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Relationship between Dislocation Density and Hydrogen Trapping in a Cold Worked API 5L X60 Steel

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Abstract

Dislocation densities have been determined and hydrogen traps have been characterized in an API 5LX60 steel. The steel has been subjected to different degrees of plastic strain (εₚ) by cold rolling. The dislocation densities has been determined by the analysis of the peak broadening on X-Ray diffractograms. The traps have been characterized through the measurement of hydrogen permeation transients and fitting of a trapping model to the experimental data. The relationship between hydrogen traps and dislocation density is discussed.

1. Introduction

The effect of cold work on the diffusion of hydrogen (H) in low alloy steels has been observed by the first time by Darken and Smith (1949). With increasing degrees of strain, a delay in the diffusion of H in the steel is observed.

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This delay is attributed to the presence of sites in which H is retained; these sites are called “trapping sites” or simply “traps” (Kumnick and Johnson, 1974). Traps are identified with microstructural defects of the steel. It is well known that with increasing degrees of plastic strain, the density of dislocations in the material is also increased. Therefore, it is reasonable to consider the hypothesis that the dislocations behave as hydrogen traps. In this work, a simple model of hydrogen trapping in dislocations is assumed: trap sites with high binding energy will be located along the dislocation line, while traps with lower binding energy will be located in the region affected by the stress field of the dislocation. In contrast with the trapping sites, the normal interstitial lattice sites (NILS) are the available sites for hydrogen in a perfect lattice. In the case of the body centered cubic structure (bcc) of pure iron and ferritic steels, these sites are the tetrahedral interstices (Kiuchi and McLellan, 1983; Ramunni et al., 2009). In absence of traps, H is located in the NILS. In presence of traps H is distributed between the NILS and the traps, but it is considered that H diffusion only occurs by jumps between NILS. From the thermodynamical point of view, the binding energy \( E_b \) is the energy needed to transfer H from a trap site to a NILS. As the binding energy is higher, it is less likely that H leaves the trap site and diffuses. Some authors have measured the trap binding energy between H and the dislocations. Gibala (1967) obtained \( E_b = 27 \text{ kJ mol}^{-1} \) by using the internal friction technique. In other works, calculations of \( E_b \) depending on the dislocation type (screw or edge) are reported. For these calculations semiempirical methods such as the embedded atom model (Lee and Jang, 2007; Ramasubramaniam et al., 2009) are used. The binding energy at dislocation core sites has been calculated as 37–42 kJ mol\(^{-1}\) for an edge dislocation and 26–29 kJ mol\(^{-1}\) for a screw dislocation (Ramasubramaniam et al., 2009). The density of trap sites \( N \) [mol cm\(^{-3}\)] at the dislocation core is related to the density of dislocations \( \rho \) [cm\(^{-2}\)] by the following equation (1):

\[
N = \frac{\rho}{a B N_{A
u}}
\]

Where \( a \) is the lattice parameter of the bcc structure, \( B \) is a geometrical parameter which depends on the orientations of the Burgers vector and the dislocation line, \( N_{A
u} \) is the Avogadro’s number and \( a B \) is the distance between adjacent trapping sites along the dislocation line.

In a previous work Castaño-Rivera et al (2012) obtained H diffusion transients in an API 5L X60 steel. The metallurgical conditions studied in that work were: as received (AR, without deformation) and cold-rolled (CR), with a 2.4% reduction in thickness. The hydrogen trapping parameters were determined by fitting simulated diffusion transients to the experimental transients. The simulated transients were calculated by using a model of local equilibrium with saturable traps and a finite difference method. In contrast to what was done in the present work, the fitted parameters included the apparent diffusion coefficient, and each permeation transient was fitted individually. From this analysis it was established that the density of both strong and weak traps was increased by an order of magnitude in the CR state with respect to the AR state. The binding energy of the weak traps was within the range of 25 to 30 kJ mol\(^{-1}\), and that of the strong traps between 60 and 75 kJ mol\(^{-1}\).

