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Etude à l'échelle de la microstructure de l'effet de l'hydrogène sur l'accommodation de la déformation plastique d'un acier lean duplex

Thèse soutenue le 12/12/2022

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Université de Lille



École Doctorale des Sciences de la Matière, du Rayonnement et de l'Environnement (ED – SMRE) Unité de recherche : Unité Matériaux et Transformations (UMET)

PhD Thesis of Rana Bchara

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Study at the microstructural scale: the effect of hydrogen on the plastic deformation of a lean duplex stainless steel

PhD defended on 12/12/2022

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Introduction

Some applications like gas and oil transportation offshore, desalination and water treatment require materials that can survive their harshest environments. The attractive combination of mechanical properties and corrosion resistance of duplex stainless steels (DSS) meet the requirements of these applications. DSS are also considered as the most adapted materials for the onshore pipelines (Figure 1) and even for the industrial equipment like food and beverage storage containers [1,2].



Figure 1 Oil platform and Refinery made of duplex stainless steels [3,4]

Duplex stainless steels are alloys based on iron, carbon, nickel and chromium in which two phases γ -austenite and α -ferrite coexist in a range between 30% and 60% [5]. DSS are known for their original structure that combines the best characteristics of austenitic and ferritic stainless steels. Since 1960, DSS were an option to replace the austenitic stainless steels in a wide range of applications because of their higher mechanical strength and the sharp increase of nickel price since the content of this alloying element is lower in DSS. As the interest in these materials increased, the lean duplex stainless steels (LDSS) with a lower cost have been developed. They are characterized by a higher content of nitrogen with a lower content of nickel and molybdenum compared to the other standard DSS.

As the growing demand shifted from petroleum fuel, coil and natural gas to cleaner energy sources, hydrogen becomes one of the best transition solutions. One of the main challenges in the hydrogen storage and transportation is the interaction of hydrogen with the structure of the materials that shorten the service life of the components [6]. This interaction can lead to the well-known phenomenon of "hydrogen embrittlement" (Figure 2). Furthermore, the cathodic protection also acts as an important source of the hydrogen embrittlement of the

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steels. Besides hydrogen embrittlement, aging at 475 °C can be deleterious for the ductility of DSS and can even embrittle the steel. Previously, numerous studies have paid the attention on the investigation of hydrogen embrittlement and 475 °C embrittlement in DSS.



Figure 2 Failure of pipelines due to hydrogen embrittlement [7,8]

Intensive efforts attempted to understand the hydrogen embrittlement of the materials and to propose multiple mechanisms based on fractographic observations and other relevant techniques. In general, it is necessary to combine two or three mechanisms to give a full account of the deformation and fracture mechanisms of the material. Nevertheless, hydrogen embrittlement showed a strong dependency on the metallurgical state of the steel. It should be noted that the competition between hydrogen diffusion and hydrogen trapping phenomena in each phase complicates the understanding of the plastic deformation accommodation of a DSS subjected to a monotonic or cyclic loading. However, many questions are still open to discussion regarding the interactions between hydrogen and the microstructure of DSS.

The main focus of this study is to understand how hydrogen modifies the ductility of a lean duplex stainless steel. Attention will be paid on the plasticity response of each phase of a lean

duplex stainless steel by changing its metallurgical state. The challenge is to perform a research work on a steel delivered by an industrial company (APERAM) without redoing a heat treatment. The as received material consists of plates of 5 mm of thickness with two lateral surfaces slightly cold worked by skin-pass. Three microstructural states of a LDSS S32304 will be investigated: annealed, cold worked and thermally aged.

In the literature, numerous studies have been focused on the degradation of DSS induced by hydrogen or long aging times at 475 °C [9,10]. Some researchers showed that the 475 °C aging for short durations could be considered as a beneficial way to improve some properties like the hardness and tensile strength specially for the ferrite phase [11,12]. This encourages us to consider a short duration of aging at 475 °C since such material exhibited resistance to embrittlement.

Investigation of hydrogen embrittlement can be focused on crack initiation and propagation by hydrogen charging the material with a gas source or a cathodic polarization [13–15]. In the present work, the specimens will be first cathodic charged with hydrogen to then study the propensity of hydrogen to diffuse into the bulk of the LDSS as a function of microstructural state by mean of hydrogen penetration depth. Moreover, the effect of hydrogen on the change of plastic deformation mechanism of austenite and ferrite will be then investigated according to the metallurgical state of LDSS charged or uncharged with hydrogen. To achieve this purpose, we will use the methodology of fatigue test to obtain a noticeable deformation avoiding an early failure as could probably occur with the monotonic loading. Atomic Force Microscopy (AFM) will be used to approach the plastic deformation accommodation. We will also implement the expertise of our lab on the ECCI (Electron Channeling Contrast Image) technique to image the dislocation arrangements. Based on our observations, it is worth proposing at the end of manuscript a mechanism that summarizes the effect of hydrogen on each studied metallurgical state of LDSS.

The content of this manuscript is divided into four chapters.

In the first chapter, a summary on the different types of stainless steels as well as the elaboration process of DSS will be presented. A background on research works related to the hydrogen embrittlement of DSS, the single austenitic and ferritic stainless steel will be then discussed.

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In the second chapter, a description on the different metallurgical states of the studied LDSS, hydrogen charging method and the experimental techniques used to characterize the material will be presented.

The third chapter focuses on evaluating the penetration of hydrogen in the three studied microstructural states by means of electrochemical permeation and fracture analysis. A comparison of the hydrogen penetration depth in the three studied materials will be given at the end of the chapter.

The fourth chapter deals with the main objective of this study and highlights the important results obtained on the investigation of effect of hydrogen on the plastic deformation of each phase in each studied microstructure of the material.

At the end of this document, a mechanism will be proposed on the hydrogen path and its effect on each microstructural state of the LDSS S32304.

Chapter I

Literature Review

In this chapter a brief description on the different types of stainless steels as well as the solidification process specially for duplex stainless steels (DSS) will be first presented. The second section of this chapter will provide background information on the mechanical behavior of DSS under cyclic and monotonic loading. Based on the previous works, the principal mechanisms of hydrogen embrittlement as well as the effect of hydrogen on the austenitic, ferritic and duplex stainless steels will be then discussed in the end of the chapter.

1. Stainless steels

Steels are mainly formed of iron and carbon with a carbon content less than 2% (in weight). Stainless steels contain at least 11% by weight of chromium which allows a high corrosion resistance. The addition of the other elements alloying such as manganese (Mn), nickel (Ni), nitrogen (N), molybdenum (Mo), silicon (Si) and titanium (Ti) improves the mechanical and chemical properties especially localized corrosion resistance. Stainless steels have been used since 1920 for many applications like pipelines, screws and bolts, medical tools, kitchen utensils, facades and roofing. The annual consumption of stainless steel has reached a growth rate more than 5% over the last 20 years which exceeds that of the other materials thanks to their good corrosion resistance, high ductility and long lasting [16]. Various criteria may be used to classify the stainless steels: chromium content, elaboration process, mechanical properties and crystallographic structure. The latter has been considered as the best criteria to identify the different groups of stainless steels. Thus, according to their microstructure, stainless steels are classified into four main types: martensitic, austenitic, ferritic and duplex stainless steels. It is possible to promote a phase formation by controlling the chemical elements composition especially the chromium and nickel content [17]. Therefore, the Schaeffler diagram (Figure I.1) has been used to predict the phases present in the steel after

welding and is often employed to have a quick idea of the class of stainless steel according to the chemical composition.



Figure I.1 Schaeffler diagram [17]

1.1. Martensitic stainless steels

Martensitic steels present usually the highest hardness and strength among the stainless steels. They contain 0.1-1.2 wt.% of carbon which lower their ductility. They are ferromagnetic and can be hardened by a simple heat treatment. Unlike austenitic and ferritic steels, martensite has a low chromium and nickel contents. The martensite microstructure can be obtained by a diffusion less transformation resulting from a rapid cooling of the austenite into the body cubic centered structure (BCC) where the carbon atoms are trapped in octahedral sites. A tempering follows the quenching in order to combine hardness and ductility. Their high mechanical resistance allowed them to be widely used in engineering and wear resistance applications [16,18].

1.2. Austenitic stainless steels

Austenitic stainless steels form the largest category of all stainless steels, they combine a good formability, weldability and high toughness at low temperature. They exhibit a face centered cubic structure (FCC) with carbon contents between 0.03-0.07%. Their microstructure is achieved by nickel (Ni) addition, a chemical element that strongly stabilizes the austenitic phase. Nitrogen and manganese are the other γ -promoter elements. Even by rapid quenching (water quench), the austenite does not transform and remains stable at room temperature.

Austenite can be destabilized by external mechanical loading giving rise to the so-called strain induced martensite and even by hydrogen charging. The martensite phase can be either the α' BCC phase or the ε HCP phase. The attempts were aimed to replace nickel by nitrogen in order to provide a good hardness and to reduce the cost of the steel [18].

1.3. Ferritic stainless steels

Ferritic stainless steels contain high chromium content (Cr > 13 %) and a low content of carbon. They exhibit a body cubic centered structure (BCC) at high temperature which forbids any phase transformation on cooling. They are magnetic and economical unlike the austenitic steels. Their welding limitations and lack of ductility have restricted the use of ferritic steels. Increasing the chromium and molybdenum contents improve their corrosion resistance, however this can be accompanied by an intermetallic precipitation which can contribute to their embrittlement. They are mainly used in transportation and making automotive parts due to their high mechanical and corrosion resistance [18].

1.4. Duplex stainless steels

Duplex stainless steels (DSS) have always attracted the attention of the researchers, suppliers and customers. Their interesting combination of corrosion resistance and mechanical properties allowed them to be widely used in transportation (oil and gas) and petrochemical industries. Bain and Griffith are the first who mentioned the existence of austenitic-ferritic (duplex) stainless steels in 1927 [19]. They are called duplex because of their dual phase microstructure that composed of α -ferrite (BCC) and γ -austenite (FCC). This beneficial behavior combines the characteristics of both phases which improve their strength and resistance to chloride stress corrosion cracking in comparison to austenite and ferrite separately. DSS possess a low level of slag inclusions, low amounts of C, O, S, impurities and residual elements. This achievement was possible due to the additional refining processes: VOD (vacuum-oxygen decarburization), ESR (electroslag remelting) and AOD (argon-oxygen decarburization).

According to the chemical composition, the elaboration process and thermo-mechanical treatments are controlled to obtain a volume fraction ratio of the phases 50%/50%, but it can be varied in a wide range, the austenite content can reach 60%. DSS usually have very high contents of chromium (Cr) and contain in much lower amount molybdenum (Mo) which are the α -stabilizing elements, and nickel (Ni), manganese (Mn) and nitrogen (N) as γ -stabilizing

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elements. Nitrogen is added with the wish to replace nickel by nitrogen for economic reasons. The development of DSS was aimed to replace austenitic stainless steels in some applications by taking advantage of their low cost and good properties (ductility and mechanical resistance, corrosion resistance).

Duplex stainless steels are divided into multiple categories based on the pitting corrosion equivalence number (PREN) calculated from the chemical composition in wt.% as follows: PREN = % Cr + 3.3 %Mo + 16 %N

According to their PREN, duplex stainless steels categories are classified as follows:

Lean duplex \leq 35 < duplex < 40 \leq super duplex < 45 \leq hyper duplex

Standard and lean duplex stainless steels (LDSS) are frequently used for structural applications and tank construction when a high strength and mildly corrosion resistance are needed. LDSS are characterized by their relatively low contents of Ni and Mo in comparison to the other DSS. However, the Mo content can reach 2% or 3% in the standard DSS. Super and hyper duplex stainless steels are highly alloyed having large contents of Cr, N and Mo to provide a PREN more than 40. These grades are used in a very corrosive environment when seawater and chemical exposures are requesting [17–19].

2. Solidification Process of DSS

As mentioned above and used for the construction of the Schaeffler diagram, the alloying element being either γ promoter or α - promoter, it is very usual to express their efficiency by their Cr and Ni equivalency:

Nieq = Ni + 0.31Mn + 22C + 14.2N + Cu

Creq = Cr + 1.37Mo + 1.5Si + 2Nb + 3Ti

It is possible to predict the solidification mode of stainless steels by using a thermodynamic operator Φ defined as follows [17]:

$$\phi = Ni_{eq} - 0.75Cr_{eq} + 0.257$$

If:

 ϕ < 0: ferritic primary solidification

 ϕ > 0: austenitic primary solidification

 $\phi pprox$ 0: ferritic-austenitic solidification

Duplex stainless steels may solidify in modes FA (ferritic-austenitic) or F (fully ferritic). The FA mode means that austenite forms either from the liquid or, for the F mode, in the solid-state

during cooling (Figure I.2). The temperature of the further heat treatment controls the ratio of each phase of the steel.

The fully ferritic solidification takes place when the percentage of chromium is relatively high which leads to α -crystals formation (S $\rightarrow \alpha$) (Figure I.2.a). After cooling, an inter and intragranular nucleation and growth of austenite phase occurs due to a solid solution transformation $\alpha \rightarrow \alpha + \gamma$.

The second solidification mode called flip-flop or often austenitic-ferritic solidification occurs at a very slow cooling rate close to the eutectic valley (S + α + γ) (Figure I.2.b). Here, ferrite is also the first crystallized phase. During the melting process, the reduction in the concentration of the α -stabilizing elements contributes to an increase in the concentration of the γ stabilizing elements (Ni, Cu, Mn, C and N) in the solution which enhances the formation of γ crystals [17].



Figure I.2 (a) Fe-Cr-Ni diagram at 70% iron illustrating the two-phase solidification and (b) simplified Fe-Cr-Ni diagram with an overview of phase formation [17]

The austenite formation leads to a reduction in the γ -stabilizing elements which triggers the ferrite solidification once again. Flip-flop solidification is based on a repeated sequence that alternates between α -crystals and γ -crystals formation until the total solidification of the material. The further cooling step involves a diffusion-driven growth of the γ -crystals or a diffusion-controlled solid solution transformation ($\alpha \rightarrow \alpha + \gamma$) which gives rise to a secondary austenite phase γ_2 [17]. Figure I.3 shows the morphology of the two types of austenite phase γ_1 and γ_2 obtained respectively from the molten metal that occurs during the first stage of flip-flop solidification and solid solution transformation of ferrite.



Figure I.3 The morphology of the primary γ_1 and secondary γ_2 austenite [17]

A tertiary austenite γ_3 can be formed at a temperature below 1000 °C due to a ferrite decomposition during the eutectoid solid-state reaction ($\alpha \rightarrow \sigma + \gamma_3$).

The 50:50 ratio of each phase is the ideal proportion to achieve the excellent mechanical and corrosion properties which requires a strictly controlled temperature of the heat treatment, which must be followed by a water quenching [17].

To express the relative solubility of the alloying elements in the α and γ phases, it is usual to refer to the coefficients K = C α /C γ . They have been defined under equilibrium conditions for solution annealed and water quenched material [5]. Ferrite is enriched in P, W, Mo, Si and Cr and austenite in N, Ni, Cu and Mn as shown in Figure I.4.



Figure I.4 Typical partition coefficients, K, for solution annealed and water quenched materials [5]

As mentioned above, nitrogen is an interesting alloying element from an economical point of view. The partition coefficient for nitrogen suggests a very high solubility in austenite and a very low one in ferrite. Therefore, increasing the average content of nitrogen in a DSS results in a stable content of nitrogen in ferrite and in an increasing content in austenite. It has been already proved that the increase in nitrogen content in DSS can harden the austenite phase

and increases its stability. The nitrogen addition leads to an increase of the microhardness of austenite phase as shown in Figure I.5. Above 0.12% (in weight) of nitrogen, the microhardness of austenite phase becomes higher than that of ferrite. In certain cases, the higher nitrogen content (0.62% in weight) induces an inversion in the matrix of DSS in which austenite can become the matrix and ferrite forms the islands of the steel [20].



Figure 1.5 Evolution of the microhardness values of α and γ phase versus the nitrogen content in DSS [20]

3. 475 °C embrittlement in DSS

The aging treatment of a given DSS in a range of temperature between 300 °C and 600 °C can be deleterious for their ductility and can even embrittle the steel. The evolution of the microstructure and the precipitation limit their application in the chemical and nuclear industries above 350 °C and attract the attention of the user in regards to the so-called 475 °C embrittlement phenomenon. The modification of the microstructure by spinodal decomposition takes place inside ferrite at 475 °C which generates the two phases α' rich in Fe and α'' rich in Cr [11]. This decomposition can occur after a long and short aging time [9– 11,21]. For long aging time, other possible phases can be formed like G (rich in Ni, Si and Mo) and R phases as well as the other secondary phases which can promote the embrittlement of the material [9]. Over the past years, 475 °C embrittlement has been extensively studied. Meanwhile, multiple studies [11,12] have shown the presence of the two distinct phases (α' and α'') without any brittleness of the steel. Pointing out the spinal decomposition for short exposure duration is not obvious. Nevertheless, Reis et al. [11] succeeded to do it in S32304 lean duplex stainless steel after 25 h of aging at 475°C which tends to be always present for longer aging times. They employed chemical dissolution method to highlight the height difference between the ferrite and austenite phase resulting from a selective dissolution of ferrite phase by oxalic acid. Indeed, the ferrite etching by this acid depends on Cr concentration because oxalic acid dissolves selectively the regions rich in Cr. Thus, the fluctuation in Cr content in the aged samples changed the etching behavior of the electrolytic polishing solution and induced a fluctuation height between austenite and ferrite. A significant decrease of the height difference between austenite and ferrite phase has occurred after 25 h and remained unchanged with the increase of aging time. The spinodal decomposition occurrence has been confirmed also by an important hardness of ferrite phase after the first hours of aging treatment and tends to be saturated after 25 h. However, 475 °C aging affects mainly ferrite phase because of its large Cr and Mo contents as well as high diffusion rates of its elements which lead to a fast kinetic reaction more than that in austenite at high temperature [9]. The 22Cr-5Ni DSS characterized by TEM (Transmission Electronic Microscopy) after 5 h of aging treatment at 475°C has revealed the presence of α' and α'' causing by the spinodal decomposition (Figure 1.6) [9].



