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HYDROGEN PERMEATION IN METALS AND ALLOYS: A BRIEF REVIEW

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ABSTRACT

This is an integrative review deals with the hydrogen-metal interaction mechanisms, reversible and irreversible traps and highlights the use of electrochemical permeation as an important tool of evaluation the Hydrogen embrittlement (HE) mechanism. Due to its simplicity, flexibility, low cost and low risk, this technique is widely used in the study of hydrogen transport and diffusion parameters, contributing to the selection of more resistant steels and alloys. On the other hand, it´s important toothose new efforts should be made to develop and implement new techniques that can be applied to different temperature and pressure conditions.

INTRODUCTION

Hydrogen is widely used in various applications, such as in ammonia production, methyl alcohol, and in the nuclear energy industry, among others. Hydrogen action can lead to changes in mechanical properties, phase transformation and eventually cause environmentally assisted failure, known as HE (Hydrogen Embrittlement). The susceptibility of steels and alloys to this phenomenon is directly related to the interaction between traps (defects) and hydrogen, and it is proven that the embrittlement phenomenon is highly affected by hydrogen trapping mechanisms. Given this, understanding the atomic hydrogen adsorption and diffusion mechanisms throughout the steel microstructure is essential to optimize the resistance of the tubes to the failures associated with hydrogen (Safyari*et al*., 2020). Hydrogen embrittlement in metals is a challenging question for proper hydrogen energy use. Despite extensive investigations, the mechanism stillis not clearly understood. HE has a very important role in the physical and mechanical properties of materials in the presence of hydrogen. HE is a phenomenon that makes steel fragile, where hydrogen atoms remain trapped inside the liquid metal during the solidification process and penetrate the interior of the material allowing for the appearance of cracks.

This causes the properties (such as tensile strength and fatigue strength) of steel to deteriorate (Metalnikov*et al*., 2020). To avoid failure due to hydrogen embrittlement, it is important to know the amount of hydrogen absorbed by certain types of steel in service conditions. The electrochemical permeation technique is easy to access and has low operation and maintenance costs; moreover, it can be applied, in principle, to all metals and alloys that have a high solubility for hydrogen. The technique describes the calculation of the effective diffusivity of hydrogen atoms in metals to distinguish reversible and irreversible trappers. It can also be used to classify the relative aggressiveness of different environments in terms of the hydrogen consumption of the exposed metal (ASTM G 148-97, 2003; ISO 17081, 2004).

METHODS

This is an integrative review, which allows the elaboration of a synthesis of the knowledge already reported in the literature on a particular topic and promotes an analysis of broad understanding of the data found (Kakushiand Évora, 2016).The present study was based on a literature search on the use of electrochemical permeation as a important tool of evaluation the Hydrogen embrittlement (HE) mechanism. Inclusion criteria were established based on the research

question, and, for analysis, we chose to include articles published in Portuguese, Spanish or English, with full text available online and free of charge. As search sources, we used: Academic Googleand Scientific Electronic Library (SciELO). The exclusion criteria were publications: that were not related to the study theme or that presented duplicity. Articles were included regardless of year of publication, as they were relevant to this review. As keywords used for research, we have: hydrogen embrittlement; hydrogen absorption, electrochemical permeation.

LITERATURE REVIEW

Hydrogen-Metal Interaction: In the H-Metal interaction, where the metal surface is in direct contact with the gas, the gas dissolves into the metal. The dissolution of hydrogen in metals consists of four stages: physical adsorption (or physisorption), chemical adsorption (or chemisorption), penetration through the surface, and diffusion. At the start of this process, gas molecules migrate to the metal surface and undergo physical adsorption due to weak attractive forces, typically from Van der Waals, between the hydrogen atom and ions in the metal matrix. After physical adsorption, dissociation occurs due to chemical adsorption where strong interactions occur between gas molecules and the solid surface. Then, the atoms that overcome the potential barrier penetrate through the surface (absorption), and, once inside the metal, diffuse (Landodlt, 1993) (see Figure 1).
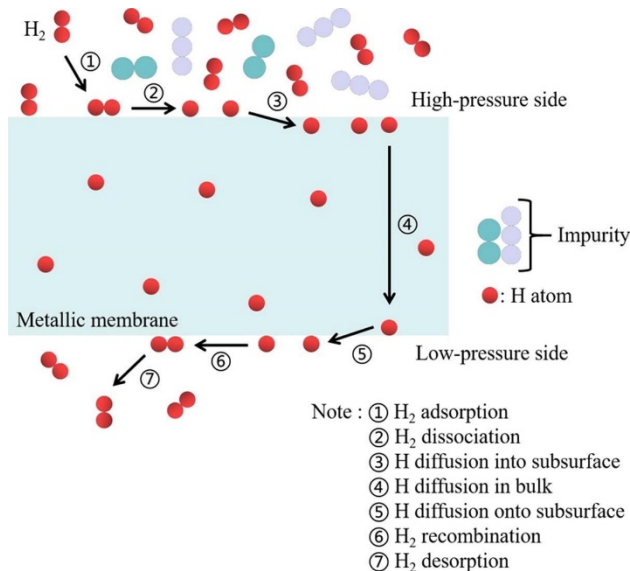

Fig. 1. Schematic of H permeation in dense metallic membrane [22]
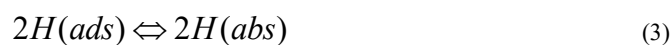
The equations for each reaction step are:

1) Physical adsorption of the molecule on the metal surface:

$$H_2(g) \Leftrightarrow H_2(ads) \qquad (1)$$

2) Chemical adsorption of the molecule with dissociation into two atoms on the metal surface:

$$H_2(ads) \Leftrightarrow 2H(ads) \qquad (2)$$

3) Penetration through the surface (absorption):

$$2H(ads) \Leftrightarrow 2H(abs) \qquad (3)$$

4) Diffusion into the metal, where the hydrogen remains dissolved:

$$2H(abs) \Leftrightarrow 2H(dif) \qquad (4)$$

Ideal diffusion, Fick's laws: The following section presents diffusion laws for the ideal case of diffusion without trapping. Then the different types of traps that can be encountered in real material are presented, along with the expression for diffusion in the presence of traps. Due to its small volume, a hydrogen atom can diffuse and occupy the interstitial sites inside the material (see Figure 2).
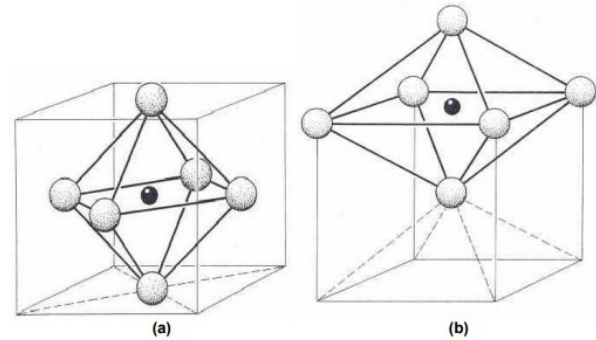

