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The influence of hydrostatic stress states on the hydrogen solubility in martensitic steels

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A specific dependency of elastic tensile stress on the hydrogen solubility is identified for martensitic steels. The lattice hydrogen concentration under applied stress may be underestimated when predicted by a classical law which associates hydrostatic stress with the partial molar volume of hydrogen. We have explored the impact of elastic distortions on hydrogen solubility from two different sources: internal stresses arising from heterogeneous microstructures and elastic fields around vacancy clusters. Only the latter seems to be in reasonable agreement with our results.

Keywords: Martensitic steels; Elastic stress field; Hydrogen solubility; Partial molar volume of hydrogen

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The understanding of hydrogen transport and trapping phenomena is a key feature in reviewing the hydrogen embrittlement models proposed and described in the literature. Both phenomena can be affected by the stress–strain states at different microstructural scales. The elastic distortion is one of the mechanical states associated with defects (vacancies, dislocations), metallurgical elements (grain boundaries, precipitates), internal and/or applied stresses that can modify the diffusion and solubility of hydrogen. The effect of applying mechanical stresses in the elastic domain has been investigated less than other parameters, such as plasticity [1–11]. These studies showed that the apparent diffusion coefficient remained quite constant and the hydrogen concentration increased with applied stress in the elastic regime. This latter evolution appears to be related to the impact of the mechanical stress fields on the chemical potential μ through the relationship deduced from a thermodynamic framework: $\mu = \mu_0 + RT\ln[C_H] - \sigma_m \bar{V}_H$ where σ_m is the hydrostatic stress, $\bar{V}_H$ is the molar partial volume of hydrogen, and μ_0 and C_H are the chemical potential without stress and the hydrogen concentration, respectively [4,12]. Despite some relevant experimental data being obtained for the elastic regimes of pure iron, steel and palladium alloys [3–6,13,14], which apear to confirm the thermodynamics theory of stressed bodies, the range of the hydrostatic stress explored was always below 50 MPa. More recently, Frappart and co-workers [1], working with high-strength low-alloy martensitic steels, reached higher hydrostatic pressures, approaching 300 MPa, which are in the "engineering" elastic domain. The hydrogen concentration equation deduced from the chemical potential expression $\ln[C_H(\bar{\sigma})/C_H(0)] = \sigma_m \bar{V}/RT$ has been verified on a tempered Fe–C–Cr martensitic steel [1], but in the pure elastic regime the apparent volume $\bar{V}$ is greater than $\bar{V}_H$. This effect disappears in the microplastic regime with the activation of edge dislocation mobility, which possibly promotes the annihilation of vacancies. The authors suggest a direct link between the superior values of $\bar{V}$ observed in the elastic regime and the elastic distortion around vacancies. In

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order to gather additional information on the subject, in this letter we explore the impact of a comprehensive variety of heat treatments and chemical compositions on the stress dependence on hydrogen solubility. According to the manufacturing process, substantial amounts of dislocations, precipitates, solute segregations, residual internal stresses and vacancies remain in these steels [15–20]. Consequently, after completing a metallurgical characterization of the last two components, their influences on hydrogen diffusivity and solubility are discussed in the elastic domain.

The studied alloys are quenched and tempered Fe–*n*C–*m*X martensitic steels (QTM), with their chemical composition given by n ϵ {0.3–0.4 wt.%} and m ϵ {0.003–1.2 wt.%} of X ϵ {Cr, Mn, Mo, Ni, P, S, Cu, Al, V, Nb, As, Co}. Alloys are first annealed at a temperature above 1130 K for 20 min and finally baked between 670 and 980 K for 20–30 min. Comprehensive experimental investigations have recently been performed to acquire an average description of the microstructure in terms of precipitate state, dislocation density, inter-lath density and prior austenitic grain size. The results and the experimental procedures of each technique used during these investigations are reported in our previous works [1,18,19]. In the present study we focus our attention on two points: the internal stresses and the density of vacancies, evaluated respectively by X-ray diffraction (XRD) analyses and differential scanning calorimetry (DSC). A Brucker AXS D8-Advanced diffractometer with Cu radiations ($K_{\alpha 1} = 0.15405$ and $K_{\alpha 2} = 0.154439$ nm) was used to perform the XRD analyses. The X-ray tube was operated at 40 kV and 40 mA. The diffraction lines were recorded from $2\theta = 40°$ to $2\theta = 145°$, with steps of 0.01° and a step time of 5 s, to cover the diffractions peaks of the (1 1 0), (2 0 0), (2 1 1), (2 2 0), (3 1 0) and (2 2 2) planes. For each material, a broadening of the diffraction pattern was observed and analyzed in order to estimate the internal stresses using the modified Williamson–Hall (WH) plots proposed by Reiman and Würschum [21]. The XRD peak-decomposition procedure using the Pearson type VII function is applied to describe the profile shape [29]. Both the full width at half maximum and the integral breadth β were calculated for each diffraction peak. Corrections were made to take into account the experimental profile broadening estimated using a LaB6 standard sample. According to WH analysis, the average value of the internal stresses is deduced from the following relationship:

$$\beta\cos(\theta) \approx \frac{\lambda}{\langle L_V\rangle} + \left[\frac{2(2\pi\langle\sigma^2\rangle)^{\frac{1}{2}}}{E_{hkl}}\right]\sin(\theta) \tag{1}$$

where θ is the angle of diffraction, λ ισ the X-ray wavelength, $\langle L_{\mathrm{v}}\rangle$ is generally associated with a material domain that coherently diffracts, $\sigma_{\mathrm{int}} = \langle\sigma^2\rangle^{1/2}$ is an average value of internal stresses and E_{hkl} is the Young's modulus depending on the $\langle hkl\rangle$ direction (we used the experimental data of Kim and Johnson [30] for the elastic constants of the martensitic structure). DSC measurements were performed using a Q100 TA Instruments DSC apparatus. The heating of the samples was carried out linearly from 273 to 723 K at a rate of 10 K min^{-1}. The existence of an exothermic peak in the evolution of the heat flow as a function of temperature was associated with the annihilation of vacancies, and the area of this peak corresponds to the vacancy-stored energy E^{st} [22–25]. The equilibrium vacancy concentration is given by:

$$c_V = \frac{E^{st}}{E^f} \times \frac{M_{\mathrm{Fe}}}{N_a} \tag{2}$$

where E^f is the formation energy of a vacancy, N_{a} is Avogadro's number and M_{Fe} is the molar mass of iron. In this work, we used data reported for α-Fe: $E^f = 1.89$ eV [31] and $M_{\mathrm{Fe}} = 55.8$ g mol^{-1}. Before performing the hydrogen characterization under applied stress, tensile and relaxation tests were carried out at particular stress levels to distinguish the specific regimes that occur in the engineering elastic domain. The experimental approach described in Ref. [1] allows one to access the parameters that are needed to define the elasticity, the microplasticity and the generalized plasticity regimes. Indeed the transition between the elastic and microplastic regimes corresponds to the activation of edge dislocation loops at a critical stress σ_{c}.

To perform electrochemical permeation (EP) tests under stress, an original experimental device was designed in our laboratory [1]. The prismatic samples were first stressed and then set within the permeation device. At the beginning, the detection side of the sample was potentiostatically maintained at a constant potential in a 0.1 M NaOH solution for 22 h in order to stabilize the anodic current at ~0.1 μA cm^{-2}. The entry side of the specimen was then galvanostatically polarized at a constant charging current density in a 1 M H_2SO_4 solution. The hydrogen flux was measured at the exit side during the sorption step until a steady state was reached. The solutions in both cells were continuously deoxygenated with argon. After the sorption step, the charging current density was stopped, the acid solution was then removed from the charging cell and the deoxygenation with argon was maintained. The desorption step was recorded until hydrogen release was complete. The flux vs. time profile was used to evaluate the amounts of lattice and trapped hydrogen in the sample, as explained in the literature [18,23]. The aim of this method is to separate the lattice from the trapped hydrogen concentrations by comparing the experimental and theoretical curves deduced from Fick diffusion laws. As described in Ref. [26], the comparison of data collected by EP and by thermal desorption spectroscopy (TDS) has been performed in the present study to validate the analysis methodology. We do not detail this approach here; however, it can be accessed elsewhere [1,18,19,26]. We focus on the evolution of lattice hydrogen C_{L} vs. stress deduced from the desorption step and the hydrogen apparent diffusion coefficient D_{app} calculated at a current density equal to 10% of the steady state during the sorption step [18,23].

The effect of stress on the hydrogen flux in the elastic domain is illustrated in Fig. 1a. As previously reported for QTM steels [1], this outcome highlights an increase in the steady-state current densities with the applied stress. Regardless of this feature, D_{app} stays stable in the pure elastic regime, where the defect density should