Figure I.6 TEM Micrograph of aged 22Cr-5Ni DSS at 475 °C for 5h illustrating a mottled contrast inside ferrite referred to a spinodal decomposition [9]

Moreover, the microhardness of ferrite in 22Cr-5Ni DSS increased from 273 HV_{0.01} with the increase of aging duration to reach a maximum 336 HV_{0.01} after 255 h, while the microhardness of austenite remained approximately stable between 263 HV_{0.01} and 290 HV_{0.01}. This verified that no microstructural change could occur inside austenite. Furthermore, the yield strength (Rp_{0.2}) and ultimate tensile strength (UTS) of the duplex steel have been significantly improved (Rp_{0.2} = 610 MPa to 735 MPa and UTS = 830 MPa to 1030 MPa) because of the ferrite microstructural change. On the other hand, a significant decrease of ductility has

been noted (elongation to fracture decreased from 50% to 12% after 255 h of aging). Ferrite has not showed the classic ductile fracture mode (ductile dimples), necking and fibrous fracture have been observed, while ductile dimples have been noticed inside austenite (Figure 1.7).



Figure 1.7 SEM images of (a) brittle fracture of a tensile specimen after 255 h of 475 °C aging treatment and (b) magnified view showing decohesion between ferrite and austenite, transgranular cleavage in ferrite indicated by the white arrows and micro-voids [9]

The fracture seemed to be essentially along the interphase boundaries where long cracks and necking have been detected. In addition, ferrite showed transgranular cleavage with brittle fracture mode caused by the presence of R phase and other precipitates. This indicates that the aged ferrite phase is mainly responsible of the embrittlement of the steel whereas austenite has accommodated most of the plastic deformation.

4. Mechanical behavior of DSS

Due to the very wide range of stainless steels, it is not so relevant to compare the mechanical behavior of DSS with the other grades. Indeed, one can read in some papers that the yield stress of DSS is double that of austenitic steel but the inverse is also possible depending on the considered grade.

What is important to note is that the mechanical properties of DSS are not simply the sum of the properties of each phase. It is necessary to point out the interaction and transfer between the two phases, especially in term of the accommodation of plastic deformation. Thus, the occurrence of two phases inside DSS complicates the understanding of its plastic deformation mechanism and so the understanding of damage and fracture. In order to well explain the degradation of a DSS, the plastic accommodation mode of each phase in the material must be

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understood first. Meanwhile, the following contributions to the yield stress of DSS are classically reported:

- a solid solution hardening especially by interstitial atoms (C, N) and to a less extent by substitutional atoms (Cr, Mo, Ni).

- a strengthening by grain size of the two phases, and their partition.

- a strain induced by the differential contraction of the two phases on cooling from the annealing temperature.

- a strain induced transformation of the austenite.

- a change in dislocation slip mode (as for austenite) or deformation accommodation mode e.g., twinning in ferrite.

4.1. Plastic deformation under monotonic loading

The accommodation of the plastic deformation under monotonic loading occurs when a specimen is subjected to a tensile or compressive stress that increases continuously. If the deformation of both phases is accommodated by dislocations glide, then plastic marks develop at the external surface which can be recorded by AFM (Atomic Force Microscopy) [22] or by DIC (Digital Image Correlation) [23]. In a previous PhD work performed by D. Salazar at Lille University [24], the strain partition under both monotonic and cyclic loading has been investigated in the DSS UR52N⁺ to understand the role of each phase in the accommodation of the plastic deformation. Ferrite and austenite have shown plasticity marks after various plastic straining ($\epsilon_p = 0.2\%$, 0.7%, 1.15% and 1.8%). Straight slip bands (Figure I.8.a) were observed inside the γ -austenitic grains while they were curvilinear (Figure I.8.b) in the α -ferrite phase.



Figure 1.8 Straight slip bands in austenite (a) and curvilinear slip bands in ferrite (b) imaged with AFM (Atomic Force Microscopy) signal error mode after plastic deformation of $\epsilon_p = 1.8\%$ [22,24]

The slip bands number increased with the increasing of the plastic deformation which led to the presence of multiple slip systems in the austenitic grains. The morphology of the austenite slip bands suggests a planar slip mode with the agreement of TEM results. Regarding the morphology of ferrite slip bands, they can be classified into two different groups, linear A and curvilinear F. Type A1 for the shorter slip bands of ferrite grains located near the phase boundary while A2 had the length size of ferrite grains. The second group F is subdivided into F1 and F2, where F1 belongs to the slips bands that did not cross the phase boundary. Slip lines type F2 present straight extremities that can intersect the phase boundary. A1, A2 and F2 seemed to be connected with the neighboring austenite grains. Figure I.9 shows the morphology of the different types of slip lines observed in ferritic phase.



Figure I.9 Different types of slip lines observed in ferritic grains after plastic deformation [22,24]

The existence of continuous slip lines across austenite/ferrite phase boundaries can be explained by the crystallographic compatibility that satisfied the Kurdjumov-Sachs (k-s) relation: $\{111\}_{FCC}//\{110\}_{BCC}$ and $\langle 011 \rangle_{FCC}//\langle 111 \rangle_{BCC}$. The slip bands can be transferred to ferrite grains when the angle between their glide systems is inferior to 10°. If this transfer is followed by a shear enhancement, the slip bands can pass through the ferrite grains (A2). Otherwise, they will stop either the gliding in the middle of ferrite grains and give a rise to the type A1, or they will continue gliding by curvilinear slip morphology and promote type F2. When the compatibility is not present between the gliding system of neighboring austenite and ferrite grains, ferrite will deform independently along their favorable systems and involves F1 slip bands [22,24].

Through EBSD (Electron Backscatter Diffraction) and KAM (Kernel Average Misorientation) analyses, Kim et al. [25] have shown that, for the duplex stainless steel LDX-2101, austenite mainly accommodates the deformation during the first stages of straining. The peak position of austenite has more shifted than that of ferrite from the initial position after 5% and 10% of straining as shown in Figure I.10. The KAM value of ferrite phase has barely achieved the same angle of that of austenite in the 20% strained sample.



Figure I.10 KAM evolution with 0-20% straining of the duplex stainless steel LDX-2101 [25]

The KAM evolution indicates that the initial deformation was essentially localized in austenite phase and further deformation was accommodate by both phases. Same plastic deformation changes have been noted for Uranus 50 (DSS) after certain level of straining. After 0.5, 0.6 and 0.9 mm of elongation, austenite grains have been activated and exhibited two or three kinds of slip planes, while ferrite did not show any deformation [26]. However, some small areas near the phase boundaries exhibited some slip traces. The activated slip systems in austenite were $(\overline{111})$ $[1\overline{10}]$ and $(\overline{111})$ $[1\overline{10}]$, having the maximum Schmid factor. The density of slip lines for both systems became higher with the increase of elongation from 0.7 mm to 0.9 mm while their height remained 10 nm. The number of dislocations in a specific grain of austenite has not changed above 0.9 mm of elongation due to the hindering of dislocations motion by each other which can be explained by the increase of friction stress. Consequently, another dislocation sources became activated [26]. Two deformation mechanisms have been suggested for ferrite, the accumulation of dislocations in the vicinity of phase boundaries induced a local stress and generated dislocations in ferrite grains. The second one is based on the shearing effect of some ferrite grains induced by the presence of dislocations in the neighboring austenite grains (Figure I.11).



Figure I.11 (a) AFM micrograph showing the emerging dislocations from austenite to ferrite grain indicated by the striped arrow. (b) A detailed area taken from image (a) revealing the sheared dislocations where the white arrow indicates the passing slip line [26]

4.2. Plastic deformation under cyclic loading

As for monotonic loading, if a metal deforms by dislocation glide under cyclic loading, alternative displacement of dislocations and their interactions leads to the presence of slip marks or extrusions at the surface of the material. The number, shape and heights of these slip marks (Figure I.12) depend on the loading conditions (applied strain and temperature) and on the properties of the crystalline structure of the material (crystallography, texture, stacking fault energy). One typical feature of the relief resulting from cyclic loading is that the extrusions are accompanied by intrusions.



Figure 1.12 Schematic diagram of three characteristic forms of mature PSM (persistent slip marks) morphology in fatigued FCC metals [27]

The heterogeneity of the DSS microstructure leads to non-uniform distribution of stresses and dislocations density between the two phases. In 1993, Polak et al. [28] have noticed straight and parallel slip lines inside the austenite grains while they were irregular and curved in ferrite grains after a strain amplitude of $\varepsilon = 7x10^{-3}$. The dislocations inside ferritic phase appeared in the form of irregular veins intercepted by channels. However, the dislocations structure in ferrite remained the same after applying two different strains amplitudes ($\varepsilon = 7x10^{-3}$ and $\varepsilon = 4x10^{-3}$). The fraction of the wall structure has increased with the higher strain amplitude.

On the other hand, the dislocations structure in austenite grains depends on the applied strain amplitude. Planar dislocation arrays followed by numerous stacking faults appeared in the upper part of austenite grains. While a cellular dislocation structure has been found in the small austenitic grains subjected to a high local deformation. The volume fraction of the wall structure seemed not important as in the case of ferrite grains due to a less strain localization in austenite grains. The DSS BöA911 strained at 0.5% showed an important plastic deformation activity in austenite grains, the extrusions were essentially present in austenite phase as shown in Figure I.13.a which was confirmed with TEM results [24]. High dislocation density gathered in planar arrays have been found in austenite, while less frequent dislocation loops were formed in ferrite.

Similar results have been obtained by Vogt et al. [29] and Mateo et al. [30] where they identified as well a plastic deformation accommodation by austenite in the DSS at low levels of strain. At high level of straining ($\Delta \varepsilon_t = 1.6\%$), austenite presented the same modifications observed at 0.5%, high dislocations density with a significant number of slip bands. Ferrite grains became more active, the surface was covered by extrusions beside the high roughness (HR) zones located in the vicinity of α/γ interphase and especially near the deformed austenitic grains (Figure I.13.b). The HR zones were always associated to a nearby deformed grain where the K-S relation was not satisfied. The enhancement of the plastic activity of ferrite phase at high strain amplitude is due to a plastic deformation transfer from austenite to ferrite.

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Figure 1.13 AFM amplitude signal error images of the surface relief of BöA911 strained at 0.5% in (a) and at 1.6% in (b) [24]

These studies have shown that the plastic deformation is mainly occurred in austenite during the first stages of straining regardless the type of the applied loading. At higher level of straining, plastic marks appear on the surface of ferrite due to the transfer of the deformation from austenite to ferrite as a function of microstructural considerations. Hence, the importance of the microstructure aspect of each phase impacts the accommodation of the plastic deformation in the DSS.

The applications of DSS can be limited under some environments like hydrogen that can affect the mechanical behavior and embrittle the material [13,31–33]. Moreover, the presence of both phases complicates the understanding of the influence of hydrogen on the mechanical properties of DSS. Indeed, the austenitic face cubic centered structure allows a low hydrogen diffusion rate but a high hydrogen solubility. In contrast, ferrite enables a high hydrogen diffusion rate and low solubility. Although, the hydrogen embrittlement of DSS is still not fully understood because of the different effects of hydrogen on the two phases.

5. Hydrogen embrittlement - HE

Hydrogen embrittlement (HE) has been a research topic since 1870. The intensive efforts have been intended to characterize and comprehend this phenomenon. It can occur when a metal is exposed to an environment containing hydrogen. Hydrogen atoms can penetrate and diffuse through the metallic structure following the interstitial sites. The presence of cracks on the surface of the material could be one of the consequences of this phenomenon. After the penetration of hydrogen, the material can be instantly damaged by a simple action of stress. HE is a concern of ductile materials which break in a brittle manner. Hydrogen is the smallest atom but it can lead to catastrophic failures of large size component as shown in Figure I.14.



Figure I.14 Failure of a pipe in a fertilizer plant after 18 months service due to HE [8]

HE is considered as a particular case of stress corrosion cracking since hydrogen involves in some cases the presence of the cracks [34].

The five main stages of the HE phenomenon are:

- adsorption of hydrogen atoms at the surface of the material,

- absorption and diffusion of hydrogen into the metallic structure,

- possible hydrogen trapping,

- presence of cracks on the surface, in some cases but not necessarily,

- embrittlement of the material enhanced by a loading.

The possible reactions related to this process are as follows:

In aqueous environment: $H^+ + e^- \rightarrow H_{ads}$

In gaseous environment this relation is substitute by the dissociation reaction: $H_2\leftrightarrow 2H_{ads}$

Once hydrogen is adsorbed on the surface of the material, it will penetrate the structure to be absorbed by the metal: $H_{ads} \rightarrow H_{abs}$

Thus, hydrogen absorbed inside the metallic materials in aqueous or gaseous environment may affect the mechanical properties of the material. The damaging effects of hydrogen can be more or less deleterious depending on the microstructure of the material and the hydrogen concentration inside the metal.
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5.1. Hydrogen sources

Hydrogen is the smallest atom, having a Bohr radius equal to 53 pm which allows it to penetrate in the metals and diffuse easily in their solid solution.

Hydrogen can be produced during the process of coating deposits used to protect the material against the corrosion e.g., galvanizing phosphating and paint-stripping solutions. Cathodic protection for the pipelines underground or under seawater is considered also an important source of hydrogen. Hydrogen gas or liquid hydrogen used as fuel in space industry may lead to the presence of cracks inside the storage tank after years of service due to HE. Moreover, the environments containing hydrogen sulfide (H_2S) or hydrochloric acid (HCl) are considered also as an important source of HE. Therefore, the drawback of replacing the fossil fuels by hydrogen to provide a clean energy is the degradation of the materials used for its production, storage and transportation [35].

According to the literature, different methods have been used to study the HE phenomenon: gaseous charging (at high pressure and high temperature), cathodic charging, hydrogenous compounds. Note that these three methods are non-equivalent in terms of hydrogen concentration and hydrogen diffusion in the materials.

<u>Gaseous charging</u> takes place in a gas chamber where a high pressure and high temperature are present to produce hydrogen gas charging. This method does not promote easily hydrogen embrittlement [36].

<u>Cathodic charging</u> is frequently used to produce hydrogen atoms by applying a cathodic potential or current density. The metal acts as a cathode submerged in an electrolyte containing hydrogen ions (H^+). In this case, hydrogen atoms can be adsorbed on the surface of the material or recombined to form H_2 gas. To prevent this recombination arsenic oxide (As_2O_3) or thiourea ($CS(NH_2)_2$) can be added to the solution.

Regarding the **hydrogenous compounds**, hydrogen atoms can be released as a result of a chemical reaction between the metal and the hydrogenated compounds. This method is not frequently reported in the literature.

In the present research, the cathodic charging method is used to introduce hydrogen into the LDSS. For this reason, the literature review of this manuscript will focus mainly on studies that have used the same method.

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5.2. Mechanisms of hydrogen embrittlement

The cracking generated from hydrogen forms the signs of a localized plasticity resulted from a macroscopic deformation. Different mechanisms of HE have been described and explained by Lynch [35] depending on the fracture modes observed through the metallographic techniques: hydride formation, hydrogen enhanced decohesion, hydrogen enhanced localized plasticity, adsorption induced dislocations emission and hydrogen vacancy interactions. The dominant mechanism can be identified depending on the material composition, its microstructure and fracture mode.

5.2.1. Hydride formation

This mechanism is observed when the solubility of hydrogen in the metallic matrix is exceeded like in Ti and Zr alloys for a major part and less frequently in V, Nb, Ta alloys [37,38]. It can only occur at temperatures where hydride phase is stable and when hydrogen can diffuse to regions near crack tips. Indeed, hydrides are known for their poor plastic properties and therefore easy to fail by brittle mode. The mechanism is based on repeated sequences of hydrogen diffusion to regions ahead cracks (high hydrostatic stress), nucleation and growth of a hydride phase, cleavage of the hydride and interruption of crack propagation at the hydride matrix interface (Figure I.15) [35].



Figure 1.15 Schematic illustrating the diffusion of hydrogen to high hydrostatic stress region following by a brittle fraction at the crack tip [35]

5.2.2. Hydrogen enhanced decohesion – HEDE

The decohesion hypothesis involves a weakness of interatomic bonds due to the transfer of hydrogen electron to the unfilled 3d shell of the metallic (as iron) atoms [39]. High hydrogen concentrations and decohesion can also occur at atomic crack tips, ahead of cracks where dislocations can form a barrier which results in a high stress, ahead cracks where a high hydrostatic stress is present like in high-strength steels and at particle-matrix interfaces (Figure I.16). A decohesion can be produced when a high elastic stress leads to a high hydrogen

concentration in interstitial lattice sites near the crack tips. A bond weakening is a result not only of trapped hydrogen but of metalloid impurities segregation at specific sites which leads also to a decohesion at grain boundaries or ahead crack tips. Therefore, in some cases a decohesion can be involved at grain boundaries and interfaces resulted from both trapped hydrogen and impurity elements [35].



Figure I.16 Schematic illustrating atoms separation caused by the weakening of interatomic bonds by (i) hydrogen in the lattice, (ii) adsorbed hydrogen and (iii) hydrogen at particle-matrix interfaces [35]

5.2.3. Hydrogen enhanced localized plasticity – HELP

It is the commonly observed mechanism of HE where solute hydrogen facilitates the movement of dislocations. The presence of hydrogen reduces the separation between dislocations by shielding the dislocations from the repulsive force between dislocation-dislocation and dislocation-obstacle. The shielding effect is strongly pronounced on edge dislocations due to the presence of dilatational stress field that can highly localized hydrogen. Therefore, a low applied stress could enhance the activity of dislocations. The high hydrogen content near or at the crack tips creates a localized plasticity which leads to an increase in dislocations mobility. The crack growth occurs by the coalescence of micro-voids in the high hydrostatic stress zones where high hydrogen environment. HELP mechanism is associated to transgranular or intergranular fracture depending on hydrogen localization inside the grains or adjacent to grains boundaries [35]. Figure I.17 illustrates the HELP mechanism inducing the micro-voids coalescence process.