Fig. 2. Octahedral interstitial sites of face-centered cubic (a) and body-centered cubic (b) matrix [23]

Lattice diffusion through interstitial jumps is the main diffusion mechanism for hydrogen in steel. A ferritic base-centred cubic (BCC) structure enables a high diffusion rate and low solubility due to its open lattice structure. In contrast, the austenitic face-centred cubic (FCC) structure has a lower diffusion rate and a higher solubility due to its closely packed lattice. Martensite is a body-centred tetragonal (BCT), but presents the tendency of hexagonal martensite formation (HCP) as carbon content increases. These structures are more closely packed than BCC. As a result, the diffusion rate of hydrogen in martensite is between ferrite and austenite (Koyama *et al*., 2018). In Table 1 several metals with crystallographic structure and their respective preferred occupied sites are presented.

Table 1. Interstitial sites occupied by hydrogen in different metals, where T are tetrahedral sites and O octahedral sites [23]

Host lattice	Crystallographic structure	Occupied sites
α – Fe	B.C.C	T
γ – Fe	F.C.C	O
Pd	F.C.C	O
Ta	B.C.C	T
V	B.C.C	T
Nb	Rhomb.	T

Equations Eq. (5) and Eq. (6) show the first and second Fick's Laws, respectively:

$$J = -D\frac{\partial C}{\partial x} \qquad (5)$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial^2 x} \qquad (6)$$

where, D is the diffusion coefficient for the ideal case, where diffusion takes place without trapping. For a given material the diffusion coefficient is constant. Some values of the diffusion coefficient for different materials are presented in Table 2.

Table 2. Diffusion coefficient of hydrogen in different materials at room temperature

Material	D (m²/s)	Ref.
Carbono steel	2.5×10^{-10}	[29]
Ferritic stainless steel	10^{-11}	[30]
Austenitic stainless steel	2.15×10^{-16}	[31]
Martensitic stainless steel	2.0×10^{-13}	[32-36]
Duplex stainless steel	$10^{-13} - 10^{-14}$ (depending on the ferrite / austenite ratio)	[30, 37-40]

The diffusion coefficient has an exponential expression dependence with the temperature expressed by Eq. (7):

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

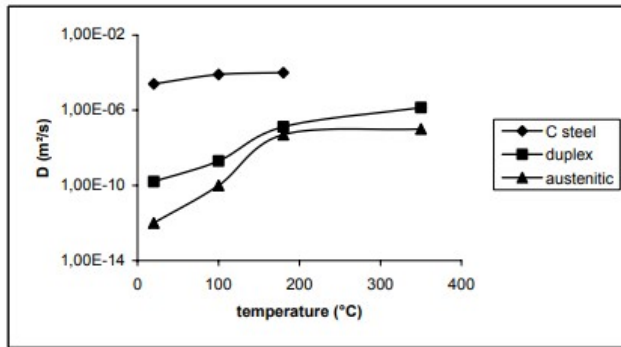Figure 3 presents the diffusion coefficient adjusted for temperature dependency for different steels.

Fig. 3. Evolution of diffusion coefficient (D) with the temperature for different steels [31]

Hydrogen Absorption

According to Stroe (2006), the adsorption of hydrogen atoms takes different paths, according to the source of hydrogen. Through cathodic polarisation and corrosion reaction, electro-adsorbed species are formed on the metallic surface. Alternatively, in the presence of a gaseous atmosphere, the molecular hydrogen can undergo physisorption or chemisorption. Usually, hydrogen atoms are considered to enter the metal either by a two-step (indirect) or a direct absorption mechanism. The equations below are written assuming that the two processes occur in parallel, which is schematized in Figure 4.
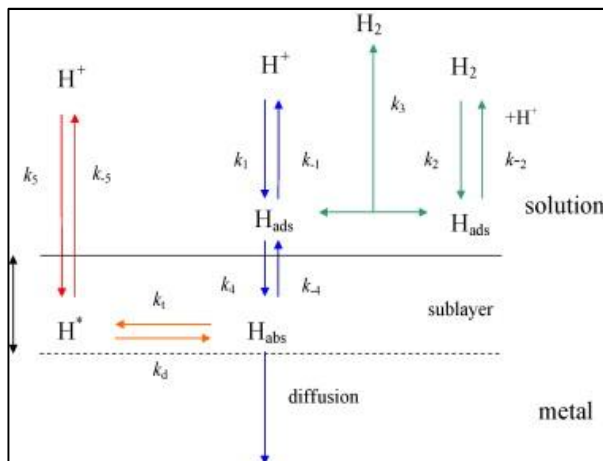

Fig. 4. Scheme of the reaction mechanism used for the general interaction of hydrogen with a metal [41]

In a solution under cathodic polarisation, the hydrated hydrogen cations, H_3O^+, are transported by diffusion/migration towards the cathode. There, the cation undergoes reduction and becomes atomic hydrogen, H. The atomic hydrogen can recombine to form molecular hydrogen, H_2 that leaves the metallic surface. For the reduction of hydrogen ions, two different reaction mechanisms are possible, depending on the nature of the metal: indirect and direct absorption mechanisms. The indirect mechanism in which hydrogen is first adsorbed on the electrode surface in the Volmer step, also known as the overpotential deposition of hydrogen (OPD), can be seen in detail in Refs: Bockris*et al.*, 1965; Montella, 2001; Gabrielli *et al.*, 2004;

Lasia, 2002. The direct hydrogen absorption, where protons are reduced to form the subsurface absorbed hydrogen, can be seen in detail in Refs: Ash and Barrer, 1960; Bagotskaya, 1962; Frumkin, 1963; Chen *et al.*, 1996.