2. Experimental procedure

The material studied in the present work was taken from an API 5L X60 steel pipe, which is used for oil and gas piping. Its chemical composition is the following: C 0.14%; Mn 1.04%; Si 0.25%; Cr 0.07%; Mo 0.08%; V 0.03%; Cu 0.03%; Ni 0.05%; Al 0.026%; P 0.014%; S 0.011%; Ti 0.015% and Nb 0.001%. The microstructure corresponds to a low carbon, low alloy steel in a quenched and tempered condition: equiaxed ferrite grains with an average size of 4 \( \mu \)m and globular cementite particles with an average size of 0.3 \( \mu \)m. It also presents low amounts of non-metallic inclusions containing Ca, S, Al, Mn and Ti. Several samples were cold rolled, where the rolling direction was coincident with the longitudinal axis of the pipe. The final thicknesses ranged from 0.5 to 4 mm and the thickness reduction from 2.4% to 50%. The corresponding levels of plastic strain (\( \varepsilon_p \)) were calculated with equation (2):

\[
\varepsilon_p = \ln \left( \frac{L_0}{L_f} \right)
\]
Where \( L_0 \) and \( L_f \) are respectively the initial and final thickness of the rolled specimen. The \( \varepsilon_p \) values ranged from 2.4% to 50%. The rolled sheets were machined to obtain disks of ca. 35 mm diameter; the disk surfaces were polished with SiC up to #600 grit. Before performing either the H permeation test or the diffractograms, both disk faces were electropolished in order to eliminate the deformed layer caused by the prior mechanical polishing. These disks served as permeation membranes for the hydrogen permeation tests with gas phase charging and electrochemical detection. For this test, both entry and exit membrane surfaces were coated with a Pd film, ca. 10 nm in thickness. Prior to the permeation test the membranes were degassed in air at 110°C during 16 h. The electrochemical technique (Devanathan and Stachurski, 1962) was used to detect the H atoms that reach the exit side of the permeation membrane. Hydrogen charging was accomplished by putting the input surface in contact with \( \text{H}_2 \) (g) at pressure of 1 bar. The electrochemical detection cell contained: a Pt counterelectrode and a Pd/PdH reference electrode. The electrolyte was NaOH (aq), 0.1 mol/liter. The exit surface of the permeation membrane served as the working electrode and was polarized at +0.200 V with respect to the normal hydrogen electrode. This potential ensures the complete oxidation of the emerging H. The hydrogen flux at the exit surface, \( j_H \) [mol H cm\(^{-2}\) s\(^{-1}\)], is obtained from equations (3):

\[
i_H = i - i_{\text{background}} ; \quad j_H = i_H / F
\]

(3)

Where \( i \) is the current density measured at the detection cell, \( i_{\text{background}} \) is a residual current density in absence of H, \( i_H \) is the net H current density and \( F = 96484 \) A s mol\(^{-1}\) is the Faraday’s constant. Four sequences of buildup-decay transients were recorded: two at 30°C, one at 50°C and one at 70°C. The theoretical permeation transients were calculated by a finite difference method [8] assuming the model of local equilibrium proposed by Oriani (1970) and the presence of saturable traps with a definite capacity of one H atom per trap. The parameters used for the calculation were: the membrane thickness \( L \) [cm], the free energy of trapping of the weak and strong traps: \( \Delta G_W, \Delta G_S \) [J mol\(^{-1}\)], the number density of the weak and strong traps sites: \( N_w, N_s \) [mol cm\(^{-3}\)], and the constants \( \Phi_0 \) [mol H cm\(^{-1}\) s\(^{-1}\) bar\(^{-1/2}\)] and \( E_\phi \) [J mol\(^{-1}\)] used for the calculation of the permeation coefficient \( \Phi \) as a function of the temperature according to equation (4):

\[
\Phi = \Phi_0 \exp \left(- \frac{E_\phi}{RT} \right)
\]

(4)

The parameters corresponding to each condition of the API 5L X60 steel were obtained by performing the fitting procedure for the whole set of permeation transients, except the first transient at 30°C. The procedure to calculate the theoretical permeation transients is described by Castaño-Rivera et al. (2012).