Figure I.17 Schematic representation of HELP mechanism [35]

In situ TEM experiments, elasticity theory and atomistic calculations have been used to prove the evidence of HELP mechanism. The proposed mechanism has existed for centuries, Birnbaum, Sofronis and Robertson [37] have reported the increasing of dislocations mobility and dislocation nucleation rate. Nibur et al.[40] have shown an increase in slip planarity resulting from hydrogen addition. They have suggested a reduction of the critical resolved shear stress necessary for dislocations gliding which enhanced their motion that related to HELP mechanism. Thus, this mechanism focuses on the interaction between hydrogen and dislocations that generates further slip bands.

5.2.4. Adsorption induced dislocation emission – AIDE

Lynch [41] was the first who proposed the AIDE mechanism. It is more complex than HEDE and HELP mechanisms. AIDE involves two steps the nucleation and the emission of dislocations away from crack tip. The first stage requires an adsorption of hydrogen then the dislocations can move easily from the crack tip by an applied stress. Once the nucleation is triggered, the dislocation core and the cooperative movement of breaking and reforming of interatomic bonds will be occurred. The crack growth induces the nucleation and growth of micro and nano-voids near the crack tips. Therefore, the voids facilitate the formation of crack growth induced by dislocation emission ahead the crack tips. AIDE mechanism is based on adsorption of hydrogen at the crack tips that weakens the interatomic bonds and leads to dislocations emission and crack growth (Figure I.18.a). This adsorption cannot be involved in inert or air environment owing to the presence of oxygen that forms strong bonds with the substrate which prevent the weakness of interatomic bonds at crack tips. Ductile cracks in inert environment were resulted from the emission of dislocations from plastic zones near the crack tips because of the strong interatomic bonds between

oxygen and the substrate (Figure I.18.b). High levels of strain are needed to generate microvoid coalescence and dimples which favors the crack growth. Like HELP mechanism, transgranular or intergranular fractures can be observed depending on the location of dislocation emission and void formation inside the grains or between the grain boundaries [35].



Figure 1.18 Schemes illustrating the (a) AIDE mechanism for HE in which the dislocations emission and coalescence of voids in the plastic zones ahead the crack favor the crack growth and (b) crack growth by coalescence of cracks and dislocations egress emitted near [35]

5.2.5. New emerging Mechanisms

In 2004, Nagumo et al. [42] proposed a new mechanism of HE: Hydrogen enhanced strain induced vacancies (HESIV). This mechanism is related to the presence of vacancies enhanced by hydrogen that can facilitate the failure of the metallic alloys. Hydrogen induces the formation of stable vacancy clusters, then their growth and agglomeration lead to a reduction in ductile crack growth resistance and accelerate the premature failure of the material. The nanovoid coalescence mechanism (NVC) has been lately suggested and it can be described as shown in Figure 1.19.



Figure I.19 Schematic representation of NVC mechanism [39]

The NVC mechanism combines the HEDE, HELP and HESIV effects. Neeraj et al [39] reported a significant dislocation activity just beneath the fracture surfaces. Based on their experimental observations, the nanovoids covered the brittle fracture surfaces of the ferritic steel. The embrittlement of the material occurred because of the localized plasticity induced by hydrogen and the presence of hydrogen vacancies which tend to growth and generate the fracture surfaces.

6. Hydrogen transport

Once hydrogen atoms are adsorbed at the surface, they have to invade the bulk by absorption and displacement. Once absorbed by the crystal lattice, they can occupy various sites like interstitial sites and defects. Their motion from site to site are hindered by trapping sites such as grain boundaries, precipitates, dislocation tangles.

From the diffusion coefficient (D) and the hydrogen concentration (C), the diffusion flux density (J) can be calculated as follows (equation I.1):

$$J = -D.grad C = -D \frac{\partial c}{\partial x} (I.1)$$

Where,

- J is the diffusion flux density, hydrogen atoms passing through a unit area in the unit time (mol.cm⁻².s⁻¹)

- D is the hydrogen diffusion coefficient (cm².s⁻¹)

- C is the hydrogen concentration (mol.cm⁻⁴)

Higher strength steels present a lower hydrogen diffusion coefficient due to their microstructure that contains in general a high dislocation density and a large volume fraction of carbide for strengthening purposes. The hydrogen diffusion rate becomes higher while

increasing the temperature especially for closed packed materials structure. At high temperature, hydrogen can be released from the deepest traps to reach the surface. Therefore, by heating the steels at high temperature, we can minimize their hydrogen content and prevent the failure of the component. This method is usually referred to "baking" process that occurred after solidification, pickling and electroplating [35]. The relation between the hydrogen diffusion coefficient and the temperature is of Arrhenius equation type (I.2) [43]:

 $\mathsf{D} = \mathsf{D}_0 \mathrm{e}^{-\frac{\mathrm{Ea}}{\mathrm{RT}}} (\mathbf{I}.\mathbf{2})$

Where,

-D₀ is the pre-exponential factor (cm².s⁻¹)

-E_a is the activation energy that depends on the crystal structure (J.mol⁻¹)

- R is the gas constant that equal to 3.814 x 10⁻³ J.mol⁻¹.K⁻¹

-T is the temperature (K)

At room temperature, the D factor (diffusion coefficient) in ferritic stainless steels is greater by several orders of magnitude than that in austenitic stainless steels where ferrite presents 10^{-7} cm².s⁻¹ and 2.15×10^{-12} cm².s⁻¹ in austenitic steels [34]. The hydrogen diffusion depends strongly on the structure of the steel in term of geometrical size and distribution of each phase and on the temperature as well. For duplex stainless steels, the ratio of austenite and ferrite phase determines the value of the diffusion coefficient, it is usually comprises between 10^{-9} - 10^{-10} cm².s⁻¹ [34].

Beside the gradient of hydrogen concentration and the temperature, the hydrogen diffusion through the microstructure of a given material is affected by a hydrostatic stress field. The presence of higher trap density at grain boundaries can slower the hydrogen transport across the lattice [35].

The hydrogen transport is not essentially carried out by the interstitial sites. Note that the short- circuits sites like dislocations and grain boundaries can also contribute to the diffusion of hydrogen inside the material.

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7. Hydrogen trapping

During the diffusion of hydrogen between the interstitial sites inside the steel, hydrogen can be trapped by various defects of the crystal lattice. These defects can be divided into three classes: attractive, physical and mixed traps (Figure I.20):

- **attractive traps:** the existence of an attractive force due to a local variation of stress, temperature and chemical potential,

- **physical traps:** refer to the crystal lattice discontinuities such as dislocations, voids and grain boundaries,

- **mixed traps:** include the combination of the two types of trapping sites mentioned above like dislocations and the three-dimensional stress field surrounded by each dislocation.



Figure 1.20 Scheme illustrating the hydrogen traps in the steel [35]

The trapping sites increase the solubility of hydrogen but decrease its apparent diffusivity. The residence time of hydrogen inside the trapping sites is higher than that of interstitial lattice sites which reduces the diffusion rate of the material and lower the hydrogen permeability of the steel [43]. Figure I.21 represents the sinusoidal curve of the energy required for hydrogen atom to pass through a trapping site. E_a characterizes the activation energy for hydrogen diffusion in the crystalline lattice. To transport the hydrogen atom into a trapping site, an additional energy (E') is needed. The energy E_a+E' is necessary to overcome the barrier energy and reach the trapping site. To escape from the trapping site, much more energy is required, $E_a+E'+\Delta E_x$ [43].



Figure I.21 Schematic representation of interaction energy between hydrogen atom and trapping sites [43]

However, two types of trapping sites exist in stainless steels, reversible and irreversible sites based on the binding energy but without concerning the energy barrier. As showed in Figure 1.22, the binding energy of reversible trapping sites (R-trap) is relatively low which means that hydrogen can leave easily the trap to become mobile. Hydrogen localized in the reversible trapping promotes the hydrogen-induced cracking (HIC) phenomenon. In contrast, much more energy has to be provided to release hydrogen from the irreversible traps (IR-trap). At these sites, the localized hydrogen cannot participate to the diffusion process owing to its permanent residency [43].



Distance

Figure 1.22 Schematic illustration of the binding energy at reversible and irreversible trapping sites [43]

8. Hydrogen effect on austenitic stainless steels

Austenitic stainless steels (ASS) are widely used in environment containing hydrogen like in acid solutions and hydrogen gas bath which can lead to their embrittlement at different levels [44]. The susceptibility of austenite to HE depends on its stability regarding to plastic deformation levels and hydrogen concentration. Ménard et al. [45] showed that the 316L ASS exhibits an increase of their slip bands features after hydrogen charging and tensile straining.

In their research, before hydrogen charging, the samples were subjected to two heat treatments: 1150 °C for 30 min and 1200 °C for 5 h followed by ice cold quenching. Consequently, two different average grain sizes have been obtained: 300 μ m after the heat treatment of 1200 °C and 140 μ m after 1150 °C. In the coarse microstructure (d = 300 μ m) strained to 2% at 10⁻³ s⁻¹, the mean value of slip bands spacing increased by 17% (1.57 \pm 0.15 to 1.84 \pm 0.23 μ m) and 100% (1.57 \pm 0.15 to 3.15 \pm 0.46 μ m) for 31 ppm and 135 ppm of hydrogen respectively. Likewise, the height of slip bands increased by 40% (20 \pm 3 to 28 \pm 3 nm) with 31 wt. ppm of hydrogen and 85% (20 \pm 3 to 37 \pm 4 nm) with 135 ppm. For the fine grains specimens charged with 135 ppm of hydrogen followed by a straining of 2% at 10⁻⁶ s⁻¹, the slip bands spacing decreased from 1 \pm 0.06 μ m to 0.56 \pm 0.06 μ m. Similar decrease has noted for the height of the slip bands from 12 \pm 1 nm to 3 \pm 1 nm. The hydrogen concentration of 135 ppm and the low applied strain rate (10⁻⁶ s⁻¹) might be insufficient to increase the slip bands features like in the case of large grains. This indicates that the grain size affects the dislocation density produced during deformation which can interact with hydrogen.

A multiple slip bands system and an increase in planar slip mode have been noted in the fine and large hydrogenated grains. The experimental observations suggested a significant plastic accommodation in the largest grains since a high dislocation density has been observed in these grains [45].

Furthermore, for a pre-strained 304L ASS subjected to a tensile loading in the presence of hydrogen, Wang et al have revealed a brittle fracture mode, while they observed a ductile fracture mode for the material subjected to the same strain level but not charged with hydrogen [44]. Figure I.23 compares the fracture surfaces of 304L ASS pre-strained in the presence and without hydrogen. It shows also that the depth of brittle zones in hydrogenated specimens depends on the pre-strain levels. It was thicker with the hydrogenated 304L ASS pre-strained at 25% (Figure I.23.d).

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Figure I.23 SEM images of (a) 0% pre-strained (b) 20% pre-strained 304L ASS hydrogen free and (c) 0% prestrained (d) 25% pre-strained of hydrogenated 304L ASS [44]

During the straining, the dislocation density has increased which enhanced the trapping of hydrogen because dislocations can act as hydrogen traps and possibly reduced its diffusivity. The diffusion loss is related to the structure of the steel and the binding energy between hydrogen and dislocations [44]. Mine et al. [46] have noticed also a reduction in hydrogen diffusivity after the pre-straining of the steel that increased the dislocations density and so the hydrogen solubility. Basically, FCC structure presents a low binding energy between hydrogen-dislocation which could suggest a more tendency for hydrogen to be trapped by dislocations. While in BCC structure, the hydrogen binding energy to dislocations appears higher than the activation energy that characterized the hydrogen diffusion. In addition, at high level of strain, the hydrogenated 304L ASS may involve the martensitic transformation which can enhance the diffusion of hydrogen along the twin and grain boundaries to be further trapped in dislocations and increased the apparent brittle zones. Consequently, α' -martensite promotes the hydrogen emerging inside austenite and thus enhanced the embrittlement of the material [44].

Hatano et al. [47] have noted a reduction of ductility for the austenitic stainless steels SUS 304 and SUS 316L after hydrogen charging. KAM analysis has revealed a strain localization induced

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by hydrogen because of the high misoriented fractions obtained after the hydrogen addition. However, in some cases the hydrogen charging can trigger a phase transformation inside austenite to give rise either to ε -martensite or to α '-martensite possibly enhanced by a straining. No α '-martensite has been observed in both hydrogenated steels but ε -martensite and stacking faults (SF) (Figure I.24.a and I.24.b) were present in some grains of SUS 304 and tangled dislocations in SUS 316L (Figure I.24.c).



Figure 1.24 TEM images showing (a) the stacking faults, (b) ε-martensite in hydrogenated SUS 304 strained to 5% and (c) the tangled dislocations in hydrogenated SUS 316L strained to 5% [47]

9. Hydrogen effect on ferritic stainless steels

The high corrosion resistance and low price of ferritic stainless steels (FSS) allow them to be more interesting than austenitic stainless steels in the automotive industry [48]. However, their applications can be also restricted due to hydrogen embrittlement. Malitckii et al. [48] studied the ferritic stainless steel (FSS) (S43940) in the as received condition and after annealing at 1050 °C and 1200 °C characterized in grain size of 18 μ m, 65 μ m and 349 μ m respectively.

For the hydrogen free materials, the grain size obtained by the heat treatment produced the expected effect, i.e., the yield stress and the ultimate tensile strength decreased with the

increase of grain size (Figure I.25). However, both the uniform elongation and the elongation to fracture were smaller for the large grain size material than for the two other ones. The three materials were hydrogen embrittled as they showed a significant decrease of their ductility after the hydrogen addition. But the grain size growth presented a minor effect on the susceptibility of the material to hydrogen and it was approximately in the same order of magnitude in the first two cases (6.9% for GS = 18 μ m and 7.3% for GS = 65 μ m) whereas 2.5% is obtained for GS = 349 μ m. In each case, the yield and tensile strength increased with the presence of hydrogen as it is shown in Figure I.25.



Figure 1.25 Stress versus strain curves of S43940 (a) in received condition, (b) after annealing at 1050 °C and (c) after annealing at 1200 °C before and after hydrogen charging [48]

Ductile and dimpled fractures accompanied by cleavage cracks have been noted in the as received steel (without hydrogen). The presence of hydrogen induced transgranular fracture mode with some intergranular fracture areas (Figure I.26.a) for the hydrogenated FSS in the received condition (GS = $18 \mu m$). Moreover, the fracture mode has become fully transgranular with the increase of the grain size (Figure I.26.c).



Figure 1.26 Fracture surfaces images of S43940 (a) in the received condition (GS = 18 μ m), (b) GS = 65 μ m and (c) GS = 349 μ m with continuous hydrogen charging [48]

Kim et al. [49] investigated the HE of two FSS 430 STS (UNS S43000) and 445 NF STS (UNS S44536). Hydrogen has been introduced into the steels using electrochemical charging in NaCl + 0.3 % NH₄SCN for 72 h with different current densities (from 0.1 to 10 mA/cm²). The SEM

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(Scanning Electron Microscopy) analyses (Figure 1.27) showed ductile fracture mode with dimples in the 430 STS charged with 0.2 mA/cm². While the 445 NF STS revealed inclusion fracture with crack initiation and propagation at grain boundaries. The results have shown a more severe HE of 445 NF than that of 430 steel. The hydrogen concentration contained in 430 STS was 1.3 ppm while 0.5 ppm has been found in 445 NF STS. Thus, the difference in hydrogen concentration found in the two materials was not the reason behind the high susceptibility of 445 NF to hydrogen. It was attributed to the precipitates formed at grain boundaries during the manufacturing and especially annealing (from 600°C to 850°C) in 445 NF steel. The Laves phase particles (precipitations of Fe₂Nb) were acting as the trapping sites for diffusible hydrogen and formed the crack initiation sites which trigger the HE of the steel [49].



Figure 1.27 SEM images showing (a) the ductile fracture mode of 430 STS charged at 0.2 mA/cm² and (b) fracture surface of 445 NF STS charged at 0.2 mA/cm² with the laves phase precipitations at grain boundaries [49]

Numerous studies [48–50] have shown the same effect of hydrogen on the mechanical properties of FSS. Hydrogen increased the yield and ultimate strength while it caused a ductility loss of the material. Wang et al. [51] have explained these effects by the dislocations pinning induced by the presence of hydrogen. In addition, the carbide particles formed in the FSS 430 affected the critical shear stress responsible to the glide of dislocations. They observed ductile dimples and micro-void coalescence in the uncharged material. In contrast, brittle fracture surfaces including transgranular and cleavage brittle areas beside the ductile fracture mode have been obtained in the hydrogen charged samples. The carbide particles were acting as hydrogen trapping sites which has decreased the diffusivity of hydrogen and formed the first nucleation cracks sites in the steel. The large number of micro-voids in the

charged sample resulted from the interaction of hydrogen with dislocations enhanced the dislocations movement and lead to their intersections. Therefore, a large number of vacancies can be generated and evolving into micro-voids coalescence which is in agreement with HELP and HESIV mechanisms.

10. Hydrogen effect on duplex stainless steels

Many studies [13,31,33,36] have shown an important interest on the investigation of hydrogen embrittlement on DSS. For instance, Okayasu et al. [33] showed a severe HE on the duplex DS SUS821L1 (21%Cr 2%Ni 3%Mn 1%Cu) due to various trapping sites and its high diffusivity. Their study also included the ASS (SUS304) and the FFS (SUS430). All the materials were cathodically charged in H_2SO_4 (0.5 mol.L⁻¹) at a current of 0.06 A for various times (1, 5, 10 and 20 h).

Figures I.28.a, I.28.b and I.28.c represent the hydrogen content measured for each steel versus the heat temperature using gas chromatography at 3.3 °C/min as a heated rate. This method determines the concentration of trapped hydrogen in the metals. Thus, the DSS presented the higher content of hydrogen with the increase of hydrogen duration in comparison with the ASS and FSS which indicates a higher hydrogen solubility in DSS. The hydrogen diffusion coefficient has been estimated for the three materials using the Arrhenius equation (mentioned in section **6**) with various temperatures and it showed a higher value in the FSS compared to that in the ASS and the DSS (Figure I.28.d). The high difference appeared in the hydrogen content and hydrogen diffusion coefficient for the three materials suggested that the ferrite/austenite interface was the favorable site for hydrogen trapping. It must then be taken into consideration for DSS the effect of the mixed lattice structures of the two phases and the existence α/γ boundaries.