Hydrogen trapping sites

When hydrogen diffuses into a metal's crystalline matrix, the atom can occupy a normal site or a trapping site. This is because the crystalline matrix is not perfect, and possesses a variety of defects such as gaps, impurities, interfaces, grain contours, or even microstructural flaws present in the metallic matrix (see Figure 5). In structures containing defects, hydrogen is responsible for unexpected failures, causing local changes in the stress field. These changes can lead to the weakening of the steel, contributing to the propagation of cracks, bubbles, and loss of plasticity of the material resulting in the rupture of vessels and tubes (Pundt andKirchheim, 2006).
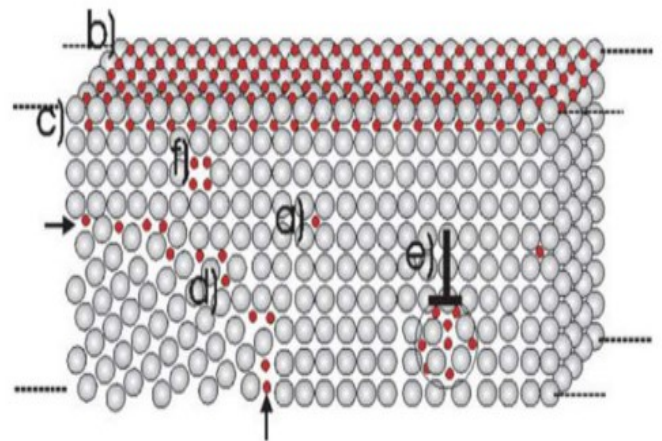

Fig. 5. Hydrogen trapping sites, where the gray and red spheres represent the atoms of the crystalline and hydrogen matrix, respectively. In (a), the occupation of the interstitial sites; (b) and (c) H atoms dissolved at surface and subsurface sites, respectively; (d) hydrogen segregation in the grain boundaries; (e) accumulation of H in edge-type disagreements; and (f) hydrogen trapped in a gap, [60] adapted from [59]

The free energy of atoms in the metal-hydrogen system is lower for atoms that reside in trapping sites than in normal sites. Trapping sites are classified as reversible or irreversible according to the magnitude of their ligation energy with hydrogen. Reversible trapping sites, which have low energy, can easily release the trapped hydrogen to diffuse. Irreversible trapping sites are those in which hydrogen is kept imprisoned and does not contribute to the diffusive process (Pressouyre and Bernstein, 1978; LiuandAtrens, 2015). A theory proposed by Pressouyreand Bernstein (1978) relates irreversible traps to the susceptibility of materials to HE. He noted that evenly distributed irreversible traps with a high level of saturation (amount of hydrogen that can be captured) are favorable to hydrogen embrittlement, reducing the amount of hydrogen that can diffuse to critical locations. Reversible traps, on the other hand, can store hydrogen until it is energetically favorable for the hydrogen to spread further. Carrasco *et al.* (2019) presented a numerical simulation of the reversible and irreversible effects of hydrogen trapping on crack propagation. The simulations showed that the appearance of cracks increases with the increase in hydrogen concentration due to the effect of hydrogen trapping. In addition, the crack start and growth in materials with irreversible traps is slower than in materials with reversible traps. These results are consistent with macroscopic observations of the trapping effect, providing a better understanding of hydrogen embrittlement in different steels. The greater the ligation energy between hydrogen and the trapping site, the greater the energy that must be provided for the hydrogen to be released from this site. The reversibility of a site is related to the hydrogen's capacity to break free from it. An irreversible trap is associated with a location with a high activation energy, such as phase boundaries and

inclusion/precipitate interfaces. Hydrogen atoms trapped at these locations are considered non-diffusible hydrogen. However, reversible traps such as grain contours and offsets have a lower activation energy. Hydrogen atoms in reversible traps are diffusible and these traps influence the effective hydrogen diffusivity (Deff) and resistance to hydrogen embrittlement (Park *et al*., 2019).

Hydrogen Embrittlement: Hydrogen is considered a promising assetto control of global warming by reducing CO_2 emissions. However, hydrogen is associated with a weakening phenomenon that causes severe degradation in the mechanical properties of metals. Hydrogen embrittlement is a generalized mode of degradation in many metallic systems that can occur through various mechanisms. It is characterized by loss of ductility and strength, fracture toughness and metal fatigue in a hydrogen environment (Pan and Pu, 2019). Hydrogen atoms can be absorbed by metals during the manufacturing process or in various service environments, such as those that include hydrogen gas, a corrosive liquid, or cathodic protection. Atomic hydrogen can segregate into crystal defects, such as vacancies, displacement nuclei and precipitates, which leads to the final rupture of metallic systems. Experimental studies show that hydrogen permeation is significantly influenced by surface conditions, particularly oxide films and internal defects and impurities that trap hydrogen and prevent diffusion (Chen *et al*., 2020). Liu *et al*. (2019) highlight the importance of evaluating the influence of microstructure on hydrogen diffusion as an essential device to understand and reduce the risk of hydrogen embrittlement in metals and structural alloys. Hydrogen embrittlement is extremely harmful to materials and can cause catastrophic failures. There are many types of embrittlement that affect metals. Of the various embrittlement processes cited in the literature, hydrogen embrittlement is responsible for a surprising number of failures and is considered the most influenced by microstructure, stress concentration, stress gradient, and strain rate. This phenomenon causes engineering alloys to fracture unexpectedly, usually at a considerable economic or environmental cost. Inaccurate predictions of component life arise from an inadequate understanding of how the material's microstructure affects HE (Seita*et al*., 2015). According to You *et al*. (2016) the degradation of materials by hydrogen is a serious problem and has been a subject of much controversy. For Venezuela *et al*. (2018) the influence of hydrogen manifests in a reduction in ductility and in the presence of brittle characteristics on the fracture surface.To date, many comprehensive works have been published on hydrogen embrittlement thathighlight the following three factors required and responsible for these types of failures (see Figure 6):
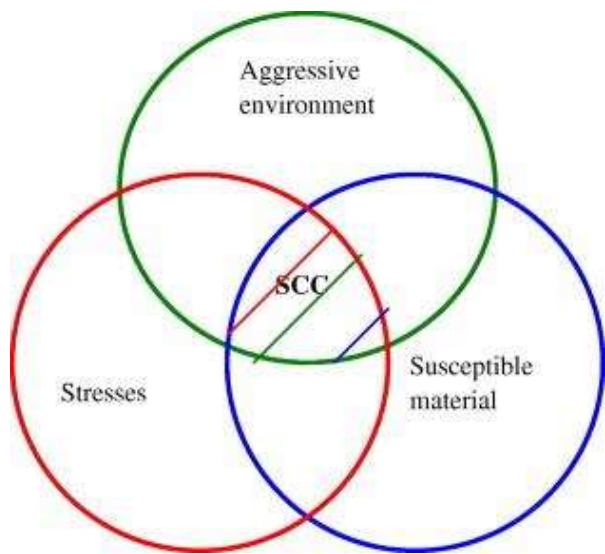