The density of dislocations in the different metallurgical conditions was determined by the analysis of the broadening of the X-ray diffraction peaks. This is an indirect method which relates the microstrain of the material with the density of dislocations (Williamson and Hall, 1953). It has been modified in order to take into account the elastic anisotropy of the material and the relative influence of the accumulation of dislocations on the breadth of the peaks corresponding to the different families of planes (Ungár et al., 1999). The usual equation for the calculation of the density of dislocation and domain sizes by X ray diffraction was improved in successive works and may be found in the literature (Ungár et al., 2001); it is presented in equation (5):

\[
\frac{\text{Breadth cos(}\theta)}{\lambda} = \Delta K = \frac{1}{d} + \left( \frac{\pi M^2 b^2}{2} \right) \rho \frac{1}{\lambda} \left[ \frac{\text{sen}\theta}{\lambda} \right]^2 C = \frac{1}{d} + \left( \frac{\pi M^2 b^2}{2} \right) \rho \frac{1}{\lambda} \frac{y^{1/2}}{K^2 C}
\]

(5)

Where the left hand member indicates the peak breadth multiplied by the cosine of the Bragg angle and divided by the X-Ray wavelength. This term corresponds to the integral breadth of each peak in the space of the wave vectors. The right hand member contains, as \( y \)-intercept, the inverse of the domain size \( d \) [nm\(^{-1}\)] and, as coefficient of the
term in second grade in the wave vector variable $\frac{\sin \theta}{\lambda}$, a combination of parameters that describes: the geometry and density of the dislocation arrays ($M$), the Burgers vector ($b$), the density of dislocations ($\rho$) and a parameter ($C$) that represents the relative “visibility” of the dislocation arrays in the diffraction peaks of the different planes. The parameter $M$ may be lower or higher than unity, depending on whether the array is of high compactness -where the elastic fields become “screened”- or of low compactness -represented by more disperse dislocation arrays-, respectively. Ribárik (2008) developed more refined methodologies based on the Fourier series expansion of the full diffractogram, but this would introduce an unnecessary complexity in this instance.

The diffractograms were measured with a Panalytical MPD instrument equipped with a Cu tube ($K_\alpha$ radiation), X-ray lens, graphite monochromator, Soller slits at the exit beam, and a Xe scintillation detector. The geometrical array corresponds to that of Bragg-Brentano with a very low divergence in the beam, which approximates to geometry of parallel rays. The mean divergence of the beam has been calculated as approximately $0.3^\circ$. The characterization of the peak breadth attributed to the equipment geometry was performed with a NIST LaB$_6$ standard which was analyzed by the same technique as that used to obtain the diffractograms of the present samples. In this way, the peak breadth of the standard may be used to calculate the true broadening attributed to the presence of dislocations and small domains in the sample.

Additional X-ray diffraction measurements were carried out on 3 samples in the Laboratório Nacional de Luz Sincrotron (LNLS), Campinas, Brazil, at energy of 7 kV ($\lambda = 1.772 \text{ Å}$) with punctual detector; also, the corresponding LaB$_6$ standard was measured in order to calculate the broadening due to the experimental array at the DRX1 line of LNLS.

3. Results and discussion

3.1. Experimental hydrogen permeation transients

Fig. 1 shows some buildup permeation transients corresponding to the cold rolled API 5L X60 steel with different values of $H_P$, together with those of the as received material, for which $H_P = 0$ is assumed. The test temperature is $30^\circ C$. Both $i_H$ and time ($t$) were normalized as $i_H \times L$ and $t/L^2$ with respect to the membrane thickness ($L$). From Fig. 1 it can be seen that the steady state H current density ($i_{Hss}$) is practically independent of $H_P$. This agrees with that reported by Riecke (1981) for the case of pure iron. This is consistent with the fact that the diffusion takes place between normal interstitial lattice sites (NILS) in the steel. Other observation is the growing delay of the permeation transients with the increase of $H_P$. This behavior agrees with previous reports found in the literature, (Kumnick and Johnson, 1980; Dietzel et al., 2006) and can be explained by the fact that as the plastic strain increases the material presents a higher trap density and eventually also a higher trap binding energy which causes a delay of the diffusion process.

Similar behavior has been observed for the other temperatures of the permeation test as well as for the decay transients.
3.2. Calculation of the diffusion and trapping parameters

In Tables 1 and 2 the values of the diffusion and trapping parameters, which were obtained by fitting the calculated transients to the experimental transients, are presented. Table 1 shows the parameters $\Phi_0$ and $E_\Phi$ as well as the value of the permeation coefficient $\Phi$ calculated at 50°C with equation (4). This latter parameter does not present a dependency on the strain level; this result is in agreement with previous literature reports (González, 1969; Miller et al, 1975, Kumnick and Johnson, 1975) for the case of pure iron.