Figure 1.28 (a), (b) and (c) the hydrogen content released from AS (austenitic steel), FS (ferritic steel) and DS (duplex steel) and (d) the hydrogen diffusion coefficients for the three steels [33]

A tensile load until the fracture was applied for the three steels. A better mechanical behavior has been observed for the DSS before the hydrogen addition. The yield and ultimate tensile strength obtained in the DSS were higher than those of the ASS and the FSS. A loss in ductility has been noted for the DSS after hydrogen addition more than that of the ASS and the FSS charged with hydrogen. The increase of hydrogen charging duration has led to a significant decrease of fracture strain of the hydrogenated duplex steel. Moreover, the fracture analysis (Figure 1.29) showed the presence of ductile dimples for the three steels before the hydrogen charging. However, a mixture of brittle and ductile fractures has been observed in the FSS charged with hydrogen. The ASS exhibited no change in its fracture mode after the hydrogen addition while the hydrogenated DSS displayed an intergranular brittle fracture with some cracks in austenite/ferrite phase boundaries due to the local accumulation of hydrogen. They suggested that the hydrogen trapped around the dislocations and triggered the intergranular HE in duplex steel [33].



Figure 1.29 Fracture surface modifications of AS (austenitic steel), FS (ferritic steel), DS (duplex steel) before and after hydrogen charging [33]

Similar results have been obtained by Claeys et al with the DSS S32205 subjected to electrochemical hydrogen charging at 0.8 mA/cm² in 0.5 M H₂SO₄ + 1 g/L CS(NH₂)₂ without applying a further mechanical loading [52]. By solving the Fick's second law equation, the estimated hydrogen diffusion coefficient was equal to $2.1 \times 10^{-14} \text{ m}^2$ /s. With 18 h of hydrogen charging where a maximum hydrogen concentration is obtained (650 ppm) and without any external mechanical loading, a surface relief has been detected essentially in austenite grains. The parallel slip lines in austenite suggested a planar slip mode possibly linked to the formation of stacking faults. EBSD analysis did not show any martensite (α' or ε) transformation inside the austenite grains after the hydrogen addition.

Luo et al. [53] have also reported the development of stacking faults inside the austenite grains of the same steel subjected to cathodic hydrogen charging at 15 mA/cm² in 0.5 M H₂SO₄ + 2 g/L CH₄N₂S for 30 min, 60 min and 360 min (Figure I.30). The increase of hydrogen duration increased the density of stacking faults (SFs) inside austenite (Figure I.30.f). The authors explained this result by a reduction of its stacking fault energy (SFE) induced by hydrogen while γ -phase has already a low SFE (10 mJ/m²). The prolonged hydrogen charging duration (e.g., 360 min) can also increase the dislocation density inside the ferrite grains which was attributed to the higher amount of absorbed hydrogen. Nevertheless, from the ECCI (Electron Channeling Contrast Image) images in Luo's paper (Figure I.30) it is difficult to appreciate the increase of SFs quantities inside austenite grains and the increase of dislocation density in ferrite caused by the addition of hydrogen.



Figure I. 30 EBSD and IPF (Inverse Pole Figure) maps revealing both phases of S32205 in (a) and (b), ECCI images of (c) no-hydrogenated sample and after hydrogen addition for (d) 30 min, (e) 60 min and (f) 360 min [53]

Moreover, XPS (X-ray Photoelectron Spectroscopy) analysis used to identify the chemical elements of the passive surface showed a reduction in the ratio of O^{2-}/OH^{-} , a change in the composition of passive film and a more important signal contribution of the substrate with the increase of hydrogen charging time. These results suggest that the hydrogen generated during the hydrogen charging process contributed to a reduction in the thickness of the passive film [53].

Conclusion

Duplex stainless steels (DSS) have received a special attention for their good corrosion resistance and mechanical properties. This excellent combination allows them to be very attractive in many applications involving a high mechanical stress in a corrosive environment. DSS tend to replace austenitic steels like 304L and 316L in some applications. Regardless the category of DSS (standard, lean, super or hyper duplex), their microstructure always presents two principal phases: austenite and ferrite in various proportions.

The elaboration process (including solidification and thermo-mechanical heat treatment) of DSS determines their microstructure and the properties of each phase of this steel. This strongly influences the individual mechanical properties of each phase and complicates the understanding of the macroscopic mechanical behavior of the DSS in different environments. The aging treatment of DSS at 475 °C for a long aging time is known also for its degradation effect, the so-called 475 °C embrittlement, particularly on the ferrite phase where brittle fracture can occur. The thermal aged DSS induces a spinodal decomposition inside ferrite phase where two distinct phases can be generated (α' and α''). However, some researchers have demonstrated the occurrence of these two phases even after a short aging time (25 h).

Many authors have highlighted the deleterious effect of hydrogen on the mechanical behavior of steels. Hydrogen can restrict the ability of plastic deformation, leads to premature fracture, promotes brittle fracture and reduces the life service of the material. These characteristics are associated to hydrogen embrittlement (HE) phenomenon. The attention has been paid since a long time on HE to provide an explanation of this phenomenon. It turns out that due to the variety of material microstructures and the different loading conditions, HE could not be modelled with a single mechanism, at least four main mechanisms are frequently considered in order to point out the pathway of hydrogen inside the microstructure of the material and to describe the fracture mode of the steel. The HELP mechanism is the commonly cited one to describe the effect of hydrogen on the mechanical behavior of numerous steels. The hydrogen diffusion and traps have shown a strong dependency of the HE phenomenon on the crystalline microstructure of the metallic materials, especially the steels. However, there is no unified opinion about the pathway and the trapping of hydrogen into the stainless steels. The principal hydrogen effects on austenitic stainless steels or on austenitic phase of DSS converge to a decrease in stacking fault energy which enhance a planar slip mode and the formation of ε -martensite or α' -martensite in some cases. While, hydrogen has induced dislocations pinning and affect the shear stress of dislocations glide in ferritic stainless steels and in ferritic phase of DSS.

In the context of this thesis, a lean duplex stainless steel (LDSS) characterized by its high nitrogen content and relatively low molybdenum and nickel content will be investigated. The hydrogen embrittlement conditions and the fracture modes will be studied. In addition, the influence of hydrogen coupled to the variation and modification of the metallurgical state of the steel will be further analyzed. Deep attention will be paid to the analysis of the plasticity of austenite and ferrite phase of the LDSS, to provide an explanation of the role of hydrogen on the plastic deformation mechanism.

Chapter II

Material and Methodology

This chapter is dedicated to present the microstructure of the lean duplex stainless steel by identifying its chemical composition and their different metallurgical states. The method used to introduce hydrogen into the material as well as the choice of hydrogen charging parameters will be showed in the second section. The last part of this chapter will present the characterization techniques used to evaluate the surface modifications and fracture mode of the steel.

1. The studied material – lean duplex stainless steel

As described in the previous chapter, duplex stainless steels (DSS) are known for their good corrosion resistance and mechanical properties. This excellent combination allowed DSS to be widely used in many industries such as petrochemical, nuclear, oil and gas transportation. The presence of two phases, austenite (γ) and ferrite (α), inside DSS complicates the understanding of its mechanical behavior. Austenite presents a face centered cubic structure (FCC) which allows a high hydrogen solubility, while ferrite exhibits a body centered cubic structure (BCC) that enables a high hydrogen diffusivity but a low solubility [13]. In general, the chemical composition is tuned and the heat treatment controlled to produce a DSS with approximately 50% ferrite- 50% austenite which was the case for the plates of the lean duplex stainless steel used in this research.

1.1. Chemical composition of the studied lean duplex stainless steel

The lean duplex stainless steel (LDSS) used in this study has been provided by the Aperam company. According to ASTM, the studied LDSS is designed by S32304 and referred to a "lean" due to a low content in molybdenum (0.47wt. %) and nickel (3.85 wt. %). Table II.1 shows the chemical composition of LDSS32304 given by the supplier while the individual chemical

composition of each phase is calculated using the Thermo-Calc software based on the annealing temperature (1050°C) and the volume fraction of each phase in the steel.

	Chemical Elements	Cr	Ni	Mn	Мо	Si	Ν	С	S	Р	Cu	Fe
LDSS32304	Wt%	22.71	3.85	1.79	0.47	0.45	0.125	0.018	< 0.001	0.028	0.46	Bal.
Ferrite	Wt%	25.39	2.82	1.63	0.60	0.44	0.033	0.009	< 0.001	0.036	0.30	Bal.
Austenite	Wt %	20.27	4.78	1.94	0.35	0.46	0.21	0.026	< 0.001	0.021	0.60	Bal.

Table II.1 Chemical composition of the studied LDSS S32304

The stacking fault energy is the energy needed to create an irregularity in the stacking sequence in the face centered cubic structures (FCC). It plays an important role in the understanding of the deformation behavior of the metals. The proposed equation (II.1) in the study of Meric de Bellefon et al. [54] is used to calculate the stacking fault energy of austenite (FCC structure) using its chemical composition listed in Table II.1.

SFE (mJ.m⁻²) = 2.2 + 1.9Ni - 2.9Si + 0.77Mo + 0.5Mn + 40C - 0.016Cr - 3.6N (II.1)

where the concentration of the alloying elements is expressed in Wt%.

The calculated SFE of austenite in LDSS S32304 is 11 mJ.m⁻², this value is considered relatively low.

1.2. Manufacturing process

The studied LDSS was elaborated in an electric arc furnace. Subsequently, the liquid is passed to the converter for the refining step of the material with VOD/AOD (vacuum/argon oxygen decarburization) furnaces and finally solidified with the continuous casting process. The slabs were transformed into sheets with a forming process that involved three main stages: hot rolling, annealing and pickling. The rolling step has reduced the initial plate thickness by 98%. The final step of the process was the solution heat treatment at 1050 °C for 20 min followed by water quenching. The material was delivered in the form of plates with 5 mm thickness. It was found surprisingly that the metallurgical state of the steel at the surface is different than that of the bulk. A detailed explanation will be discussed in the section **1.3** of this chapter. To identify the different faces of the plate, we have employed the classical terminology encountered in metal forming which refers to the rolling direction. In this way, the wide side of the plate is the (RD) side, the thin side parallel to the rolling direction is the (ND) side and the thin side perpendicular to the rolling direction is the (TD) side (Figure II.1).



Figure II. 1 Scheme of duplex stainless-steel microstructure based on the three directions ND, RD and TD In this work, the mechanical tests have been carried out along the rolling direction (RD).

1.3. Surface analysis

To get an overview about the homogeneity of the steel (phase, hardness) according to the thickness of the plate, microhardness measurements using a Vickers indenter have been performed on the surface parallel to the rolling direction (ND) and in the bulk of the material (mid-thickness of the plate). The applied load used to indent each phase was 0.025 kgf and 10 indents were produced and measured in austenite and in ferrite. Before testing, the surface was mechanically polished using SiC papers (from 320 to 2400) and finished with 1 μ m diamond paste then etched with Beraha reagent for 10 s to differentiate between ferrite and austenite phases. The mean value of measured microhardness of each phase is listed in Table II.2.

Micro-hardness Vickers	Surface	Bulk		
Austenite HV 0.025	302 ± 14	259 ± 7		
Ferrite HV0.025	274 ± 13	236 ± 5		

Table II.2 Microhardness of austenite and ferrite on the surface and in the bulk of the studied LDSS on thenormal direction of the surface plane (ND)

First, a significant difference (~40 HV) appears between the measurements of each phase in both cases i.e., austenite is harder than ferrite. Second, the hardness of each phase is lower in the bulk than on the surface. This difference reveals the heterogeneity of the metallurgical state of the steel between the surface and the bulk which points out the presence of a work hardened layer. The thickness of the latter has been estimated by performing a micro-hardness profile on the TD plane of the plate using a load of 0.2 Kgf in the depth of the material.





Figure II.2 shows a uniform hardness distribution over 200 μ m of the depth of the material. Therefore, the estimated thickness of the work hardened layer is about 200 μ m. The work hardened surface can be explained by the presence of a higher dislocation density in the vicinity of the surface resulting from the manufacturing process. It is suspected that a final step in the manufacturing process has been performed (skin pass). To verify this proposition, additional techniques have been used to attest the heterogenous distribution of dislocations in the steel like Electron Channeling Contrast Imaging (ECCI) and Transmission Electron Microscopy (TEM) analysis.

1.4. Dislocations structure

To better understand the structure of each phase on the surface and in the bulk of the material, Electron Channeling Contrast Imaging (ECCI) analyses have been conducted and confirmed then by TEM micrographs.

The ECCI observations have been performed after mechanical and electrolytic polishing using a solution of 80% acetic acid, 10% perchloric acid and 10% distilled water. Images have been taken from the transverse plane direction as shown in Figure II.3, where the work hardened layer (labeled as work hardened part) and the bulk (labeled as Annealed part) are present.



Figure II. 3 SEM image of the LDSS in transverse direction (TD)

Figure II.4 shows a broader view of the dislocations distribution in each phase in the two parts of the sample (work hardened and annealed part). Dislocations are highly present in both phases on the surface compared with the bulk of the steel.



Figure II.4 ECCI images showing dislocations in white arrows for: (a) ferrite, (b) austenite present on the surface and (c) ferrite (d) austenite in the bulk of the LDSS in the transverse direction (TD)

To confirm definitely the difference observed in the dislocations density between the surface and the bulk of the steel, Transmission Electron Microscopy (TEM) analysis has been used on two extracted samples from the surface and from the bulk in the normal direction (ND). The prepared disk for TEM were cut in the rolling direction. The preparation of the thin foils will be further detailed. According to TEM images (Figure II.5), the dislocation density in both phases seems higher on the surface of LDSS than in the bulk which can confirm the large amount observed with ECCI images in the transverse direction.



Figure II.5 TEM dark field images for BCC ferrite on the surface (a) and in the bulk (c) and bright field images for FCC austenite on the surface (b) and in the bulk (d)

From now on, the bulk of the material is designed as "LDSS annealed" and the surface as "LDSS cold worked". Consequently, in the present work, the cathodic charging and the mechanical tests are performed separately on the two states of the steel.

1.5. Microstructure

In general, the microstructure of duplex stainless steels contains islands of austenite embedded in ferritic matrix. The microstructure of the LDSS was observed using optical microscopy (OM) after etching with Beraha reagent (solution of 4 g NH₄HF₂, 1 g K₂S₂O₅, 80 mL H₂O and 40 mL HCl) for 10 s as shown in Figure II.6.a. Moreover, the combination of the two electrolytic etching solutions (HNO₃ 40% for 20 s and NaOH 40% for 10 s) with an applied tension of 4.3 V has revealed the grain and twin boundaries inside the austenite phase. The

two different types of etching (chemical and electrolytic) were preceded by a mechanical grinding using abrasives papers from 320 to 2400 SiC, then finished with 1 μ m diamond paste. Figure II.6 shows the microstructure of the LDSS cold worked where the dark phase corresponds to α -ferrite and the light one to γ -austenite phase in the normal direction. The observed microstructure of the LDSS with OM after Beraha and electrolytic etching is the same for both annealed and cold worked states.



Figure II.6 Optical micrograph of the LDSS32304 cold worked showing ferrite (α) and austenite (γ) phases in the normal direction (ND) (a) after Beraha etching and (b) after electrolytic etching revealing the grain and twin boundaries inside austenite

Electron Backscatter Diffraction (EBSD) analysis has been performed to highlight the crystallographic texture of the steel and identify the crystalline orientation of the grains of each phase. Figure II.7 compares the IPF (Inverse Pole Figure) of each phase in the two states of the material (cold worked and annealed), it shows no preferential texture for austenite. However, ferrite in the annealed state (Figure II.7.c) reveals a slight preferential orientation along (101) plan. Its grains size seems higher than that of ferrite in the LDSS cold worked (Figure II.7.a).



Figure II.7 EBSD inverse pole figures illustrating: (a) ferrite and (b) austenite of LDSS cold worked, (c) ferrite and (d) austenite of LDSS annealed

The kernel average misorientation (KAM) approach is often used as a qualitative measure of plastic deformation localization. In the present work, KAM was used to discriminate the level of plastic deformation inside ferrite and austenite in the two metallurgical states: annealed and cold worked. In short, KAM which is easily obtained from EBSD data measures the average misorientation between a central point and its nearest neighbors. KAM is sensitive to several factors, those depending on the material and those depending on SEM experiment parameters. In general, KAM is high in deformed grains due to higher dislocation density. To obtain comparable results, the SEM-EBSD parameters were similar for each case. Figure II.8 shows blue zones that indicate misorientations less than 1°, that are free from strain and lattice distortion. The dominant zones of green and yellow show a misorientation for ferrite and austenite of the cold worked material (Figure II.8.a and II.8.b). The difference of the KAM values of both phases existing between the annealed and cold worked material highlights also the misoriented areas presenting on the surface of LDSS 23204 plates. Average values of 0.73° and 0.59° have been found for ferrite and austenite respectively of the LDSS cold worked. On

the other hand, 0.56° and 0.47° values have been noted for ferrite and austenite respectively of the LDSS annealed.



Figure II.8 Kernel average misorientation maps showing the microstructure misorientation of: (a) ferrite and (b) austenite corresponding to LDSS cold worked, (c) ferrite and (d) austenite corresponding to LDSS annealed

To sum up, the surface microstructure shows a larger misorientation compared to the bulk of the steel induced by the manufacturing process most probably from skin pass stage. The KAM results are relevant with ECCI and TEM observations and confirm the presence of a high amount of dislocations in ferrite and austenite phase present in the surface layer of the material (LDSS cold worked).

The X-ray diffraction (XRD) method has been also used to identify and quantify the different phases of the steel. The X-ray diffraction pattern was obtained using Cu(k α) which corresponds to a wavelength of 1.5406 Å with a step size of 0.01°, a scan step time of 0.5 s and an angular interval 2 θ between 40°-120°. Figure II.9 presents the diffraction patterns of the two states of the material.



