compare the calculations to the experimental data, we calculate the total content of hydrogen, using the data in Table 1 and the following equation:

$$\frac{\overline{C}_{H900}}{\overline{C}_{SA}} = \frac{\overline{C}_{H1000}}{\overline{C}_{SA}} \frac{1}{V_{cell}} \int exp\left(\frac{E_{int}^{el}(r)}{RT}\right) dV = \frac{1.47}{V_{cell}} \int exp\left(\frac{E_{int}^{el}(r)}{RT}\right) dV$$
(14)

Fig. 3 describes the calculated equilibrium distribution of hydrogen in the vicinity of an isolated η -Ni₃Ti precipitate, according to Eq. (13). The two regions that were characterized earlier in Fig. 2a by tensile stresses are enriched with hydrogen up to ~10⁴ ppm. In contrast, the two regions characterized by compressive stresses are depleted of hydrogen.

The integral of the local concentration over a representative unit cell should be equal to the measured total hydrogen absorption in the H900 condition. The value of the unit cell volume, V_{cell}, is chosen such that the volume fraction of a single precipitate is 6% of the cell volume, in accordance with the chemical composition and Calphad calculations [57]. Fig. 4 describes the calculated average C_{H900}/C_{SA} ratio as a function of the n-Ni₃Ti precipitates volume fraction. The calculated ratio is compared to the experimentally measured value. Two kinds of calculations are presented: pure dilation misfit strains with ΔV^{H} of 1.6, 1.8 and 2 cm³ mol⁻¹, and calculation that takes the misfit strains associated with hydrogen atoms as tetragonal. As the volume fraction of precipitates increases, the total hydrogen absorption due to the elastic interactions increases too. The curves of the tetragonal approach raise moderately compared to the curves for pure dilation misfit strains. The use of $\Delta V^{H} = 1.6 \text{ cm}^{3} \text{ mol}^{-1}$ yields results that best match the experimental value of the concentration of hydrogen. Obviously, as the volume fraction of precipitates increases, the strength of the alloy increases, but the susceptibility to HE is expected to increase too.

Experimentally, increasing temperature generates peaks of hydrogen desorption at certain temperatures that indicate the binding energies of the active traps. Temperature Programed Desorption (TPD) experiment was conducted on Custom 465® steel in [30], and is reproduced by the H900 black solid curve in Fig. 5. A desorption peak is observed in the temperature range of 330-420 K. The elastic contribution to the equilibrium concentration of hydrogen in the H900 state is calculated for a range of temperatures; the results are represented by the black solid with square symbol curve in Fig. 5. It shows an exponential decrease of the hydrogen concentration in the range of 270-400 K that stabilizes above 400 K, in good agreement with the experimental TPD curve. This range of temperatures reflects shallow traps, which is expected for trapping by elastic stresses [20]. Experimentally, desorption peaks appear also in the SA and H1000 states within a similar temperature range, but with ~3-4 times lower intensity [30].



Fig. 3 – The calculated equilibrium distribution of hydrogen in the vicinity of a single η -Ni₃Ti precipitate on the (110) plane.



Fig. 4 – Calculated average $C_{\rm H900}/C_{SA}$ ratio as a function of the $\eta-Ni_3Ti$ precipitates volume fraction, and compared to the experimentally measured value. Two kinds of calculation are presented: pure dilation misfit strains with $\Delta V^{\rm H}$ of 1.6, 1.8 and 2 cm³ mol⁻¹, and calculation with tetragonal misfit strains of the hydrogen atoms [92].

In both aging conditions, the amount of reverted austenite is small and nearly constant (<5.2 vol%), and the austenite is dispersed as discrete particles. Since the SA treatment at 982 °C involves also recovery of most of the dislocations and stabilization of the grain boundary structure, the aging treatments at H900 (482 °C) and H1000 (540 °C) do not cause significant changes in these microstructure features. The only difference between the H900 and H1000 is the higher degree of coherency in the H900 condition. Therefore, we suggest that the main source of hydrogen absorption in the H900 state of Custom 465[®] steel is the coherency stress fields surrounding the precipitates.

The result based on hydrogen concentration may be assessed by comparing with the *apparent diffusion coefficient* in the alloy (Table 1). Oriani [12] suggested the following relationship between the lattice diffusion coefficient of atomic hydrogen, D_L , and the effective (apparent) diffusion coefficient of atomic hydrogen, D_{eff} , due to the influence of several trapping sites under a condition of low hydrogen concentration:

$$\frac{D_{\rm L}}{D_{\rm eff}} - 1 = \sum_{i} \frac{N_{\rm R}}{N_{\rm L}} \left[\exp\left(-\frac{E_{\rm b}}{RT}\right) \right] \tag{15}$$

Oriani also suggested [93] that the diffusion is influenced by elastic stress fields. We assume that Eq. (15) should be generalized to include the interaction with the elastic stresses, in similarity with Eq. (10):

$$\frac{D_{L}}{D_{eff}(\mathbf{r})} - 1 = \sum_{i} \frac{N_{R}}{N_{L}} \left[\exp\left(-\frac{E_{b}}{RT}\right) \right] \left[\exp\left(\frac{E_{int}^{el}(\mathbf{r})}{RT}\right) \right]$$
(16)