Fig. 6. Factors responsible for hydrogen embrittlement [89]

Hydrogen Embrittlement Mechanism: Hydrogen damage in metals is divided into reversible and irreversible HE. For reversible HE, hydrogen atoms migrate and then accumulate at the potential cracking

locations, leading to the delayed fracture of the alloys. By contrast, in irreversible HE, hydrogen atoms combine with each other to form hydrogen molecules at defect sites, generating high hydrogen gas pressure and hydrogen-induced cracking. After a hydrogen removal treatment is conducted, the reversible hydrogen damage in steels is healed, but irreversible HE still remains. So far, many HE mechanisms including the hydrogen pressure theory, hydrogen-induced phase transformation (HIPT) theory, hydrogen-enhanced decohesion mechanism (HEDE), hydrogen-enhanced localized plasticity mechanism (HELP), and hydrogen-enhanced strain-induced vacancies (HESIV) have been proposed to explain HE phenomena. The hydrogen pressure and HIPT theories can explain irreversible HE, while reversible HE is mostly rationalized by the HEDE, HELP, and HESIV mechanisms. However, it is of consensus that no one HE mechanism is widely accepted for explaining all reversible HE phenomena (Dwivedi and Vishwakarma, 2019) (see Figure 7).
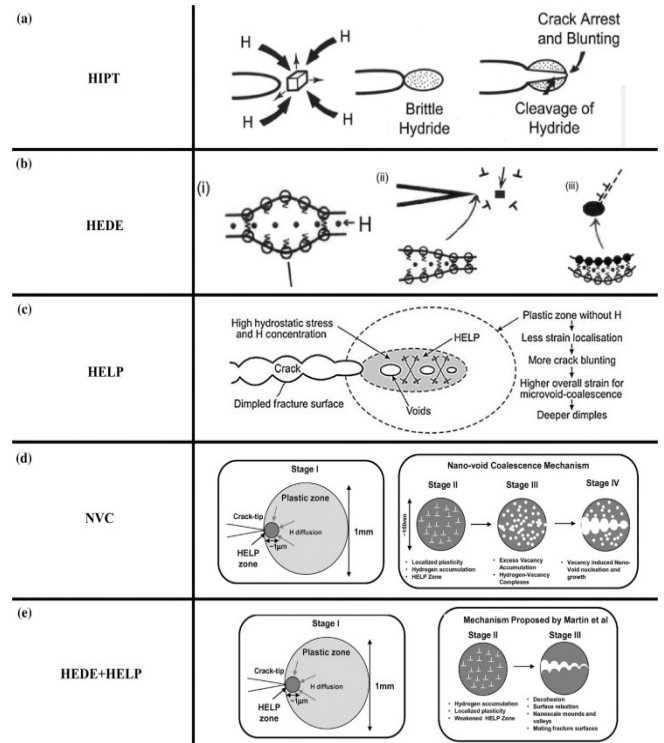

Fig. 7. Schematic diagrams of HE mechanisms. (a) HIPT [113]: hydrogen-induced phase transformation theory; (b) HEDE [113]: hydrogen-enhanced decohesion mechanism; (c) HELP [113]: hydrogen-enhanced localized plasticity mechanism; (d) NVC [114]: nanovoid coalescence mechanism; (e) HEDE + HELP [114]: combined effect of hydrogen-enhanced decohesion and hydrogen-enhanced localized plasticity mechanisms

Due to the combined effects of hydrogen concentration and stress gradients, hydrogen diffuses toward and accumulates at the stress concentration region. As the local hydrogen concentration reaches the critical value, which is still unknown, fracture failure occurs as schematically shown in Figure 8. Usually, hydrogen sources are divided into internal hydrogen and external hydrogen. Internal hydrogen is produced in the material preparation processes, such as smelting, welding, pickling and plating.

Whereas external hydrogen is generated during service due to corrosion, hydrogen gas and H_2S gas acid environments. Accordingly, the prevention of HE can be considered based on two approaches. The first is the use of surface coating and surface modification treatments. These methods are used to prevent external HE. The second approach is the modification of the material microstructure by adding/eliminating the appropriate alloy elements and optimizing the alloy microstructure. Hydrogen embrittlement prevention measures can be seen in detail in Refs: Bhadeshia, 2016; NelsonandMurray, 1984; ChenandWu, 1992; Ratoi*et al*., 2020.
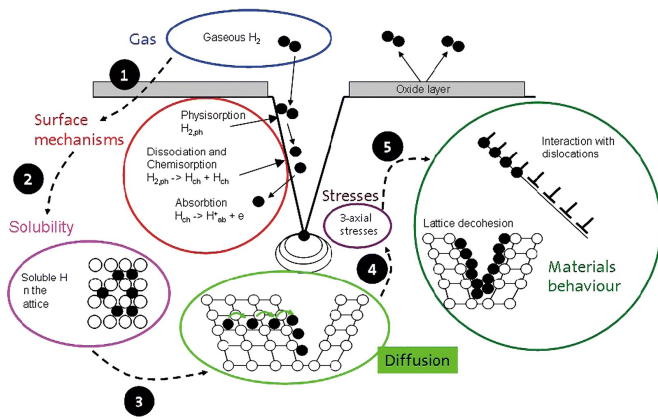
Fig. 8. Schematic diagram of the evolution of the hydrogen atom and HE failure [115]

Electrochemical permeation of hydrogen: The simplest measurement techniqueamongst the techniques and tools for measuring hydrogen embrittlement is the permeation test, which is also used to measure diffusible hydrogen in steel. If the amount of diffusible hydrogen is known, the steel's susceptibility to HE can be determined and assessed (De Bruycker*et al*., 2018; Bueno *et al*., 2014; DevanathanandStachurski, 1962). The electrochemical permeation technique was developed by Devanathan and Stachurski in 1962 and allowed for the development of a standard test from which parameters related to the susceptibility of a material to the harmful action of hydrogen can be obtainedsuch as: solubility, diffusivity, permeability and hydrogen flow. This method uses two adjacent cells, a cathode cell (Load Cell) and an anode cell (Detection Cell), separated by a metallic membrane called the working electrode (WE). Each of these compartments is also composed of a reference electrode (RE) and an auxiliary electrode (AE) (see Figure 9). The loading solution can be an acidor an alkaline solution. The usual detection solution is 0.1M NaOH (Espinosa-Medina *et al*., 2017;Silva *et al*., 2020). The method consists of producing hydrogen in the load cell where the hydrogen atom adsorbed on the sample surface will then be absorbed into the metal due to the difference in concentration until it reaches the detection cell. In the detection cell, an anodic potential is applied to oxidize the diffused hydrogen (Liu *et al*., 2020). The hydrogen oxidation reaction is given by:

$$H = H^+ + e^- \qquad (8)$$

The electrochemical permeation technique is an effective method to study the influence of microstructure on hydrogen permeation, since hydrogen absorption and diffusion are strongly dependent on hydrogen solubility and entrapment in different matrix microstructures. Through the electrochemical permeation of hydrogen, it is possible to determine, among other parameters, the number of trapping sites on metal surfaces, the hydrogen flow, and the apparent and effective diffusivity (Folena*et al*., 2020; Monzamodeth *et al*., 2021).
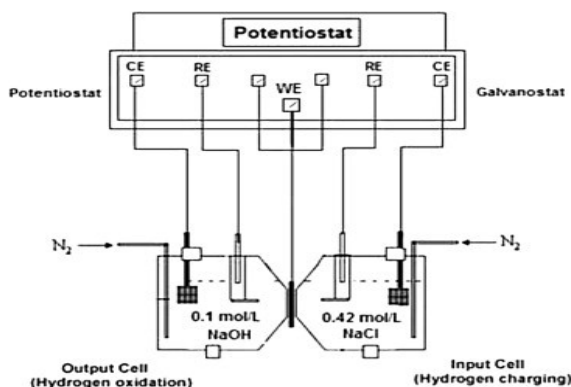

Fig. 9. Devanathan-Stachurski double-cell setup [124]

During the first charge (first transient) all sites, normal and reversible and irreversible, are filled with hydrogen until the flow at the outlet reaches its maximum value. After reaching the steady state, where the flow of hydrogen is constant, the charge is canceled and the hydrogen is oxidized on the detection side where the measurement of the experimental device is made. The hydrogen flow decreases (desorption) to a value called the bottom. During the discharge process only the hydrogens in the matrix and the reversible sites are removed, whilst the hydrogens present in irreversible trapping sites require a greater amount of energy to be removed. After obtaining the second transient, the cathodic current is interrupted to promote complete hydrogen desorption (Doyle *et al*., 1995). The Figure 10 shows an illustration of the curves obtained for both permeation transients. The apparent diffusion coefficient (Dapp) is calculated from the first transient; this coefficient includes the effects of all existing, reversible and irreversible trapping sites. For the second transient, the value of the effective diffusion coefficient (Deff) is obtained considering only the reversible trapping sites, since the irreversible sites have already been filled with hydrogen in the first transient. The results of the permeation tests are usually presented in normalized coordinates: normalized flow and normalized time (see Figure 11). Each curve will provide the data that will be used to find the parameters of diffusivity, permeability and solubility (Oriani, 1970; ThomasandSzpunar, 2020).
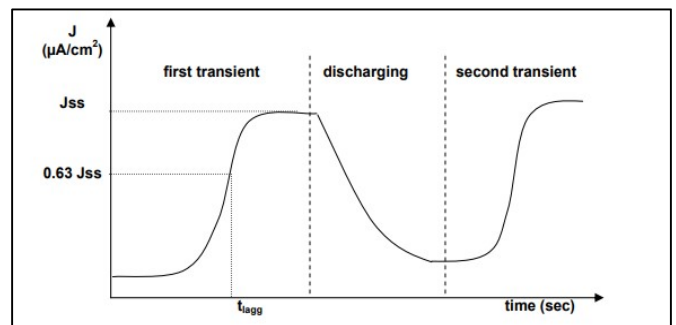
Fig. 10. Typical permeation curves represented in time-current density coordinates [24]
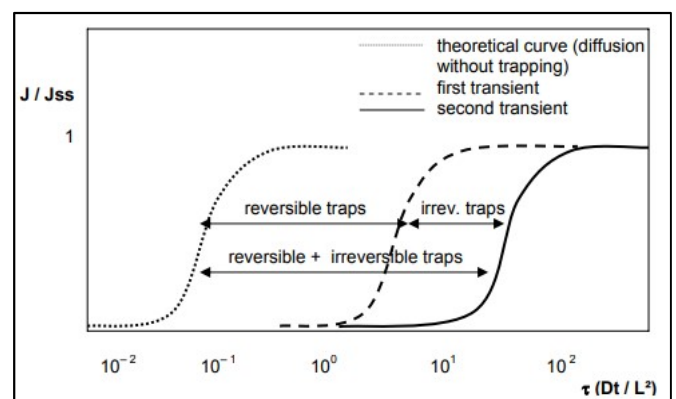
Fig. 11. Permeation curves represented in normalized coordinates [24]

Equation of the diffusion coefficient in electrochemical hydrogen permeation methods: During an electrochemical hydrogen permeation test, the variation in the concentration of this element in the metal will depend on both position and time. The double-cell electrochemical permeation model of Devanathan and Stachurski (1962) is the classic model used to study hydrogen diffusion in metals, which is based on Fick's second law:

$$\frac{\partial c(x,t)}{\partial t} = D_H \frac{\partial^2 c(x,t)}{\partial x^2} \qquad (9)$$

where D_H corresponds to the diffusion coefficient of hydrogen in steel, c corresponds to the hydrogen concentration, and t represents the time.

There are three methods to produce hydrogen: Galvanostatic-Potentiostatic (GP), Double-Potentiostatic (DP), and under Open Circuit Potential in Acid medium (OCPAc). Following the standards Refs. ASTM G 148-97 (2003) and ISO 17081 (2004), hydrogen diffusivity in various publications is estimated only by the DP method, even if the GP and OCPAc methods were also used. The references Boes and Züchner (1976), McBreen *et al.* (1966), Leblond and Dubois(1986) showed that the first two methods have different boundary conditions and, therefore, different solutions to Fick's second law. Note that these standards do not justify the use of only one equation regardless of the method used to generate hydrogen. The following equations (Fick's second law solutions) describe the transient flow of hydrogen for the DP (Eq. (10)) and GP (Eq. (11)) methods. The boundary conditions for the DP method consider the hydrogen concentration on the sample surface constant, while the conditions for the GP method consider the constant flow rate:

$$j(t) = j_\infty \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 D_{app} t}{L^2} \right) \right] \tag{10}$$

$$j(t) = j_\infty \left[1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{(2n+1)^2 \pi^2 D_{app} t}{4L^2} \right) \right] \tag{11}$$

where euj_∞ is the maximum steady-state current density, L is the membrane thickness, and $j(t)$ is the current density at time t (see Figure 12).
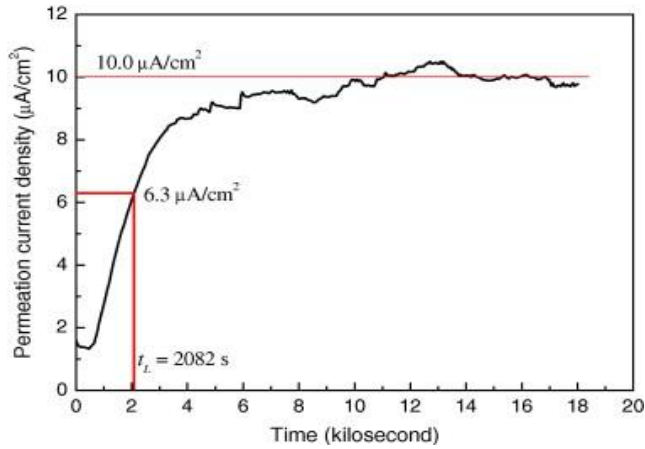