Figure II.9 X-ray diffraction patterns for LDSS annealed and LDSS cold worked in the normal direction (ND).

To determine the volume fraction of each phase, the peak area of each phase was estimated using Eva software. The percentage of each phase was calculated by the ratio of the sum of peaks area of phase (α) over the sum of peaks area of phase (γ). The volume fraction estimated for the LDSS annealed and the LDSS cold worked are summarized in Table II.3.

Table II.3 Volume fraction of Austenite and Ferrite in LDSS annealed and LDSS cold worked

	Austenite	Ferrite
LDSS Annealed (<i>RD</i>)	45%	55%
LDSS Cold worked (RD)	42%	58%

2. Experimental Methods

2.1. Hydrogen charging

The cathodic polarization method was chosen in our study to charge the LDSS with hydrogen because it has been widely used to investigate the influence of hydrogen on the steel and it is safer than the gaseous charging method.

2.1.1. Electrochemical cell and Hydrogen charging cell

To determine the hydrogen charging parameters, and to perform cathodic charging, different electrochemical cells were used depending on the dimensions and form of the samples (Figure II.10). The electrochemical cells are constituted of a three-electrode set-up: a reference electrode *(RE)*, a specimen welded with a steel wire as work electrode *(WE)*, and one or two platinum counter electrodes *(CE)*. The electrodes are connected to a potentiostat/galvanostat (Origaflex 1000 mA by Origalys). The used reference electrode is the Hg/Hg₂SO₄ electrode whose potential is 0.6513 V compared to the standard hydrogen electrode. All the potentials given in this thesis are relative to the electrodes were used to charge the flat specimens before the mechanical tests, two counter electrodes were used to charge the two lateral surfaces (perpendicular to the ND direction) of the samples (Figure II.10). In all cases, the steel wire and the grip parts of the specimen were electrically isolated using a varnish coating except the studied one. The specimens subjected to hydrogen charging were mechanically polished with final 1 µm diamond paste.



Figure II.10 Electrochemical cells used for hydrogen charging (a) for tensile specimens and (b) for fatigue specimens

2.1.2. Hydrogen charging parameters

The hydrogen charging method requires different parameters: the choice of the solution, the specific cathodic current density (ic) or cathodic potential, and the charging duration.

According to the literature [13,31,36], 0.5M H_2SO_4 electrolyte is commonly used to generate hydrogen atoms with adding 0.2 g/L As_2O_3 or $CS(NH_2)_2$ as a poison to prevent H_2 recombination.

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The application of a cathodic current density allows a better repeatability in the hydrogen loading/charging compared to the application of a potential. A reason why we applied a current density. In order to determine the value of this current density, potentiodynamic curve of the material in the 0.5 M H₂SO₄ solution with 0.2 g/L As₂O₃ at 0.166 mV/s of scan rate was carried out (Figure II.11). For that, a potential is applied and the current is measured. Then, knowing the surface of the sample in contact with the electrolyte, the current density is evaluated. The plotted curve (as in Figure II.11) presents the current density (i) versus the potential for each measured point.

In the anodic domain, the current corresponds to the oxidation reactions (dissolution or oxidation of the material). In the cathodic domain, the current corresponds to the reduction reactions, and so the reduction of the electrolyte which takes place at the surface of the material. In the present cases, the reduction of the electrolyte is the reaction with hydrogen. Near the corrosion potential, the both reactions occur. The potentiodynamic curve of a material in a given solution provides information about the susceptibility of the material to corrosion in a specific electrolyte. It gives not only the corrosion potential but also determines the cathodic and anodic domain of the material in the used electrolyte. In the case of the passive material, it gives the passive domain. Thus, we can note that the investigated LDSS is a passive material in the 0.5 M H_2SO_4 electrolyte. The passive domain is between around -0.3 V and 0.4 V.



Figure II.11 Potentiodynamic curve of the LDSS in 0.5M H₂SO₄ + 0.2g/L As₂O₃ solution

According to the potentiodynamic curves (Figure II.11), an applied current density ic equal to 10 mA/cm² was chosen. The hydrogen charging reaction requires the hydrogen reduction which belongs to the cathodic domain. A low cathodic current density is chosen (-10 mA/cm²) to introduce hydrogen atoms into the steel with less cracks on the surface after a short hydrogen charging duration. The charging of all our experiments was performed at room temperature.

The cathodic charging duration used in this study are 5 h, 24 h, 72 h and 168 h. According to the literature [13,31,36], most of the hydrogen charging duration range is between 24 h and 72 h, a reason why we have chosen these four durations. After 5 h of hydrogen charging, the surface of the steel can be maintained smooth, less blisters and cracks can be observed (Figure II.12).



Figure II.12 SEM micrograph showing the smooth surface of LDSS charged 5h with hydrogen after the electrolytic polishing

The aim of 168 h (7 days) of hydrogen charging is to verify the enrichment of the specimen by hydrogen. It should be noted that the penetration depth of hydrogen in the material depends on the current density.

2.1.3. Aging Effect

It is well known that the hydrogen diffusion and hydrogen solubility are very different in both phases. Thereafter, hydrogen requires a time to pass through the two phases and saturate each one of them. Ghorani et al. [55] have previously reported that the interphase boundary in DSS is the first site for hydrogen trapping. Then, hydrogen atoms will diffuse to more stable trapping sites during the holding time (post-charging time). To get an overview about the saturation of each phase in hydrogen, multiple microhardness measurements have been

performed on the surface of the LDSS annealed. We have chosen the annealed state because of the low dispersion obtained in their microhardness values due to the low dislocation density in the bulk. The sample has been charged in hydrogen with a current density of -10 mA/cm² for 24 h to ensure that hydrogen is present in both phases. The microhardness has been evaluated using Vickers microhardness (load of 25 g) by taking 10 measures in each phase to get a general hardness of austenite and ferrite. A gap of 2 h has been taken into account between each measurement set as it shown in Table II.4.

Duration after hydrogen addition	Without hydrogen charging	0h	2h	4h	6h	24h
Austenite (HV)	259 <u>+</u> 7	300 ± 20	311 ± 23	284 ± 16	259 ± 10	286 ± 9
Ferrite (HV)	236 ± 5	249 ± 15	260 ± 15	274 ± 18	268 ± 11	270 ± 12

Table II.4 Microhardness of each phase after hydrogen addition using Vickers microhardness

The microhardness of both phases increased significantly after hydrogen addition, from $HV_{0.025} = 259 \pm 7$ to $HV_{0.025} = 300 \pm 20$ for austenite and from $HV_{0.025} = 236 \pm 5$ to $HV_{0.025} = 249 \pm 15$ for ferrite. After 4 h from hydrogen addition, the microhardness evolution of each phase becomes more stable, $HV_{0.025} = 284 \pm 16$ for austenite and $HV_{0.025} = 274 \pm 18$ for ferrite. The microhardness evolution for each phase remains almost the same after 6 h and 24 h of hydrogen charging. This indicates a stability in hydrogen for each phase after 4 h of the cathodic charging. Therefore, all the mechanical tests were performed after a delay of 4 hours from hydrogen charging.

3. Thermal aging treatment

The susceptibility of DSS to precipitation and undesirable transformations above 280 °C restricted the applications of DSS [11]. As described in chapter **1** section **3**, at 475 °C, ferrite decomposes into α ' Fe-rich and α '' Cr-rich phase by spinodal decomposition and leads to an embrittlement of the material for relatively long aging time [10]. Recently, some studies [11,12] have demonstrated the occurrence of spinodal decomposition even for a short time aging (25 h or 50 h). This fact is one of our objectives in order to change the metallurgical state of ferrite without evidencing of any brittleness. Thereby, the samples were heated in a muffle furnace at 475 °C for 25 h and then cooled at room temperature. The surface preparation was

performed as mentioned in paragraph **2.1.1.** after the aging treatment and before the mechanical test.

4. Characterization techniques

The characterization methods described below aim to analyze various properties of the interpreted material. The different phases of the steel and crystallographic texture have been identified using XRD and EBSD techniques. The microstructure of ferrite and austenite present in the material was highlighted using ECCI and TEM observations. The surface modifications of the as received LDSS S32304 material have been investigated before and after the mechanical test by the two metallographic techniques AFM and SEM. The fracture mode after the tensile test was detected using SEM observations.

4.1. Atomic Force Microscopy

Atomic Force Microscopy (AFM) has been mainly used in our study to evaluate the relief induced by the accommodation of the plastic deformation during cyclic (fatigue) loading.

AFM is a scanning probe microscopy. It allows the analysis of the surface of the material at the nanoscale using interatomic forces between the studied material and a tip mounted on a cantilever. The AFM's principle is based on the control and the detection and measurement of interaction forces between the tip and the surface of the sample that the tip scans. The evolution in the interaction tip/surface induces modifications in the cantilever's deflection which can be quantified by the reflection of laser spot on a split photodiode detector (Figure II.13).



Figure II.13 Schematic showing the principle of AFM analysis

AFM can operate in three different modes: contact mode, non-contact mode and intermittent mode, depending on the forces generated between the tip and the sample. The most used mode is currently the intermittent mode. It is also named "tapping[™] mode" when using a Vecco or Brucker AFM in the intermittent or tappingTM mode, the cantilever and then the AFM tip oscillate in vertical direction. The tip touches the surface of the material at each oscillation. This allows avoiding the interruption of interactions between the tip and the surface and keeping a good stability of the system "tip+surface". The main idea of the tapping[™] mode is to limit the contact between the tip by working with non-contact forces, i.e., essentially with the Van der Waals forces. Because of very low values of Van der Waals forces, the variations of interactions between the tip and the surface cannot be detected directly by evolutions of cantilever's deflection. But their variations in oscillation amplitude are easier to measure. During scanning, because of the evolution of topography (or other surface properties), the interactions between the tip and the surface change and induce the modifications of resonance frequency of the tip+cantilever system and the change of cantilever's vibration at a given frequency. Near the cantilever's resonance frequency, this change in amplitude is large and thus easier to be detected. Hence in tappingTM mode the AFM works at a fixed frequency of oscillation and a constant oscillation amplitude (a constant tip-sample interaction) is imposed. The vertical position of scanner, and thus of tip, is adjusted to keep the oscillation amplitude constant, and so gives the evolution of the topography of the surface. Thus, AFM can provide high resolution images of the topography of the materials and give a quantitative information.

In our study, the analyses were conducted in tapping[™] mode using Veeco Nanoscope III AFM. Pyramidal tips of silicon nitride (Bruker RTESPA-300 probe) with curvature radius less than 15 nm and angle equal to 35° were used and replaced regularly to avoid the precision loss induced by the wear of the tip. The surface modifications due to the accommodation of the plastic deformation such as slip steps and extrusions can be observed through the AFM analyses as yet used by others authors [22,45,56]. Note that, because of the form of the tip, the AFM cannot measure always the good topography of the extrusions and slip bands (Figure II.14). Moreover, if the intrusions are generally detectable by AFM, their topography cannot be measured by AFM [56].

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Figure II.14 AFM tip motion in contact with a metallic surface [24]

4.1.1. Image Types

In tapping[™] mode, AFM provides two images: topographic image and signal error image. The first image provided by the movement of the z-piezoelectric scanner allows the measure of the topography of the surface of the sample. The signal error image (in Volt) resulted from the difference between the amplitude setpoint and the registered amplitude of oscillations enables a clear detection of evolution of the topography because the signal corresponds to the experimental derivative of the topography. Thus, the signal error images allow to easily detect the evolution in topography so in this study the presence of slip bands or extrusions.

In the present work, multiple areas of 40 μ m x 40 μ m have been captured in the upper, middle and lower part of the gauge length of the fatigue specimen after the mechanical loading (Figure II.15). Then 10 μ m x 10 μ m areas were retaken inside the 40 μ m x 40 μ m areas, particularly where the plastic marks have appeared and few images of 5 μ m x 5 μ m have been captured in some cases because of the smoothness of the slip lines and the small size of some austenitic islands.



Figure II.15 Scheme of the captured images in the gauge part of the specimen in the normal direction (ND)

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To characterize the slip marks, according to the profiles obtained by AFM, two parameters are considered: the slip bands heights (SBH) and the slip bands spacing (SBS). A specific software coupled with AFM has been used to find out the values of SBH and SBS by counting 20-25 slip marks in 10 zones approximately in each phase. The captured images with 10 μ m x 10 μ m of scan size have been used to measure the values of SBH and SBS because of their high resolution. Figure II.16 shows the accurate measurements of the slip marks by extract from the AFM image specific profiles. Moreover, the SBH value can change along the slip marks, a reason why several profiles have been collected along each slip mark. For this reason, SBH is written as [mean of the lowest value-mean of the highest value]. On the other hand, SBS was measured only once for each line but it is written as [mean of the lowest value-mean of the highest value].



Figure II.16 Profiles showing the measurement of the slip lines features (SBS and SBH) through AFM analysis

4.1.2. AFM resolution

Vertical resolution

The piezoelectric scanner resolution and the conditions of analyses (especially the noise) determine the vertical resolution. The piezoelectric scanner is very sensitive and provide a high resolution that can reach 0.1 nm which depends also on the surface roughness. In our study, the samples subjected to AFM analysis were electrolytic polished before the fatigue loading to obtain a smooth surface and a roughness less than 2 nm. This low roughness before

testing allows the measurement of the slip marks which are from a few nanometers to a few tens of nanometers.

Lateral resolution

Lateral resolution depends on various factors such as curvature radius of the AFM tip, surface roughness, environment conditions of AFM scanning, scan size and number of scan samples per lines. As previously reported, a high lateral resolution requires also less roughness. The value of samples/line chosen in our study is 512 and the image size was maximum 40 μ m x 40 μ m therefore a 79 nm (40x1000/511) of spatial resolution could be obtained in the better cases of measurement. The best resolution achieved could be about 13 nm with images of 5 μ m x 5 μ m.

4.2. Transmission electron microscopy

Transmission electron microscopy (TEM) is known for its high resolution which allows the characterization of the microstructure of the material. It provides information for this thesis on the deformation substructures such as dislocations, twins and stacking faults. The sample preparation consists obtaining a very thin specimen of the material (120-150 nm) to be transparent to electrons. To create an image, the transmitted electrons pass through the thin foil then a system of magnetic lenses to form an electronic image. The image is collected either by a phosphor screen either by a wide-angle camera. They are then recorded by a CCD detector (charged coupled devices) that can convert the electrons into an electronic pulse per pixel to obtain an optical image [57]. The most pronounced difference between SEM and TEM methods is the acceleration voltage offered by TEM that can reach 300 kV.

The most common imaging modes of TEM are bright field (BF) and dark field (DF). By placing the objective aperture in the back focal plane, a BF image can be formed where only the unscattered electrons are collected and appear bright in BF TEM image. The area that can strongly scatter the electrons like dislocations will appear in dark. On the other hand, DF images can be generated by specific scattering electrons where an objective aperture is placed in the back focal plane to block the unscattered electrons. The selected scattered electrons can form the DF image by choosing a specific diffraction spot. In this case, those which have been dark in BF images will appear bright in DF images [58].

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Besides BF and DF images, the diffraction patterns can be formed in the back focal plane of the objective lens by magnifying the projector lenses onto the recording devices. By analyzing the diffraction pattern, we can determine the crystallographic details of the sample.

In this work, thick slices were cut in the rolling direction then mechanically grinded and thinned to 150 μ m or less using SiC paper # 800. Discs with 3 mm in diameter were then extracted by shear punching. The final thinning was performed using the double jet technique and Struers Tenupol device. A solution of 80% acetic acid, 10% perchloric acid and 10% distilled water was employed as electrolyte and the electropolishing occurred at 10 °C and 25 V of applied tension to form a hole in the center of the foil with edges thin enough to be visible through TEM.

TEM micrographs were collected using FEI Tecnai G2-20 twin microscope operated at 200 kV. We have attributed a diffraction pattern to each TEM image. The diffraction patterns were associated to each phase of the steel by comparing them to the theoretical ones.

4.3. Scanning electron microscopy

Scanning electron microscopy (SEM) is designed to characterize the surface of the material by using an electron beam. Once the electron beam is focused on the surface of the specimen inside the vacuum chamber, different signals are emitted and collected by different detectors to form images. The detected signals inside SEM are secondary electrons (SE) and back scattered electrons (BSE). Secondary electrons are generated from a few nanometers of the sample surface. They result from the inelastic interaction between the electron beam and the sample. SE provide high resolution topographic images. However, BSE are produced from about one micrometer under the surface, resulted from quasi-elastic interaction between the electron beam and the sample. Compared to SE, BSE have higher energy and give lower resolution images. The BSE give information on the chemical composition of the sample because their energy depends on the atomic number (Z).

A SEM HITACHI SU 5000 was used in this study to identify the fracture mode for the samples subjected to tensile loading and the surface modifications of the deformed specimens after fatigue test.

4.3.1. Electron backscatter diffraction

Experimentally, electron backscatter diffraction (EBSD) is coupled with SEM where this latter equipped with a detector that can collect the backscattered electrons. Nowadays, most of all SEMs are equipped with a detector that can collect the backscattered electrons to produce EBSD. This is a powerful technique to comprehend the characterization of crystalline materials. It allows the access on the crystallographic texture, misorientation distribution, shape and size of grains inside the crystalline material [59]. To form an image, an electron probe is focused on the small surface of the sample which enables the diffraction of the backscattered electrons that fulfil the Bragg's law to be recorded by the detector. Inside the microscope chamber, the sample must be titled by 70° which is the optimal position to analyze the backscattered signal. The diffraction pattern obtained is made up of Kikuchi bands [58].

The inverse pole figure maps (IPF) are frequently used to understand the preferred orientations. IPF maps are presented as color images followed by a standard stereographic triangle where the colors represent the orientation perpendicular to the surface.

Kernel Average Misorientation

During EBSD analysis a local grain misorientation can be detected by using kernel average misorientation (KAM). The KAM investigations identify the lattice distortions and can inquire about the high dislocation density of a given material. Usually, a high KAM value is obtained for the deformed grains with a high dislocation density resulting from a high straining. This method quantifies the misorientation between a pixel and its surrounding pixels [58]. The KAM approach is used to localize detected regions of plastic deformation.