As assumed above, one may propose that D_{eff} in the SA condition represents the lattice diffusion coefficient D_L since in the SA condition there is low dislocation density and there are no precipitates, therefore there are only low stresses in the lattice. According to Table 1, for all thermal conditions, the measured effective diffusion coefficient D_{eff}^{l} was lower than the



Fig. 5 – The calculated elastic contribution to the equilibrium concentration of hydrogen in the H900 condition as function of the temperatures (black solid curve) compared to TPD experimental spectra of charged specimens for heating rate of 5 °C·min⁻¹ (black dot curve). TPD data for the SA and H1000 conditions is also shown, for comparison. The calculated curve describes the relative amount of hydrogen remaining in the steel, while the TPD data shows the amount of hydrogen desorbed by heating of the steel. A value of $\Delta V^{\rm H} = 1.6 \text{ cm}^3 \text{ mol}^{-1}$ was used in the calculation.

effective diffusion coefficient at high occupancy of hydrogen in the lattice, D_{eff}^{h} . Comparing the diffusion coefficients in the state of low occupancy of traps, one observes that $D_{H1000}^{l} < D_{SA}^{l}$, indicating that there are more traps in the H1000 condition than in the SA condition due to the appearance of precipitates.

The diffusion coefficient in the H900 condition is lower than in the H1000 condition, $D_{\rm H900}^{\rm l} < D_{\rm H1000}^{\rm l}$. This may be attributed to the coherency stresses in the H900, since it was found before that the integrated elastic effect is attractive. Comparing Eq. (14) for the concentration of hydrogen to Eq. (16) for the diffusion coefficient, it is noticed that the right-hand-sides of the two equations are similar. Therefore, if we apply the same considerations as those for Eqs. (12)–(14), the ratio between the *average* diffusion coefficients $\overline{D}_{\rm L}/\overline{D}_{\rm H900}$ may be expressed in terms of the ratio $\overline{D}_{\rm L}/\overline{D}_{\rm H1000}$ (using the data in Table 1):

$$\frac{\overline{D}_{SA}}{\overline{D}_{H900}} - 1 = \left(\frac{\overline{D}_{SA}}{\overline{D}_{H1000}} - 1\right) \frac{1}{V_{cell}} \int exp\left(\frac{E_{int}^{el}}{RT}\right) dV = \frac{2.26}{V_{cell}} \int exp\left(\frac{E_{int}^{el}}{RT}\right) dV$$
(17)

where we assume that the elastic influence on the effective diffusion coefficient can be obtained by the volume average of the elastic term.

Fig. 6 compares the calculated $\overline{D}_{SA}/\overline{D}_{H900}$ as a function of the volume fraction of the precipitates to the experimentally measured ratio. As the volume fraction of the precipitates increases, more hydrogen is attracted by their elastic fields, and the effective diffusion coefficient decreases. The experimental ratio of the diffusion coefficients is placed slightly below the line corresponding to pure dilation misfit strains with $\Delta V^{\rm H} = 1.6 \, {\rm cm}^3 \, {\rm mol}^{-1}$, which was also found as the best fit for the concentration calculations above despite the crude estimation of the elastic influence. The experimental ratio is also favorably compared to the line corresponding to the tetragonal misfit



Fig. 6 – Calculation of the $\overline{D}_{SA}/\overline{D}_{H900}$ ratio as a function of the $\eta-Ni_3Ti$ precipitates volume fraction, and compared to the experimentally measured value. Two kinds of calculation are presented: one for pure dilation misfit strains with ΔV^H of 1.6, 1.8 and 2 cm³ mol⁻¹, the other takes the misfit strains associated with hydrogen atoms as tetragonal [92].

strains found by Wang et al. [93]. We trust the pure dilation misfit since the concentration calculations are better fitted with it. We assume that the elastic term that has been added in Eq. (16) describes only the path of hydrogen atoms that were trapped by the elastic stresses. Comparison with the experimental value points to an additional effect that lowers the diffusion coefficient, which is the distortion of the diffusion paths by the influence of the stress field (known as tortuosity [62–72]).

Conclusion

Considering the experimental difficulty to determine the local distribution of hydrogen and its diffusion coefficient in the presence of internal stresses, we suggest a computational approach to estimate these quantities. The method is applied to hydrogen in the lath martensite matrix around $\eta - Ni_3Ti$ precipitates in Custom 465^{\oplus} precipitation-hardened martensitic stainless steel. The calculations assess the hypothesis that the coherency stresses are responsible for the enhanced absorption and reduced hydrogen diffusivity in the peak-aged condition.

- Regions of compressive and tensile hydrostatic stress, giving rise to repulsive and attractive interactions, respectively, are found in the vicinity of each coherent precipitate. The integrated effect of these elastic stresses sum up to increased *average* hydrogen concentration and decreased apparent diffusion coefficient.
- The equilibrium concentration of hydrogen due to the elastic stresses decreases with increasing temperature, in conformance with experimentally measured TPD data.
- The hydrogen concentration, diffusivity and temperature of desorption confirm the role of the coherency stresses of

the precipitates in the peak-aged H900 condition. Best quantitative conformance with the experimental results for Custom 465[®] is obtained when regarding the misfit between hydrogen and the steel as pure dilation that gives rise to a partial molar volume of hydrogen of 1.6 cm³ mol⁻¹. The conformance with tetragonal misfit strains is less favorable.

• It is predicted that the amount of hydrogen in reversible traps will increase with increasing concentration of coherent precipitates.

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