Fig. 12. Transient hydrogen permeation current density curve measured on X80 steel [134]

From characteristic parameters (maximum current density at steady state, j_∞, and time-lag, t_L), obtained from the electrochemical permeation curve, the apparent diffusion coefficient, D_{app} is obtained. The time-lag time interval, t_L, is the point where the saturation of the metallic matrix by hydrogen begins to occur, defined as the time necessary to reach a current density corresponding to 63% of the maximum current density at steady state. Time-lag can also be calculated from characteristic equations depending on the method used for hydrogen loading, Galvanostatic-Potentiostatic (Eq. (12)) or Double-Potentiostatic (Eq. (13)), (Züchner and Boes, 1972).

$$D_{app} = \frac{1}{2} \frac{L^2}{t_L} \tag{12}$$

$$D_{app} = \frac{1}{6} \frac{L^2}{t_L} \tag{13}$$

The norms ASTM G 148-97 (2003) and ISO 17081 (2004) standardize electrochemical hydrogen permeation experiments. The equations Eq. (12) and Eq (13) are applied according to the method used in References (Boes and Züchner, 1976; Züchner and Boes, 1972). These norms ASTM G 148-97 (2003) and ISO 17081 (2004) only recommend the use of Eq. (13), where the time interval, t_L, is defined as $j(t)/j_\infty = 0.63$. According to Carvalho *et al.* (2017) the equations proposed by the norms cited, in principle, underestimate the value of diffusivity, and only standardize hydrogen permeation using the Double-Potentiostatic method. The authors sought to clarify this question by proposing an empirical methodology for calculating the apparent diffusivity using the OCPAc method and from the permeation curves, they sought a representative mathematical model or a phenomenological equation. The sigmoid logistic function (Eq. (14)) was the one that most fits the experimental data. The correlations proposed by the authors Refs. (Carvalho *et al.*, 2017) for the calculation of apparent diffusivity prove to be adequate not only for this method, but also for other projects.

$$f(x) = A_2 + \frac{A_1 - A_2}{1 + \left(\dfrac{x}{x_0} \right)^p} \tag{14}$$

where, the dependent variable $f(x)$ was related to the normalized current density, $j(t)/j_\infty$, and the independent variables x and x_0 were related to time. The parameters A_1, A_2 and p were adequately correlated with the physical and chemical properties of the phenomenon. In Eqs. (12) and (13), the parameter A_2 (Eq. (15)) relates the slope of the dimensionless permeation curve associated with the saturation time and the physical-chemical characteristics of the material to its diffusivity and thickness. The dimensionless parameter A_2 is defined as follows:

$$A_2 = \frac{L^2}{D_{app} t_L} \tag{15}$$

Given the values of t_L (s), j_0 (mol/cm².s) and D_H (cm²/s), important properties can be determined, such as permeability, P in mol/cm. s, and the solubility, S, (mol/cm³). Permeability is related to the transport of hydrogen at steady state due to a pressure gradient. Solubility is related to the material's capacity to store hydrogen in the crystalline matrix (Boes and Züchner, 1976; Kupka and Stępień, 2009).

$$S = \frac{P}{D_{app}} \tag{16}$$

$$P = j_0 L \tag{17}$$

where, j_0 (mol/cm².s) is the maximum flow of hydrogen in the steady state as a function of the maximum current density in the steady state, j_∞ (mA/cm²), and F is the Faraday constant, (96,485C/mol).

$$j_0 = \frac{j_\infty}{F} \tag{18}$$

The concentration of the subsurface, C_0, which corresponds to the concentration of hydrogen at the cathode side, can be estimated by the expression (Yen and Huang, 2003):

$$C_0 = \frac{j_\infty L}{D_{eff}} \tag{19}$$

The previously described parameters are applied to the mathematical models to determine the density of hydrogen trapping sites. The density of hydrogen trapping sites in metals can be determined according to the model proposed by Oriani (1970).

$$N = \frac{C_0}{3}\left(\frac{D_L}{D_{eff}} - 1\right) \qquad (20)$$

where N is the density of trap sites per cm³, C_0 is the concentration of subsurface trap sites in number per cm³, D_L is the normal diffusivity, that is, that which would be obtained in a homogeneous lattice, and D_{eff} is the effective diffusivity, both in cm²/s.

This model allows the density of trap sites in any steel or alloy to be determined. However, the absence of the Avogadro constant (N_A) directly influences the final result. If this mathematical model were used in the way proposed by its developers, the value obtained for the density of hydrogen trapping sites would be so small that we could overlook the effect of hydrogen trapping on the metal; that is, the number of capture sites would become insignificant. Also, the scaling unit of the N parameter, if not corrected, becomes inconsistent because its units would be the number of capture locations per unit of volume. In this case, Eq. (20) should be written as follows (Araújo *et al.*, 2014):

$$N = \frac{C_0}{3}\left(\frac{D_L}{D_{eff}} - 1\right)N_A \qquad (21)$$

where N_A is Avogadro's constant = 6.022 × 1023 mol⁻¹(IUPAC, 1997). Another mathematical model used in recent papers by some researchers (Quick and Johnson, 1978; BegićHadžipašić*et al.*, 2012; Haq*et al.*, 2013) to determine the density of trapping sites in steel and alloys is governed by the following equation:

$$N_T = N_L\left(\frac{D_L}{D_{eff}} - 1\right)\exp^{-\left(\frac{E_b}{RT}\right)} \qquad (22)$$

where N_T is the density of trapping sites, N_L is the density of the interstitial sites in steel, E_b is the hydrogen trap binding energy, R is the universal gas constant, and T is the absolute room temperature. However, as can be seen in Refs. (Araújo *et al.*, 2014) the choice and application of these models must be made judiciously, because the adopted model must be suitable for the proposed case study. This criterion is essential to avoid mistakes that can lead to inaccurate results or estimates.