The EBSD analyses were carried out on Hitachi SU-5000 FEG-SEM system operated at 20 kV with an Oxford Instruments Symmetry system.

4.3.2. Electron channeling contrast imaging

Electron channeling contrast of backscattered electrons in SEM enables the observation of crystal defects such as dislocations, stacking faults, twins and grain boundaries. The electrons channeling contrast can be generated when the electron beam excites the two-beam diffraction condition in the crystal [60]. The contrast of the image depends on the crystallographic orientation of the lattice. The presence of defects such as dislocations can produce a lattice distortion which strongly affect the intensity of backscattered electrons by

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changing the crystal orientation. Under two-beam conditions, the whole crystal becomes quasi electron transparent which appears dark in the ECC image. The dislocations disturb the crystal which lead to a backscattering and appear as bright areas in the image.

ECCI is a rapid and non-destructive characterization method and can replace TEM technique for the investigation of dislocations and stacking fault lying underneath the surface. ECCI micrographs enable the observation of a wide area unlike TEM micrographs where a small area can be detected. Furthermore, the dislocation structures of deformed samples can be analyzed directly by ECCI without necessity for preparing thin foils that can be destroyed during the preparation.

4.4. X-ray diffraction

X-ray diffraction experiments are widely used to characterize the crystalline materials as well as phase identification and structure properties. It is a non-destructive technique, used for the crystalline material.

The principle is based on the Bragg's Law. The XRD technique consists in diffracting an incident monochromatic x-ray beam on the different crystalline planes of the grains that constitute the studied material. If no Bragg condition is met, the detector collects the background noise of X-ray scattering from the X-tube in the material. If a Bragg condition (for a given n of the Bragg law) is respected, the incident filtered photons of the tube diffract almost entirely towards the detector which collects all the photons from the tube. The signal becomes more intense than when the Bragg condition is not respected. A crystalline material can be studied by X-ray diffraction when the distance between crystal lattice planes and the angle of the diffracting x-ray beam fulfills Bragg's Law [61]:

$$n\lambda = 2d_{hkl}sin\theta$$

Where,

- n: integer

 $-\lambda$: wavelength

-dhkl: interplanar spacing between the diffracting planes

- θ : Bragg angle

Thus, by varying the incident angle of the x-ray beam with the normal to the surface of the sample the diffraction pattern is generated.

In this study, an estimation of the volume fraction of each phase has been done using the software Eva, where the area under each peak is calculated. Then the ratio of the sum of austenite peak areas over the sum of ferrite peak areas has been evaluated to determine the volume fraction of each phase in the LDSS S32304. The analyses were conducted using D8-Passeur diffractometer in a 40-120° 2 θ range with Cu k α radiation (λ = 1.54056 Å) and a step size of 0.01° for 0.5 s.

5. Representation of the LDSS microstructure

To summarize all the analyses carried out on the material, Figure II.17 displays the characteristics of the microstructure of LDSS used in this research. The γ -austenitic phase presented as islands embedded in a α -ferritic matrix. The microhardness measurements confirmed by TEM, ECCI and KAM analyses have revealed the heterogeneity of the microstructure of LDSS. Indeed, the metallurgical state of the surface of the studied LDSS is different than that of the bulk which has been explained by the high dislocation density and high microhardness values presented in both phases on the surface of the material as shown in the Figure II.17. For this purpose, the LDSS plates have been separated into two types of material, LDSS-Cold worked (work hardened part) and LDSS-Annealed (bulk) for the further experiments.



Figure II.17 Schematic representation of the different characteristics of the studied LDSS

Chapter III

Evaluation of hydrogen depth

The objective of this chapter is to well understand how hydrogen can impact the microstructure of LDSS presented in the previous chapter. It is essential to investigate the interaction of hydrogen-metal on the microstructural scale in terms of hydrogen penetration depth and its localization in the steel. Different complementary techniques could be used to determine the hydrogen effect on the microstructure in a given material like: electrochemical permeation (EP), Thermal Desorption Spectroscopy (TDS), Glow Discharge Spectrometry (GDS), Secondary Ions Mass Spectroscopy (SIMS or nano SIMS), Elastic Recoil Detection Analysis (ERDA) and Tritium Autoradiography. For further investigations, alternative methods like Kelvin Probe Force Microscopy (KPFM) and fracture analysis would be very useful to localize and detect the influence of hydrogen on the different microstructural states present in this study.

1. Electrochemical permeation

Electrochemical permeation is one of the classical techniques widely used to determine the hydrogen interaction with the microstructure: concentration and diffusion of hydrogen in the material based on different mathematical models. This method is known for its possibility of studying hydrogen diffusion even in aggressive solutions. In this context, the electrochemical permeation measurement was employed to investigate the interaction between hydrogen/microstructure in the three materials: annealed, cold worked and thermally aged LDSS and to further understand the relationship between the microstructural state change and hydrogen diffusion. Let us recall again the terminology "cold worked" is referred to a hybrid specimen made of an annealed bulk and covered by a single layer (200 μ m) of cold worked material. While the annealed specimens are formed of the bulk of LDSS.

The EP technique was initially developed by Devanathan and Stachurski [62] in order to determine different parameters like diffusion coefficients, hydrogen concentrations by measuring the hydrogen flux passing through a metallic membrane. The Devanthan-Stachurski cell is composed of two electrochemical units or cells separated by a metallic membrane which is the studied sample. The first unit called the hydrogen entry cell in which the surface of the metal is galvanostatically or potentiostatically charged with hydrogen. The second unit is called the detection cell (or oxidation cell) in which the surface of the metal is exposed to an anodic polarization in order to oxidize and allow the detection of hydrogen flux passing through the metallic membrane.

The hydrogen evolution reactions (HER) that occurred in both cells are formed from a sequence of several elementary reactions.

In the hydrogen charging side, a cathodic reaction is involved to promote the adsorption of hydrogen atoms at the surface of the metal and then absorbed into the bulk of the material:

$$H^+ + e^- \rightarrow H_{ads} \text{ and } H_{ads} \rightarrow H_{abs}$$

The hydrogen atoms can be simultaneously recombined to form molecules of hydrogen which facilitates their desorption from the surface. By adding some chemical poisons (As_2O_3 or $CS(NH_2)_2$), this reaction can be relatively avoided.

$$H_{ads} + H_{ads} \rightarrow H_{2(g)}$$

The diffused hydrogen atoms will oxidize on the detection side (in the "oxidation cell") where the anodic polarization occurs:

$$H_{abs} \rightarrow H_{ads}$$
 and $H_{ads} \rightarrow H^+ + e^-$

Therefore, the principle of hydrogen diffusion through the metallic membrane in electrochemical permeation cell can be summarized as follows:



Figure III.1 Schematic illustration of adsorption/desorption reactions of hydrogen through the metallic membrane in the electrochemical permeation cell

III – EVALUATION OF HYDROGEN PENETRATION DEPTH

In the detection cell, the initial current density is set to a low value, typically $0.1 \,\mu\text{A/cm}^2$ by applying an anodic potential in order to detect the released electrons from the sample that are proportional to the passing hydrogen flux. Figure III.2 illustrates the recorded permeation curve corresponding to the diffusion of hydrogen through an iron metallic membrane [63]. From the curve, especially the first transient, the diffusion coefficient can be calculated by different methods. Several build-up transients can be achieved by polarizing immediately the entry side after reaching the steady-state which describes the saturation state of the diffusible hydrogen. The apparent hydrogen diffusion coefficient can be calculated based on the first transient while the hydrogen concentration in the irreversible sites is determined by using the multiple build-up transients [63].





1.1. Electrochemical permeation set-up

Figure III.3 shows the electrochemical permeation set-up carried out on the LDSS32304 at the UMET lab. The set-up is composed of two cells, in each a three-electrode system has been used: Hg/Hg_2SO_4 as the reference electrode *(RE)*, a platinum counter electrode *(CE)* and the welded specimen with a steel wire *(WE)*. In each cell, the electrodes are connected to a potentiostat/galvanostat (Origaflex 1000 mA by Origalys). The specimen was connected to the two potentiostats by an inverse configuration.

Both sides of the specimen were prepared by mechanical polishing with SiC papers up to grade 2400 and finished with 1 μ m diamond paste. The solutions of both cells were deoxygenated continuously by argon gas during the experiment. The surface of the metallic membrane

exposed to the solutions presents a circular form (diameter equal to 15 mm) and has an area of \sim 1.8 cm².



Figure III 3 Electrochemical permeation cell

First, the EP tests have been performed on a standard steel (S355) with a thickness of 800 μ m before starting the measurements on the studied LDSS in order to ensure the function of the experimental set-up. The hydrogen charging reaction in the entry cell (cathodic charging) has been occurred in 5% NaCl solution at a cathodic current density equal to -1 mA/cm². While a solution of 0.1 M NaOH has been used in the detection cell by applying an anodic potential of -50 mV (relative to the Hg/Hg₂SO₄ reference electrode) to oxidize the hydrogen passing through the steel. The values of the cathodic current density and anodic potential have been chosen according to the potentiodynamic curves of the considered steel in both solutions. After a period of 24 h of recording a stable background current density (0.1 μ A/cm²) in the detection cell, the 5% NaCl solution was poured in the entry cell and the hydrogen charging process can begin. Both solutions are maintained at room temperature and deoxygenated by argon gas before 30 min and during the measurements acquisition in each cell.

The hydrogen permeation curve (evolution of the current density as a function of time in the "oxide" cell) revealed a sharp increase of the current density after 4 h of hydrogen charging. This evolution is associated to the diffusion of hydrogen through the metal and therefore

confirms the well-functioning of the experimental set-up. Now, the EP measurements can be successfully conducted on the studied LDSS (state: annealed) by adopting first the suitable EP parameters.

1.2. Electrochemical permeation parameters

Different parameters are required to be defined before the electrochemical hydrogen permeation takes place like the choice of the solutions, the cathodic current density and the anodic potential.

First, the surface of the LDSS-Annealed in the charging side is exposed to a solution of 0.5M $H_2SO_4 + 0.2 \text{ g/L} \text{ As}_2O_3$ at a constant cathodic current density of -10 mA/cm² as explained previously in chapter **2**, section **2.1.2**. According to the literature [63–66], an alkaline solution of 0.1M NaOH is commonly used in the detection cell (exit side) to facilitate the oxidation of the hydrogen atoms.

An anodic potential of -100 mV vs Hg/Hg₂SO4 reference electrode is chosen according to potentiodynamic results obtained in 0.1M NaOH in such a way to apply an anodic potential at the beginning of the passive domain to first limit the growth of the passive film and then ensure the oxidation of hydrogen atoms into H⁺. The anodic potential was applied for 24 h before the hydrogen charging starts to obtain a stable current density in the oxidation side $(0.1 \ \mu\text{A/cm}^2)$ and allow the detection of hydrogen flux passing through the metal during the experiment.

The permeation procedure described above for the standard steel was conducted on LDSS of 500 μ m of thickness by applying first an anodic potential on the oxidation side for 24 h before the hydrogen charging begins. Then, the solution of 0.5M H₂SO₄ + 0.2 g/L As₂O₃ was poured into the charging cell, a cathodic current density of -10 mA/cm² is applied to promote the formation of hydrogen atoms and their adsorption on the surface of the metal. After a few hours of the electrochemical hydrogen charging process, we noticed no evolution in the background current density (oxidation side) where it remained always 0.1 μ A/cm². Such result suggests that hydrogen did not diffuse through the full thickness of the sample. This is why different parameters have been considered. At first, we performed the cathodic charging for a few more days to trigger the saturation of the material in hydrogen, but no hydrogen flux was detected after 7 days of hydrogen charging. Note that the drawback of the long hydrogen charging duration in the solution H₂SO₄ is the accumulation of the corrosion product FeSO₄ on

the surface of the material. This accumulation tends to form a corrosion film that acts as a barrier on the surface and prevents more hydrogen atoms to penetrate the steel. Thus, the increase of hydrogen duration seems not to be the efficient way to ensure the diffusion of hydrogen. For this reason, a higher cathodic current density has been applied ($i_c = -70 \text{ mA/cm}^2$) expected to create more hydrogen atoms and reduces the hydrogen charging time. Likewise, these parameters did not allow the detection of the diffused hydrogen passing through the sample.

In the study of Yao et al. [67], it has been recommended to pre-charge the DSS2205 by hydrogen before starting the electrochemical permeation measurements in order to saturate the irreversible traps and therefore enhance the diffusion of hydrogen during the experiment. Based on this purpose, the studied LDSS has been pre-charged for 3 days by keeping the same applied current density (-10 mA/cm²) and hydrogen charging solution (0.5M H₂SO₄ + 0.2 g/L As₂O₃). Then the surface of the sample has been polished with 3 μ m and 1 μ m diamond paste to remove the surface relief and avoid the formation of a thick corrosion film in the later electrochemical hydrogen charging permeation. After the background current density reached 0.1 μ A/cm² (24 h), the cathodic current density was applied on the entry surface of LDSS in the charging cell. As the charging time progress, no evolution of the current density for the "oxidation" cell has been detected.

Previously, it has been reported [63,64] that the diffusion path of hydrogen depends on the membrane thickness because hydrogen takes longer time to be released from the thick samples. Addach et al [63] have shown a reduction in the steady-state of the background current density with increasing the thickness of membrane. Where the maximum of hydrogen flux has reached 1.84 μ A/cm² when the thickness of the pure iron was 500 μ m. While the hydrogen permeation current achieved 1.18 μ A/cm² and 0.79 μ A/cm² for the specimens of 1.5 mm and 2 mm respectively. In our case, the samples are thin enough (500 μ m) to detect the diffusion of hydrogen and even the reduction of the thickness of the specimens to 300 μ m did not provide any changes on the permeation curve of the material.

At this stage, two hypotheses can be proposed to explain the results: first, a recombination of hydrogen or the thickness of the passive film which forms on the surface of the sample in the "oxide cell" might be too thick or not enough to allow the detection of hydrogen flux. Second,

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the penetrated hydrogen could not reach the total thickness of the sample in order to be released in the other side. Indeed, some authors [68–70] mention the importance of a layer of palladium or nickel at the detection surface of the material to promote the oxidation of hydrogen atoms and therefore provide a significant permeation current density. Because, a part of the hydrogen atoms in the detection cell could be recombined to form molecular hydrogen (H₂) and therefore not be measured in the permeation current density. Note that the use of a palladium layer is not systematic, some authors did not recommend the palladium coating especially in the case of duplex steels [66,71,72].

Furthermore, the evaluation of the microhardness of a permeation sample could provide an additional explanation on the non-detection of hydrogen, since the presence of hydrogen induces an increase in the microhardness of LDSS as shown in chapter 2 section 2.1.3. The microhardness measurements have been performed on a permeation tested sample 300 µm of thickness that has been hydrogen charged for 4 days during the EP test. First, the sample has been cut and polished up to 1 μ m on the cross section. More than 30 microhardness profiles along the thickness (load of 25 g) have been performed at different locations of the sample (in the cross section) to estimate the penetration depth of hydrogen (Figure III.4). The higher values of microhardness have been obtained on the half thickness of the sample which indicates that hydrogen is relatively located in only one-half thickness of the sample of the cathodic charging side. Moreover, an increase in the microhardness values have been noticed on the surface of the sample that was not exposed to the hydrogen charging solution (Figure III.4). First, these results suggest that hydrogen is only present in the half thickness of the sample (150 µm). Moreover, the diffusion of hydrogen has not only occurred in the center of the specimen exposed to the solution but also to the other parts that are not in contact with the solutions. This shows that hydrogen atoms do not follow a single path to diffuse out metal since the material is formed of an interconnected structure between ferrite and austenite. Thus, taking into account some results of the literature and our observations, the hydrogen diffusion probably occurs preferentially through the ferrite network and rarely from ferrite to austenite because the hydrogen diffusion coefficient in ferrite is higher than that in austenite. Moreover, the hydrogen traps within the phases and at the ferrite/austenite interface play an important role on hydrogen permeation [73], [74].



Figure III.4 Schematic representation of the microhardness performed in the cross section of a permeation sample

The morphological feature of the microstructure of the material should be taken also into consideration. Indeed, in the study of Zheng et al [66], the DSS 2205 presents small globular islands of austenite embedded in a ferrite matrix which has allowed an easier diffusion of hydrogen via the ferrite phase. Wu et al. [73] have shown that the direction of hydrogen penetration into the microstructure of the steel can strongly affect the apparent hydrogen diffusion coefficient (Figure III.5). They explained that the diffusion of hydrogen with respect of the rolling direction (RD) is faster than in the transverse direction (ND) owing to the longer austenite islands.



Figure III.5 Schematic of the geometry of the microstructure of the DSS 2205 illustrating the diffusion direction of hydrogen along the normal direction (ND) in (a) and (b) and along the rolling direction (RD) in (c) and (d) [73]

In sum, it seems that the complex geometry of the studied LDSS 32304 beside the effect of the hydrogen traps within or at the phase boundary have tortured the diffusion of hydrogen into the microstructure which made impossible the acquisition of the permeation measurements with the used thickness which are close to those of the mechanical test specimens and representative of the microstructure.

The attempt to build a relationship between the microstructural change and the pathway of hydrogen by evaluating the coefficient diffusion and the concentration of hydrogen has been unsuccessfully conducted.

The fracture analysis of the three different microstructural states cathodically charged or not with hydrogen by using tensile test thus appeared to be an accessible way to estimate the penetration depth of hydrogen. Another benefit of the tensile test is the opportunity to identify the fracture mode and the effect of hydrogen on the mechanical properties of each studied material.

2. Tensile Test

Series of tensile tests have been carried out on the steel to evaluate the influence of the metallurgical state as well as the hydrogen effect on the mechanical properties of the LDSS S32304. From, the mechanical response and the fracture analysis, we will attempt to compare the depth of hydrogen penetrated into the steel between the three metallurgical states of LDSS S32304.