Table 1. Parameters related with the hydrogen permeation coefficient in the API 5L X60 steel in the different metallurgical conditions. Symbols are defined in text.

| Condition     | $\varepsilon_p$ (%) | $\Phi_0$ (mol H cm$^{-1}$ s$^{-1}$ bar$^{-1/2}$) | $E_\Phi$ (J mol$^{-1}$) | $\Phi$ (50°C) (mol H cm$^{-1}$ s$^{-1}$ bar$^{-1/2}$) |
|---------------|---------------------|-----------------------------------------------|-------------------------|-------------------------------------------------|
| As received   | 0                   | 6.91x10$^{-8}$                                | 32.27                   | 4.2x10$^{-13}$                                   |
| Cold rolled   | 2.14%               | 1.37x10$^{-7}$                                | 33.74                   | 4.8x10$^{-13}$                                   |
| Cold rolled   | 5.7%                | 2.45x10$^{-7}$                                | 35.33                   | 4.8x10$^{-13}$                                   |
| Cold rolled   | 11.4%               | 4.97x10$^{-7}$                                | 37.09                   | 5.0x10$^{-13}$                                   |
| Cold rolled   | 11.4%               | 1.07x10$^{-7}$                                | 33.06                   | 4.8x10$^{-13}$                                   |
| Cold rolled   | 23.5%               | 1.80x10$^{-7}$                                | 33.95                   | 5.9x10$^{-13}$                                   |
| Cold rolled   | 70.0%               | 9.57x10$^{-8}$                                | 33.34                   | 3.9x10$^{-13}$                                   |

The trapping parameters are presented in Table 2. The trap binding energies of both weak ($E_{b,w}$) and strong ($E_{b,s}$) traps were calculated by $E_b = -\Delta G - T\Delta S$, where the term $T\Delta S$ is neglected.
Table 2. Trapping parameters of the API 5L X60 steel in the different metallurgical conditions.

| Condition      | \( \varepsilon_P \) | \( E_{bw} \) j mol\(^{-1} \) | \( N_{bw} \) mol cm\(^{-3} \) | \( E_{bs} \) j mol\(^{-1} \) | \( N_{bs} \) mol cm\(^{-3} \) |
|----------------|----------------------|---------------------------------|-------------------------------|-------------------|-------------------------------|
| As received    | 0%                   | 34.5                            | \( 2.5 \times 10^3 \)         | 58.2              | \( 1.1 \times 10^3 \)          |
| Cold rolled    | 2.14%                | 30.0                            | \( 8.0 \times 10^4 \)         | 62.4              | \( 9.2 \times 10^4 \)          |
| Cold rolled    | 5.7%                 | 28.9                            | \( 2.5 \times 10^3 \)         | 62.5              | \( 2.1 \times 10^4 \)          |
| Cold rolled    | 11.4%                | 23.0                            | \( 3.7 \times 10^4 \)         | 61.6              | \( 3.9 \times 10^7 \)          |
| Cold rolled    | 11.4%                | 25.3                            | \( 1.9 \times 10^4 \)         | 62.6              | \( 5.0 \times 10^7 \)          |
| Cold rolled    | 23.5%                | 24.4                            | \( 3.5 \times 10^4 \)         | 60.8              | \( 6.8 \times 10^7 \)          |
| Cold rolled    | 70.0%                | 25.0                            | \( 6.2 \times 10^7 \)         | 61.1              | \( 1.4 \times 10^8 \)          |

In Fig. 2 the trapping parameters are presented as a function of \( \varepsilon_P \). The confidence intervals were assessed by changing the parameters around their optimal values, in such way that the quality of the fit was not significantly impaired. The chosen quantitative criterion was that the mean quadratic deviation of the fit, normalized by the steady state H current density, does not increase more than 0.1 percent units with respect to its minimal value. Fig. 2 shows that the trap density, either weak or strong, increases with the increase of plastic strain. The binding energy of the strong traps practically does not vary with \( \varepsilon_P \).