CONCLUSION

The Hydrogen embrittlement is a widely known phenomenon that occurs in steels and alloys. This brief review dealt with the mechanisms of the hydrogen diffusion into these materials responsible by the it′s mechanical properties degradation causing accidents in the industrial environment related to phenomenons such as the appearance of cracks, fissures, and rupture of vessels and tubulations. Therefore, to reduce the phenomenon of hydrogen embrittlement, the selection of the apropriate material is very important. The research and results obtained from the hydrogen permeation technique contributes significantly to this selection but unfortunately the temperature and especially the pressure variation are little explored when using this technique. In many applications the metals and alloys can be exposed to temperatures or pressures differentsother than 25°C and 1 atm respectively. Thus, efforts should be made to develop and implement new techniques that can be applied to different temperature and pressure conditions.

REFERENCES

Araújo, D. F., Vilar, E. O., & Carrasco, J. P. 2014. A critical review of mathematical models used to determine the density of hydrogen trapping sites in steels and alloys. *International Journal of hydrogen energy*, *39*(23), 12194-12200.

Ash, R., & Barrer, R. M. 1960. Diffusion with a concentration discontinuity: The hydrogen-palladium system. *Journal of Physics and Chemistry of Solids*, *16*(3-4), 246-252.

ASTM G 148-97. Standard Practice for Evaluation of Hydrogen Uptake, Permeation, and Transport in Metals by an Electrochemical Technique, 2003.

Bagotskaya, I. A. (1962). Effect of the solution composition on the diffusion rate of electrolytic hydrogen through metallic diaphragms. 1. diffusion of hydrogen through iron diaphragms. *ZhurnalFizicheskoiKhimii*, *36*(12), 2667-2673.

BegićHadžipašić, A., Malina, J., &Nižnik, Š. (2011). The influence of microstructure on hydrogen diffusion in dual phase steel. *Acta MetallurgicaSlovaca*, *17*(2), 129-137.

Bhadeshia, H. K. D. H. (2016). Prevention of hydrogen embrittlement in steels. *ISIJ international*, *56*(1), 24-36.Xu, Q., & Zhang, J. (2017). Novel methods for prevention of hydrogen embrittlement in iron. Scientific reports, 7(1), 1-9.

Bockris, J. M., McBreen, J., &Nanis, L. (1965). The hydrogen evolution kinetics and hydrogen entry into a-iron. *Journal of the Electrochemical Society*, *112*(10), 1025.

Boes, N., &Züchner, H. (1976). Electrochemical methods for studying diffusion, permeation and solubility of hydrogen in metals. *Journal of the Less Common Metals*, *49*, 223-240.

Bueno, A. H. S., Moreira, E. D., Siqueira, P., & Gomes, J. A. C. P. (2014). Effect of cathodic potential on hydrogen permeation of API grade steels in modified NS4 solution. *Materials Science and Engineering: A*, *597*, 117-121.

Carrasco, J. P., Diniz, D. D. S., Barbosa, J. M. A., Silva, A. A., & dos Santos, M. A. (2019). Numerical simulation of the hydrogen trapping effect on crack propagation in API 5CT P110 steel under cathodic overprotection. *International Journal of Hydrogen Energy*, *44*(5), 3230-3239.

Carvalho, J. P. D., Vilar, E. O., & Araújo, B. A. (2017). A critical review and experimental analysis of the equation recommended by ASTM G148-97 and ISO 17081: 2004 for the calculation of the hydrogen diffusivity in metals and alloys. *International Journal of Hydrogen Energy*, *42*(1), 681-688.

Chen, J. M., & Wu, J. K. (1992). The application of electroplating for prevention of hydrogen embrittlement in AISI 4140 steel. *Plating and surface finishing*, *79*, 74-74.

Chen, J. S., Diard, J. P., Durand, R., &Montella, C. (1996). Hydrogen insertion reaction with restricted diffusion. Part 1. Potential step—EIS theory and review for the direct insertion mechanism. *Journal of Electroanalytical Chemistry*, *406*(1-2), 1-13.

Chen, Y. S., Lu, H., Liang, J., Rosenthal, A., Liu, H., Sneddon, G., ... & Cairney, J. M. (2020). Observation of hydrogen trapping at dislocations, grain boundaries, and precipitates. *Science*, *367*(6474), 171-175.

De Bruycker, E., Huysmans, S., &Vanderlinden, F. (2018). Investigation of the hydrogen embrittlement susceptibility of T24 boiler tubing in the context of stress corrosion cracking of its welds. *Procedia Structural Integrity*, *13*, 226-231.

Devanathan, M. A. V., & Stachurski, Z. (1962). The adsorption and diffusion of electrolytic hydrogen in palladium. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, *270*(1340), 90-102.

Doyle, D. M., Palumbo, G., Aust, K. T., El-Sherik, A. M., &Erb, U. (1995). The influence of intercrystalline defects on hydrogen activity and transport in nickel. *Acta metallurgica et materialia*, *43*(8), 3027-3033.

Dwivedi, S. K., & Vishwakarma, M. (2019). Effect of hydrogen in advanced high strength steel materials. *International Journal of Hydrogen Energy*, *44*(51), 28007-28030.

Espinosa-Medina, M. A., Carbajal-De la Torre, G., Sánchez Castillo, A., Ángeles-Chávez, C., Zeferino-Rodríguez, T., & González-Rodríguez, J. G. (2017). Effect of chloride and sulfate ions on the SCC of API-X70 pipeline welds in diluted carbonated solutions. *Int. J. Electrochem. Sci*, *12*, 6952-6965.

Folena, M. C., & da Cunha Ponciano, J. A. (2020). Assessment of hydrogen embrittlement severity of an API 5LX80 steel in H2S environments by integrated methodologies. *Engineering Failure Analysis*, *111*, 104380.

Frumkin, A.N. (1963). In Advances in *Electrochemistry and Electrochemical Engineering*. Delahay, ed., Interscience, New York, 3, 287.

Gabrielli, C., Grand, P. P., Lasia, A., & Perrot, H. (2004). Investigation of hydrogen adsorption-absorption into thin palladium films: I. Theory. *Journal of The Electrochemical Society*, *151*(11), A1925.

Haq, A. J., Muzaka, K., Dunne, D. P., Calka, A., &Pereloma, E. V. (2013). Effect of microstructure and composition on hydrogen permeation in X70 pipeline steels. *International journal of hydrogen energy*, *38*(5), 2544-2556.