The mechanical behavior of the steel uncharged and charged with hydrogen was evaluated by using a tensile test carried out on a MTS machine of maximum capacity of 20 kN. The set-up for the tensile tests consists of a system of chucks/grips designed for flat specimens of different thicknesses (Figure III.6). During the test, the displacement of the cross-head of the machine is controlled. It moves at a constant speed inducing an evolution of the load which is applied on the specimen. The evolution of the load (N) according to the displacement (mm) of the cross-head of the machine is measured during the test. Assuming that only the sample deforms in its gauge zone, the strain (%) of the sample is calculated from the value of the displacement of the crosshead and that of the gauge length. Knowing the cross-section of the specimen in the gauge zone, the tensile stress (MPa) is also evaluated from the applied load.

The stress versus strain curve allows to determine the ductility and the tensile properties: ultimate tensile strength (UTS), yield stress (YS) and total elongation to fracture (ϵ_t) of the material.

The tensile tests were performed until fracture to evaluate the ductility and the fracture mode for the different microstructural states of the steel. Through the tensile test and by using SEM, we intend to estimate the size of the embrittled zones generated by the hydrogen addition.



Figure III.6 MTS tensile equipment used in this study

Specimen geometry

The flat specimens were extracted from the steel plate in the normal direction by spark machining. The specimens had a gauge length of 20 mm and a cross section of $3 \times 0.5 \text{ mm}^2$ as illustrated in Figure III.7.



Figure III.7 Scheme of the flat specimen in the normal direction (ND) used in the tensile test, the dimensions are given in mm

The cross-head displacement speed is fixed at 0.014 mm/s to obtain a strain rate of 10^{-3} s⁻¹. Before the test, the samples were mechanically polished using SiC papers with particle sizes between 320 and 2400 and finished by diamond suspensions from 6 to 1 μ m. Both lateral surfaces of the specimen were prepared by a mechanical polishing with SiC papers up to grade 2400 and finished with 1 μ m diamond paste. The tensile tests have been applied according to the rolling direction (RD) of the specimens and performed twice in order to optimize the results. To study the effect of hydrogen, the two lateral surfaces of the specimen were cathodically charged as mentioned in chapter **2** section **2.1.1**.

The nomenclature adopted for the samples tested in air or after hydrogen charging is: LDSS-X-Air, LDSS-X-Hy where X represents the metallurgical state of the material (Annealed, CW or 475° C) and y represents the hydrogen charging time. For instance, LDSS-Annealed-H5 stands for the LDSS S32304, annealed and hydrogen charged for 5 hours.

3. Tensile properties of LDSS

As previously mentioned, the delivered material plates are formed of two different metallurgical states, thus it is necessary to determine the mechanical characteristics of each state (cold work and annealed). In addition, the annealed specimen is considered as "monolithic" since it is formed only of the bulk of the steel. While, the cold worked is considered as "hybrid" since the cold worked layer forms 200 µm of the thickness of the steel (or the specimen). The stress-strain curve is plotted for LDSS-CW-Air and LDSS-Annealed-Air as shown in Figure III.8.



Figure III.8 Stress-strain curve of LDSS-Annealed-Air and LDSS-CW-Air elongated to fracture

The difference in the mechanical behavior between the two materials might be due to the high dislocation density existed in the cold worked material. The values of the tensile characteristics of both states are summarized in Table III.1.

Tensile characteristics	LDSS-CW-Air	LDSS-Annealed-Air
YS 0.2% (MPa)	580	490
UTS (MPa)	730	690
A (%)	33.6	34.6

Table III.1 Tensile characteristics values evaluated in the two metallurgical states of the delivered material

An improvement in the yield and ultimate strength is noticed in LDSS-CW-Air. Where the yield strength (YS 0.2%) is 580 MPa in the LDSS-CW-Air and 490 MPa in LDSS-Annealed-Air (Table III.1). The ultimate strength (UTS) is higher in LDSS-CW-Air (730 MPa) than in the annealed material (690 MPa). In contrast, the elongation to fracture is similar in both studied states, 33.6% in LDSS-CW-Air and 34.6% in LDSS-Annealed-Air. The difference in the mechanical behavior between the two materials is supposed due to the effect of the cold worked layer more precisely to the high dislocation density existed in this layer which increased the hardness of the steel. Similar findings have been obtained by Koh et al. [75] where they explained that the high rates of skin pass can release the tangled dislocations from the surroundings of solute carbon. And so, the yield strength increased because of the high dislocation density resulted from the multiplication of dislocations.

4. Observation of fracture surface of LDSS

Figure III.9 illustrates the fracture surfaces of LDSS-Annealed-Air specimen elongated until fracture. The entire fracture surface was covered by ductile dimples (Figure III.9.b) reflecting a ductile fracture mode for the two states of the steel. It is very difficult to figure out the fracture surfaces of austenite and ferrite since both phases exhibit a ductile failure mode. Note that the observations of the fracture surfaces of LDSS-CW-Air showed the same behavior of the annealed steel.



Figure III.9 SEM images of LDSS-Annealed-Air showing (a) the fracture surface and (b) ductile dimples in the transverse direction (TD) after the tensile test

5. Influence of hydrogen addition on tensile properties of LDSS

5.1. Surface characterization before the monotonic loading

Before performing the tensile test, the surface characteristics of the samples charged with hydrogen were realized. The two hydrogen charging durations applied on LDSS-Annealed and LDSS-CW are 5 h and 24 h. The surface observations of the samples charged with both conditions exhibit cracks but they were fewer on the surface charged for 5 h. The surface characterization of LDSS-CW charged 24 h with hydrogen is shown in Figure III.10. The surface cracks are mostly present in austenite grains with the existence of some blisters occasionally in both phases (Figure III.10.a and III.10.b). The hydrogen blisters are supposed to result from the accumulated hydrogen atoms underneath the surface, where they tend to recombine and form hydrogen molecules (H₂) (Figure III.10.c and III.10.d). Then, the pressure underneath the surface of the material. The hydrogen blisters can appear as cavities as shown in Figure III.10.c or they pop up to give rise to an open blister as illustrated in Figure III.10.d. These surface characteristics (cracks, hydrogen blisters) result from a strong stress field induced by the presence of hydrogen in the material.



Figure III.10 SEM images of the surface characterization of LDSS-CW-H24 etched with Beraha reagent showing in (a), (b) the microcracks indicated by the black arrows and (c), (d) hydrogen blisters indicated by red dashed zones

5.2. The tensile behavior of LDSS-Annealed-H5 and LDSS-CW-H5

Figure III.11 shows the stress-strain curves obtained in the tensile tests conducted until fracture for the two states of LDSS (annealed and cold worked) in the air and after hydrogen charging of 5 h. The evolution of the stress-strain curves shows similar mechanical behavior between the hydrogen charged and uncharged material in both cases. The only difference can be noticed is the ductility loss in hydrogen charged steels.



Figure III.11 Evolution of stress response as a function of strain for LDSS-Annealed and LDSS-CW in the air and with hydrogen charging for 5 h

Table III.2 shows the tensile characteristics of LDSS-CW and LDSS-Annealed uncharged and hydrogen charged for 5 h calculated from the curves of Figure III.11. The yield strength exhibits no change upon the short hydrogen charging duration in both annealed and cold worked material. Where, the YS 0.2% value remains unchanged for LDSS-CW-Air (580 MPa) and LDSS-CW-H5 (586 MPa). Likewise, the YS 0.2% of LDSS-Annealed-Air was 490 MPa and after 5 h of hydrogen addition it remains 493 MPa. On the other hand, the ultimate strength (UTS) decreases from 730 MPa in LDSS-CW-Air to 700 MPa in LDSS-Annealed-H5. A similar behavior has been observed in the annealed state where the UTS reduces from 690 MPa in LDSS-Annealed-Air to 657 MPa in LDSS-Annealed-H5. The ductility loss based on elongation to fracture drops from 33.6% in LDSS-CW-Air to 16.3% in LDSS-CW-H5. Similarly, the elongation to fracture decreases from 34.6% to 19.2% in LDSS-Annealed after 5 h of hydrogen charging.

Tensile characteristics	LDSS-CW-Air	LDSS-CW-H5	LDSS-Annealed-Air	LDSS-Annealed-H5
YS 0.2% (MPa)	580	586	490	493
UTS (MPa)	730	700	690	657
A (%)	33.6	16.3	34.6	19.2

Table III.2 Tensile characteristics values evaluated in the two metallurgical states of the delivered material

The only modifications observed after the hydrogen are a decrease in the elongation to fracture and a premature fracture. This indicates that 5 h of hydrogen charging is insufficient to modify the tensile properties of both states especially the yield strength and the strain hardening.

5.3. The fracture surface characterization of LDSS-Annealed-H5 and LDSS-CW-H5

The fracture surfaces of LDSS-Annealed-H5 and LDSS-CW-H5 were characterized using SEM as shown in Figure III.12. A mixed fracture mode is observed in both cases. A brittle zone is observed at the surface fracture of the specimen accompanied with a small shear zone and ductile dimples in the center of the specimen. The brittle regions likely highlight the presence of hydrogen since the latter enhances the transition fracture mode from ductile to a brittle one. However, the ductile dimples have the same characteristics of those observed in the uncharged specimen which suggests that hydrogen did not reach the center of the specimen since no clear effect of hydrogen is visible. Figure III.12.a and III.12.b show that the size of brittle zone effectively depends on the metallurgical state of the studied material, where 50 μ m is found in the LDSS-Annealed-H5 and 40 μ m in the LDSS-CW-H5. Moreover, the brittle zones seemed to be more uniformly distributed in LDSS-CW-H5 and appeared as a more regular ribbon. These results point out the effect of the higher dislocation density present in the cold worked material on the distribution of hydrogen in the material. Indeed, the dislocations promote the trapping of more hydrogen atoms and so slow down their diffusion which could imply a more uniform distribution of hydrogen in the material and generate smaller brittle zones.



Figure III.12 SEM images of the fracture surface in the transverse direction (TD) of (a) LDSS-Annealed-H5 and (b) LDSS-CW-H5 after tensile test

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A closer look in the brittle fracture surfaces of LDSS-Annealed-H5 (Figure III.13.b) and LDSS-CW-H5 (Figure III.13.e) displays similar morphologies. The challenge was to identify the brittle fracture surfaces of austenite and ferrite in the steel. As we can notice in Figures III.13.b and e two different brittle morphologies appear in both cases, a ladder or steps pattern as illustrated in Figure III.13.a and III.13.d, and a river pattern in Figure III.13.c and III.13.f.



Figure III.13 SEM images of brittle fracture surfaces of LDSS-Annealed-H5 in (a), (b) and (C). Brittle fracture surfaces of LDSS-CW-H5 in (d), (e) and (f). The small black arrows indicate the river pattern

Based on the literature and the experience of the personnel of the laboratory, fractography images for the single embrittled austenitic and ferritic stainless steels have been used in this study to identify the brittle fracture surfaces of ferrite and austenite phase in LDSS. The river pattern shown in black arrows in Figure III.14.a and III.14.b reveals the typical cleavage brittle mode that are expected for ferritic stainless steels. The second type of the fracture morphology that appeared as steps pattern is closely related to the fracture mode of austenitic stainless steels embrittled with hydrogen (Figure III.14.c and III.14.d).



Figure III.14 (a) brittle fracture surface of a ferritic stainless steel S43940 charged with hydrogen [48], (b) enlarged view of the brittle surface of ferrite in LDSS-Annealed-H5, (c) brittle surface of a monocrystal FeCrNi-N austenitic stainless steel charged with hydrogen at 70 °C [76] and (d) enlarged view of the brittle surface of austenite in LDSS-Annealed-H5. The small black arrows indicate the river pattern in ferrite

5.4. The tensile behavior of LDSS-Annealed-H24 and LDSS-CW-H24

The results of tensile tests performed until fracture of LDSS-Annealed and LDSS-CW uncharged and hydrogen charged for 24 h are illustrated in Figure III.15. LDSS-CW hydrogen charged or uncharged with hydrogen exhibits the same elastic limit. A slight difference appears between the mechanical behavior of LDSS-Annealed-Air and LDSS-Annealed-H24.



Figure III.15 Stress versus strain curve of LDSS-Annealed-Air, LDSS-Annealed-H24, LDSS-CW-Air, LDSS-CW-H24 subjected to a tensile test until fracture

In order to compare the tensile characteristics of each material charged or uncharged with hydrogen, the calculated values are summarized in Table III.3. The longer hydrogen charging duration resulted in a higher ductility loss in both states of LDSS. Similar ductility losses have been observed for several duplex stainless steels charged with hydrogen [13,77]. Such result is attributed to the deeper penetration of hydrogen into the material with increasing the hydrogen charging time [78]. The elongation to fracture decreases from 33.6% in LDSS-CW-Air to 10.9% in LDSS-CW-H24 and from 34.6% in LDSS-Annealed-Air to 9.4% in LDSS-Annealed-H24. A slight increase in the yield strength is noticed only in the annealed charged with 24 h. The value of yield strength increases from 490 MPa in LDSS-Annealed-Air to 510 MPa in LDSS-Annealed-H24, while the ultimate strength decreases from 690 MPa to 650 MPa after 24 h of hydrogen charging which is close to that obtained LDSS-Annealed-H5. However, the hydrogen charging for 24 h in the cold worked material did not show any significant effect on yield and ultimate strength. The yield strength remains almost unchanged (588 MPa) and the UTS slightly decreases from 700 MPa in LDSS-CW-Air to 689 MPa in LDSS-CW-H24.

Tensile characteristics	LDSS-CW-Air	LDSS-CW-H24	LDSS-Annealed-Air	LDSS-Annealed-H24
YS 0.2% (MPa)	580	588	490	510
UTS (MPa)	730	689	690	650
A (%)	33.6	10.9	34.6	9.4

Table III.3 Tensile characteristics values evaluated in LDSS-CW and LDSS-Annealed charged or uncharged with24h of hydrogen

Here, the increase of yield strength in LDSS-Annealed values after a long hydrogen duration can be related to the pinning effect of hydrogen on dislocations by impeding the cross slip and dislocation motion as explained in previous works [13,79]. This effect is not clearly showed on LDSS-CW because the specimen is formed of 200 μ m of cold worked layer and 300 μ m of annealed (bulk) part and thus its mechanical curve reflects the effect of hydrogen on the annealed part and cold worked part at the same time.

5.5. The fracture surface characterization of LDSS-Annealed-H24 and LDSS-CW-H24

The fracture surfaces of LDSS-Annealed and LDSS-CW hydrogenated for 24 h characterized using SEM are represented in Figure III.15. As we noticed, with the increase of hydrogen charging time, the depth of brittle zone increases, where the latter does not exceed the 50 μ m in LDSS-CW-H24 while the brittle zone represents 100 μ m of the thickness of LDSS-Annealed-H24. The size of shear zone reduced in LDSS-Annealed-H24 more than in LDSS-Annealed-H5. On the other hand, the fracture morphology in LDSS-CW-H24 represents an abrupt transition from ductile zone in the center of specimen to a brittle region at the edges without involving a shear zone (Figure III.16.a). A detailed image of the brittle region in LDSS-CW-H24 (Figure III.16.b) shows a transgranular brittle mode (TG) in which the distinction between austenite and ferrite phase can be established. The brittle zones of austenite in LDSS-CW-H24 appear as steps pattern and those of ferrite show the presence of river pattern as a result of the TG and cleavage brittle mode. Likewise, transgranular fracture areas are observed in austenite and ferrite phases of LDSS-Annealed-H24 as shown in Figure III.16.d, III.16.g and III.16.h.



Figure III.16 SEM images showing the fracture surface in the transverse direction and embrittled region of LDSS-CW-H24 in (a), (b) and LDSS-Annealed-H24 in (c), (d). (e) and (f) show austenite and ferrite phase respectively in LDSS-CW-H24. (g) and (h) illustrated ferrite and austenite phase respectively in LDSS-Annealed-H24

5.6. Discussion

The both hydrogenated materials LDSS-Annealed and LDSS-CW subjected to tensile tests showed a premature fracture with the increase of the hydrogen charging time, similar to what observed in other duplex stainless steels [13,80]. Based on fractography observations, hydrogen induces the transition of fracture mode from ductile to brittle one which is the typical effect of hydrogen as reported in many studies [13,78,80,81]. It was easy to identify the brittle fracture of austenite and ferrite in the 5h hydrogen charging materials (LDSS-Annealed-H5 and LDSS-CW-H5).

The hydrogen charging of LDSS-CW for a short or long duration (5 h and 24 h) did not affect the brittle zone, where the latter was 40 μ m after 5 h and 50 μ m after 24 h of hydrogen charging. Moreover, the embrittled zone in LDSS-Annealed-H24 was double that of LDSS-CW-H24. Therefore, it seems that the higher dislocation density present in both phases of LDSS-CW acts as barrier on the diffusion of hydrogen towards the bulk of the specimen. However, a difference in hydrogen depth was remarked after 24 h of hydrogen charging in the annealed state, where the size of the embrittled zone increased from 50 μ m in LDSS-Annealed-H5 to 100 μ m in LDSS-Annealed-H24. The increasing of hydrogen charging time indeed increases the penetration of hydrogen in the material as demonstrated in some references [13,78].

The 24 hours of hydrogen charging was however insufficient to saturate the specimen in hydrogen since ductile dimples were still observed in the center of the specimen and presenting the same characteristics of that found in the uncharged materials. Yet the 72 h of hydrogen charging (3 days) was also unable to saturate the entire annealed specimen by hydrogen, the total size of the brittle region did not exceed the 140 µm. The size of brittle zone and the ductile characteristics evaluated after the hydrogen addition are indeed a good indicator about the depth of hydrogen. But we cannot ignore the likely presence of hydrogen in deeper areas of the microstructure e.g., shear zone in which the hydrogen concentration is lower than that required to induce cracks development or brittle fracture. Meanwhile, the 7 days of hydrogen charging has ensured the penetration of hydrogen atoms in the center of the specimen where the entire sample was hydrogen embrittled (Figure III.17.a) regardless the metallurgical state of LDSS. More developed cracks (Figure III.17.b) were observed in the embrittled zones due to the higher hydrogen concentration provided from 7 days of charging.