Fig. 2. Trapping parameters of the API 5L X60 steel as a function of the plastic strain (\( \varepsilon_P \)). In order to allow the comparison in a logarithmic scale, the strain level of the as received material has been arbitrarily fixed at \( \varepsilon_P = 0.001 \).

3.3. Calculation of the dislocation density

The dislocation densities and domain sizes were obtained for all the samples detailed in Table 1, by means of X ray diffraction in the Panalytical MPD equipment described above. Besides, the sample without deformation (\( \varepsilon_P = 0\% \)) and those cold rolled to 2% and 23% reduction in thickness were measured at the LNLS as described in paragraph 2. The data on weak and strong trap densities (\( N_{bw}, N_{bs} \)) are shown in Fig. 3. Also shown in this figure is the evolution
of the values of the surface density per unit volume. Since the aim is just to analyze the trend, an approximation has been made, i.e. all domain surfaces correspond to spherical domains and surface density is calculated as the inverse of the domain size. The calculation of this magnitude is performed in an attempt to explain the existence of at least two types of defects that alternatively produce weak or strong trapping. Most of the so called weak traps are sites created along the dislocation line. These sites would present at first sight an easy path for diffusion along the line; however, H diffusion in bcc iron is fast enough to preclude the existence of short circuit paths along the dislocation. The expected effect is a transitory retention of H atoms that causes a delay in the diffusion process. The strong traps are sites in which hydrogen remains trapped during longer times with a higher binding energy. In the case of plastic deformation, these sites might turn up being due to dislocation arrays that develop at high levels of plastic strain. These arrays are of low energy and they could lead to the development of traps where H is not easily evacuated. The observation that the strong trap density increases with plastic strain is logical and expected. Also, it is logical that the strong traps are much less abundant that the weak traps, by a factor of the order of $10^{-4}$. The observed increase of the dislocation density with plastic strain is also an expected behavior. In fact, the curve of $\rho$ vs. $\varepsilon_p$ practically follows a typical mechanical hardening curve, since that hardening is proportional to the dislocation density.

The domain size decreases mainly due to the formation of sub-grains until it reaches an asymptotic value. The domain size should not be confused with the sub-grain size because a misorientation of a few degrees of in adjacent regions is sufficient for the X-rays to detect them as distinct crystalline domains. As the dislocation density increases, a point is reached in which the region between adjacent dislocations is no longer periodic. In this situation, the dislocations are not individually detected; rather they exert a screening effect on each other. In fact, the long range stress field of two dislocations close to each other is much less than the stress field of two separate dislocations. Approximately, the strain value at which the decrease of the domain size stops agrees with the strain value at which the growth rate of the dislocation density decreases. The weak traps seem to be related to nearly isolated dislocations. The strong traps might be proportional to the density of arrays, i.e. to sub-grain boundaries or sequences of arrays, not closed but dense. A boundary or a compact array should contain a number of strong traps, probably in the form of kinks or jogs. When the density of sub-grains and arrays does not further increase with

![Figure 3. Dislocation density ($\rho$, Laboratory X rays and LNLS), density of weak and strong trap sites ($N_w, N_s$) and dislocation array surface density ($d^1$) as a function of plastic strain ($\varepsilon_p$).](image-url)
increasing strain, then the density of strong traps should stabilize. Another possibility for the strong traps is that they are related to vacancies created by plastic deformation, also on the regions of highly dense dislocation arrays. In fact, the binding energy for strong traps measured in this work agrees well with reported values, experimental and theoretical, of the binding energy for vacancies: 53.65 kJ mol$^{-1}$ and/or 58.75 kJ mol$^{-1}$, respectively (Ramasubramaniam et al, 2009).

4. Conclusions

The behavior of the dislocation density approximately follows that of stress-strain curves of metallic materials. The independent determinations via laboratory X-Ray diffraction (Cu K$_\alpha$ radiation) and synchrotron radiation are in good agreement. In the domain of low plastic strain, both the density of weak traps and the density of dislocations show a similar increasing trend as the plastic strain increases. At higher plastic strain, both the density of weak traps and the density of dislocations reach an asymptotic value. The density of strong traps has been correlated with the specific surface of dislocation arrays per unit volume; a log-log plot of strong trap density vs. plastic strain shows a linear dependency.

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