ISO 17081. International Organization for Standardization. Method of measurement of hydrogen permeation and determination of hydrogen uptake and transport in metals by an electrochemical technique. 2004.

IUPAC, I. (1997). Compendium of chemical terminology. *the "Gold Book"*.

Kakushi, L. E., & Évora, Y. D. M. (2016). Social networking in nursing education: integrative literature review. *Revista Latino-Americana de Enfermagem*, *24*.

Koyama, M., Hirata, K., Abe, Y., Mitsuda, A., Iikubo, S., & Tsuzaki, K. (2018). An unconventional hydrogen effect that suppresses thermal formation of the hcp phase in fcc steels. *Scientific reports*, *8*(1), 1-7.

Kupka, M., &Stępień, K. (2009). Hydrogen permeation in Fe-40 at. % Al alloy at different temperatures. *Corrosion science*, *51*(3), 699-702.

Landodlt, D. (1993). Corrosion et chimie de surfaces des matériaux. *Presses Polytechniques et UniversitairesRomandes, Lausanne*, 413-462.

Lasia, A. (2002). Applications of electrochemical impedance spectroscopy to hydrogen adsorption, evolution and absorption into metals. In *Modern aspects of electrochemistry* (pp. 1-49). Springer, Boston, MA.

Leblond, J. B., & Dubois, D. (1986). A general mathematical description of hydrogen diffusion in steels—I. Derivation of diffusion equations from Boltzmann-type transport equations. In *Perspectives in Hydrogen in Metals* (pp. 193-203). Pergamon.

Liu, M. A., Rivera-Díaz-del-Castillo, P. E., Barraza-Fierro, J. I., Castaneda, H., & Srivastava, A. (2019). Microstructural influence on hydrogen permeation and trapping in steels. *Materials & Design*, *167*, 107605.

Liu, Q., &Atrens, A. (2015). Reversible hydrogen trapping in a 3.5 NiCrMoV medium strength steel. *Corrosion Science*, *96*, 112-120.

Liu, X., Huang, Y., Li, J., Yang, D., Xu, Y., &Kunte, H. J. (2020). Effect of microbial hydrogen consumption on the hydrogen permeation behaviour of AISI 4135 steel under cathodic protection. *International Journal of Hydrogen Energy*, *45*(7), 4054-4064.

McBreen, J., Nonis, L., & Beck, W. (1966). A method for determination of the permeation rate of hydrogen through metal membranes. *Journal of the electrochemical society*, *113*(11), 1218.

Metalnikov, P., Eliezer, D., Ben-Hamu, G., Tal-Gutelmacher, E., Gelbstein, Y., & Munteanu, C. (2020). Hydrogen embrittlement of electron beam melted Ti–6Al–4V. *Journal of Materials Research and Technology*, *9*(6), 16126-16134.

Montella, C. (2001). EIS study of hydrogen insertion under restricted diffusion conditions: I. Two-step insertion reaction. *Journal of Electroanalytical Chemistry*, *497*(1-2), 3-17.

Monzamodeth, R. S., Campillo, B., & Flores, O. (2021). Hydrogen diffusion in Ni-Cr-Fe system. *Materials Today: Proceedings*.

Nelson, J. G., & Murray, G. T. (1984). Prevention of hydrogen embrittlement by a TiO/sub 2/surface layer. *Metall. Trans., A;(United States)*, *15*(3).

Oriani, R. A. (1970). The diffusion and trapping of hydrogen in steel. *Acta metallurgica*, *18*(1), 147-157.

Pan, Y., & Pu, D. (2019). Hydrogen embrittlement of C40 transition-metal disilicides. *Journal of Materials Research*, *34*(18), 3163-3172.

Park, C., Kang, N., Kim, M., & Liu, S. (2019). Effect of prestrain on hydrogen diffusion and trapping in structural steel. *Materials Letters*, *235*, 193-196.

Pressouyre, G. M., & Bernstein, I. M. (1978). A quantitative analysis of hydrogen trapping. *Metallurgical transactions A*, *9*(11), 1571-1580.

Pundt, A., &Kirchheim, R. (2006). Hydrogen in metals: microstructural aspects. *Annu. Rev. Mater. Res.*, *36*, 555-608.

Quick, N. R., & Johnson, H. H. (1978). Hydrogen and deuterium in iron, 49–506 C. *Acta Metallurgica*, *26*(6), 903-907.

Ratoi, M., Tanaka, H., Mellor, B. G., & Sugimura, J. (2020). Hydrocarbon Lubricants can control Hydrogen embrittlement. *Scientific reports*, *10*(1), 1-14.

Safyari, M., Moshtaghi, M., &Kuramoto, S. (2020). On the role of traps in the microstructural control of environmental hydrogen embrittlement of a 7xxx series aluminum alloy. *Journal of Alloys and Compounds*, *855*, 157300.

Seita, M., Hanson, J. P., Gradečak, S., &Demkowicz, M. J. (2015). The dual role of coherent twin boundaries in hydrogen embrittlement. *Nature communications*, *6*(1), 1-6.

Silva, S. C., Silva, A. B., & Gomes, J. P. (2020). Hydrogen embrittlement of API 5L X65 pipeline steel in CO2 containing low H2S concentration environment. *Engineering Failure Analysis*, 105081.

Stroe, M. E. (2006). Hydrogen embrittlement of ferrous materials. *Université Libre de Bruxelles*.

Thomas, A., &Szpunar, J. A. (2020). Hydrogen diffusion and trapping in X70 pipeline steel. *International Journal of Hydrogen Energy*, *45*(3), 2390-2404.

Venezuela, J., Blanch, J., Zulkiply, A., Liu, Q., Zhou, Q., Zhang, M., &Atrens, A. (2018). Further study of the hydrogen embrittlement of martensitic advanced high-strength steel in simulated auto service conditions. *Corrosion Science*, *135*, 120-135.

Yen, S. K., & Huang, I. B. (2003). Critical hydrogen concentration for hydrogen-induced blistering on AISI 430 stainless steel. *Materials Chemistry and Physics*, *80*(3), 662-666.

You, Y., Teng, Q., Zhang, Z., & Zhong, Q. (2016). The effect of hydrogen on the deformation mechanisms of 2.25 Cr–1Mo low alloy steel revealed by acoustic emission. *Materials Science and Engineering: A*, *655*, 277-282.

Züchner, H., &Boes, N. (1972). Electrochemical methods for diffusion measurements. *Berichte der Bunsengesellschaft für physikalische Chemie*, *76*(8), 783-790.

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