Figure III.17 SEM images illustrating in (a) the fracture surface of the entire embrittled specimen after seven days of hydrogen charging and (b) enlarged view of a brittle region, the black arrows indicate the microcracks and the dashed red zones illustrate the cleavage fractures (c)

Under different hydrogen charging durations the fracture morphologies of the annealed and cold worked specimens showed a cleavage brittle mode (C) accompanied with micro-cracks that might be present not only at the ferrite/austenite interface but also within the austenite and ferrite grains as observed in the study of Claeys et al. [13].

However, the characterization of the fracture surfaces cannot be fully discussed without taking into consideration the HE mechanisms. Sometimes, combining two or more mechanisms would be possible to explain the mechanical degradation of the steel. The two commonly cited HE mechanisms are HEDE and HELP hydrogen [15,51,82]. In HEDE, hydrogen reduces the cohesive strength between atoms and therefore a decohesion at grains boundaries or interfaces can be observed. The second mechanism (HELP) is associated to transgranular or intergranular fracture in which hydrogen enhances the dislocation nucleation and the shielding effect by reducing the repulsive forces between dislocation-dislocation. Luo et al. [83] have associated HELP to the micro void coalescence (MVC) fracture observed in the duplex S2205 soaking in H₂SO₄, where the fracture surface has been covered by fine ductile dimples. While, they proposed HEDE as a mechanism of degradation of the S2205 charged 10 days with hydrogen based on the fracture morphology of the cracking surface. The fractography showed brittle areas as a result of cleavage fracture (C) with the evidence of ductile dimples. In their study, they considered that HELP is responsible of plastic failure and HEDE of the brittle fracture. Likewise, Djukic et al. [84] associated the mixture of brittle and ductile fractures observed in the hydrogenated low carbon steel to the simultaneous mechanisms HELP and HEDE. The presence of transgranular brittle fracture surfaces is due to HEDE while the MVC fractures (finer ductile dimples) characterize the HELP mechanism. One of these two mechanisms can be predominantly occurred depending on hydrogen concentration.

Using fractography observations is however insufficient to explain the HE mechanisms especially in the dual phase steels. Additional techniques like EBSD and interrupted tensile tests are needed to be employed in order to detect the crack growth and crack propagation and therefore the recognition of HE mechanism. Moreover, the occurrence of phase transformation in austenite can affect the hydrogen embrittlement resistance of the material and complicates the prediction of HE mechanism. In the study of Laureys et al [85] the crack initiation has occurred in the transformed martensite phase of the TRIP steel, others [86] stated the crack nucleation at ferrite/martensite interfaces. In sum, many factors like phase transformation in austenite and twinning deformation in ferrite can influence the degradation of the material and complicate the prediction of HE mechanism. In our case, it is extremely difficult to well predict the HE mechanism but based on the literature we can suggest that the

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degradation of the steel likely followed HEDE mechanism since transgranular brittle fracture mode has been detected in the 5 h, 24 h and 7 days of hydrogen charged samples. Here, it is difficult to predict the contribution of HELP mechanism because the ductile dimples present in the center of specimens did not show any modifications which reflects the absence of hydrogen in this region.

5.7. Highlights

The main findings obtained from the hydrogen charging of both materials LDSS-Annealed and LDSS-CW are summarized as follows:

-The microcracks resulting from hydrogen charging effect have mainly appeared at the surface of austenite phase in both states.

-The introduction of hydrogen in both states of LDSS 32304 resulted in a significant ductility loss (a premature fracture) regardless the hydrogen charging times.

-In all cases, the embrittled zone of LDSS-CW after hydrogen addition was smaller than that of hydrogenated LDSS-Annealed. Moreover, there was no difference between the size of the embrittled zone in LDSS-CW-H5 and LDSS-CW-H24. This indicates that hydrogen has penetrated less deep in the LDSS-CW probably due to the hinder of hydrogen diffusion by the dislocations that highly located in the cold worked material and therefore formed a barrier on the hydrogen penetration.

-The 7 days of hydrogen charging has successfully forced the hydrogen atoms to reach the center of our designed samples that have 500 μ m of thickness.

-The fracture surfaces of the uncharged material revealed a micro void coalescence (MVC) fracture mode which tends to be replaced by a transgranular fracture mode with the increasing of hydrogen charging time.

6. Influence of 475 °C aging treatment

Only the LDSS-Annealed samples were subjected to 475 °C aging treatment for 25 h since they showed lower dislocation density than the LDSS-CW and so a more stable microstructure. This purpose has been explained in chapter **2** section **1.3**, where the microhardness evaluated in each phase of both states of LDSS showed a more homogeneous distribution in LDSS-Annealed compared to LDSS-CW. However, it was possible to verify that the aging treatment affects only

the hardness of ferrite without evidencing of any brittleness. Indeed, the microhardness measurements evaluated in each phase in the normal direction (ND) showed an increase of the microhardness of ferrite from $HV_{0.025} = 236 \pm 5$ to $HV_{0.025} = 270 \pm 6$ while that of austenite remained unchanged $HV_{0.025} = 259 \pm 7$.

6.1. The mechanical behavior of LDSS-475°C

Mechanically, the tensile test can be used to evaluate first the improvement of yield and ultimate strength as well as the premature failure of thermally aged materials as shown in the study of Reis et al. [11]. Second, it allows the detection of the fracture surfaces using SEM analysis to ensure the ductile behavior of the aged steel. Figure III.18 shows the results of the tensile test performed until fracture of LDSS-Annealed-Air and LDSS-475°C-Air.



Figure III.18 Stress-strain curve of LDSS-Annealed-Air and LDSS-475°C-Air subjected to a tensile test until the fracture

The evolution of the tensile properties shows that the short duration of aging treatment (25 h) leads to a significant increase in YS 0.2% and UTS with an important ductility loss. The YS 0.2% increases from 490 MPa in LDSS-Annealed-Air to 643 MPa in LDSS-475°C-Air (Table III.4). Likewise, the UTS raises from 690 MPa in LDSS-Annealed-Air to 814 MPa in LDSS-475°C-Air. While the elongation to fracture (A) decreases from 34.6% to 10.2% after the aging treatment for 25 h. This mechanical behavior has been already observed for other aged duplex stainless steels even for short aging durations because of the presence of spinodal decomposition as

demonstrated in the literature [9,11]. As suggested by Chandra et al [87] and Weng et al. [88], during the aging treatment, the dislocations become pinned in a complex structure between the two phases α' and α'' which decreases the mobility of dislocations and therefore contributes to the strength of the steel accompanied with a ductility loss. This proposition has been confirmed by Hsieh et al. [89], where the TEM observations on the aged duplex stainless steel showed that the spinodal nanostructure creates a barrier and hinders the movement of dislocations which leads to a significant strengthening effect.

Tensile characteristics	LDSS-Annealed-Air	LDSS-475°C-Air	
YS 0.2% (MPa)	490	643	
UTS (MPa)	690	814	
A (%)	34.6	10.2	

Table III.4 Tensile characteristics values of LDSS-Annealed-Air and LDSS-475 $^\circ\text{C-Air}$

6.2. The fracture surface characterization of LDSS-475°C

The fractographies in Figure III.19 show that the entire aged specimen is ductile similar to what observed in LDSS-Annealed-Air. The ductile fracture mode in the LDSS-475°C-Air confirms that the 25 h of aging is indeed not enough to embrittle the material. Reis et al. [11] have noticed a decrease in the size of ductile dimples as a result of increase in the formation of microcavities in ferrite after the aging treatment. This observation is unlike that of our sample, the size of ductile dimples in the aged material did not show any decrease: 4-2 μ m is found in LDSS-475°C-Air while 3-1 μ m was estimated in the LDSS-Annealed-Air.



Figure III.19 SEM fractographies showing in (a) the fracture surface and (b) enlarged view of the black zone indicating the ductile dimples in LDSS-475°C-Air

7. Influence of hydrogen on aged LDSS-475°C

7.1. The tensile behavior of LDSS-475°C-H72

The comparison of the tensile properties of LDSS-Annealed and LDSS-475°C uncharged and charged with 72 h of hydrogen is summarized in Figure III.20.



Figure III.20 Stress-strain curve of LDSS-Annealed and LDSS-475 °C in the air and charged for 72 h of hydrogen after the tensile test

Besides the significant reduction in the elongation to fracture (2.3%) observed in LDSS-475°C-H72, a strong increase in the yield and ultimate strength is recorded (Table III.5). Where the yield strength (YS 0.2%) increases from 643 MPa in LDSS-475°C-Air to 741 MPa in LDSS-475°C-H72. In the same way, the ultimate strength (UTS) increases from 814 MPa to 859 MPa. However, if we compare the tensile curve of LDSS-475°C-H72 to LDSS-Annealed-H72, the ductility loss and the other tensile properties appeared to be more affected by hydrogen when the material is thermally aged. Because, at first, the aging treatment contributes to the hardening of the steel and especially the ferrite phase as we mentioned previously in section **6**. Then, the introduction of hydrogen leads to the increase of the microhardness of both phases as we demonstrated in chapter **2**, section **2.1.3.** since hydrogen induces a strong stress field. In sum, the combined effect of aging treatment and hydrogen implies a higher hardness and therefore strengthening the material.

Tensile characteristics	LDSS-Annealed-Air	LDSS-Annealed-H72	LDSS-475°C-Air	LDSS-475°C-H72
YS 0.2% (MPa)	490	612	643	741
UTS (MPa)	690	747	814	859
A (%)	34.6	5.59	10.2	2.3

Table III.5 Tensile characteristics values in LDSS-Annealed-Air, LDSS-Annealed-H72, LDSS-475°C-Air and LDSS-475°C-H72

7.2. The surface fracture characterization of LDSS-475°C-H72

Figure III.21 compares fracture surfaces and the brittle zone depth of LDSS-Annealed and LDSS-475 °C charged 72 h of hydrogen. Brittle fractures are observed at the edges of both specimens. The size of the brittle zone is higher in LDSS-Annealed-H72, where 140 μ m is estimated in LDSS-Annealed-H72 and 115 μ m in LDSS-475 °C-H72. This difference suggests that the "chromium clusters" resulted from the aging treatment form a trap site for hydrogen atoms and inhibit their diffusion. Transgranular cleavage facets are observed in both charged materials (Figure III.20.b and III.20.d). The river cleavage morphology together with the so-called tongues were clearly identified in ferrite of LDSS-475 °C-H72 as shown in Figure III.21.g.



Figure III.21 Fracture surface images of LDSS-Annealed-H72 in (a), (b) and LDSS-475°C-H72 in (c), (d). (e) and (f) enlarged view of the brittle surfaces of ferrite and austenite respectively in LDSS-Annealed-H72. (g) and (h) enlarged view of the brittle surfaces of ferrite and austenite respectively in LDSS-475°C-H72

7.3. Discussion

The 25 h of aging treatment induced the hardening of LDSS 2304 especially the ferrite phase as a result of spinodal decomposition. This latter is characterized by a redistribution of chromium atoms to form regions rich in Cr and others depleted in Cr as stated by many authors [11,12,90]. The austenite phase did not show any modification which justified by the unchanging of microhardness values as already found in the literature [9,11]. The strength of the material has improved owing to the reduction in the mobility of dislocations in the interconnected structure between α and the new formed phase α'' .

The combined effect of aging treatment and hydrogen charging was then investigated in order to determine the influence of the redistribution of chromium atoms on the depth of hydrogen penetration. The cumulative effect of both conditions (aging treatment and hydrogen charging) was highlighted on the tensile properties. We observed a significant increase in the strengthening of the LDSS-475°C-H72 more than that of LDSS-475°C-Air and LDSS-Annealed-H72 apart. This result could be explained by first, the fine structure resulted from aging treatment has reduced the dislocations mobility. Second, the presence of hydrogen in a given steel (non-thermally aged) can also pin dislocations and slower their mobility. The size of the brittle zone in LDSS-475°C-H72 was fairly lower than that in LDSS-Annealed-H72. This can be explained by the presence of "chromium clusters" that act as trapping sites and alter the diffusion of hydrogen. The aged ferrite phase tends to accumulate more hydrogen atoms and slower their diffusion toward the deepest zones.

However, the fractography morphology of LDSS-475°C-H72 showed a brittle zone of 115 μ m with the presence of a ductile zone in the center of the sample that related to a transgranular (TG) fracture mode and a micro void coalescence (MVC) mode respectively. Hydrogen accumulated in the "chromium clusters" of ferrite will reduce the cohesive strength and eventually resulting in crack initiation and cleavage fracture which are in consistent with HEDE mechanism.

7.4. Highlights

In this research, the strengthening effect of the aging treatment without evidencing of brittle fracture on the LDSS was first verified, then the combined effect of aging treatment and
hydrogen charging on the evolution of the mechanical strength and the fracture mechanism of the material has been conducted. The main conclusions are listed below:

- The annealed state of LDSS S32304 can be turned into another strengthener one by a simple heat treatment (475°C) for 25 h only. The strengthening effect is a result of a more or less advanced spinodal decomposition in the ferrite phase.

-SEM observations confirmed the fully ductility of the aged LDSS-475°C.

-The introduction of hydrogen in LDSS-475°C has increased significantly the yield and ultimate strength with a large ductility loss as a result of a combined effect of aging treatment and hydrogen charging.

-The strengthening of the LDSS-475°C-H72 as well as the reduction in the size of its brittle zone can be explained by the trapping of hydrogen in the "chromium clusters" that forms a barrier to the dislocations movement because of the increase in the critical shear responsible for dislocation glide.

-The "chromium clusters" seem to induce a strong hydrogen capture ability and so the aging treatment seems to promote the formation of hydrogen trapping sites in the ferrite phase.

Conclusion

This chapter aimed to study the penetration of hydrogen in the different metallurgical states of the lean duplex stainless LDSS S32304 (annealed, cold work and thermally aged) by means of hydrogen electrochemical permeation (EP) method and fracture analysis after tensile tests. The various microstructural traps like austenite-ferrite interface, the strong hydrogen trapping ability of austenite and microstructure defects can strongly tortuous the diffusion of hydrogen which seemed to take place through the ferrite network. Moreover, the geometry of the microstructure i.e., austenite islands embedded in ferrite matrix, oriented in the rolling direction plays a key role on the hydrogen permeability.

The EP tests showed a low penetration of hydrogen in the thickness of the duplex steel and highlighted the importance of ferrite channels that form a diffusion path for hydrogen.

The fracture analysis appeared as a powerful tool to estimate the hydrogen penetration depth in each microstructural state by detecting the size of brittle zone. Note that, the hydrogen atoms could penetrate deeper (in shear zone) but their concentration is insufficient to induce any brittleness.

From the results obtained by fracture analysis after tensile tests, we can estimate that the maximum of hydrogen concentration can be found in the brittle zones of each state of the material. And the hydrogen concentration decreases over the brittle zone to reach 0% in the ductile zones since the ductile dimples exhibit same characteristics as those of the uncharged material.

The brittle zone in the cold worked and the thermally aged material after hydrogen addition was smaller than that of the hydrogenated annealed as shown in Figure III.22. The difference in the hydrogen depth observed in the three materials clearly indicates that the presence of higher dislocation density in the cold worked material and the "chromium clusters" in the aged material have indeed slow down the diffusion of hydrogen towards the center of the sample. This reflects their strong hydrogen capture ability. However, the 5 h of hydrogen charging led to 50 μ m of brittle zone in the annealed LDSS S32304 which made us expect a 240 μ m after 24 h and a full embrittlement 720 μ m (>> sample thickness) after 72 h of hydrogen addition. Or only 100 μ m of brittle zone is obtained after 24 h and 140 μ m after 72 h of hydrogen charging. Thus, the evolution of the hydrogen depth as a function of time is not linear owing to the strong hydrogen traps of austenite phase and austenite-ferrite interface.



Figure III.22 Estimation on the hydrogen presence in (a) LDSS-Annealed-H24 and LDSS-CW-H24. (b) LDSS-Annealed-H72and LDSS-475°C-H72 charging

Chapter IV

Role of Hydrogen on Cyclic Plasticity

This chapter focuses on bringing to light the mechanism(s) of hydrogen-modified plasticity of the LDSS S32304, i.e., either hydrogen-reduced or hydrogen-enhanced plasticity. The goal is of course to identify the role and/or the behaviour of each phase of LDSS on the partition of plasticity by considering the three metallurgical states of the material (annealed, cold worked and thermally aged). To accumulate a large plasticity without excessively straining the material like under a monotonic loading, we have used the methodology employed for fatigue testing. The aim of the fatigue test in our study is not determining the fatigue life or mechanical strength of the LDSS S32304 but to accumulate cycle after cycle a plastic deformation in each phase without leading to instability or fracture in the steel.

The chapter starts providing a brief description of the fatigue phenomenon and how it can be analysed. Then the experimental procedure used to assess the plastic deformation behaviour of each phase of the material will be described. After performing the tests on the three uncharged or hydrogen charged microstructural states, the effect of hydrogen on the accommodation of cyclic plasticity will be approached with AFM and SEM analyses. In addition to the evolution of the surface relief, the dislocation arrangements will be detected using SEM-ECCI according to the metallurgical state of LDSS S32304 charged or uncharged with hydrogen.

Finally, this chapter claims at providing an explanation of how the cyclic response of LDSS S32304 is affected by the introduction of hydrogen. The classical mechanisms of hydrogen embrittlement mentioned in the literature chapter cannot be ignored in the discussion. However, it is proper to question if the discussion at this scale is enough to explain the plastic deformation mechanism of LDSS S32304 cyclically loaded since the two phases can interact to accommodate the cyclic plasticity. Therefore, beside any discussion at the scale of atoms-dislocations interaction, it is necessary to consider also the mesoscopic scale. In addition, it is necessary to keep in mind that the investigated materials also differ in their degree of

homogeneity at the scale of the specimen. Indeed, only the specimen of annealed material and 475°C aged material can be considered homogeneous at this scale since the heat treatment affects the bulk of the material. They will be considered as "monolithic". The cold worked material charged or uncharged with hydrogen as well as the other hydrogenated specimens (annealed and 475°C aged LDSS) are considered as "hybrid specimens". Because first, in the cold worked material, the cold worked layer forms 200 μ m of the thickness of the steel, second, the depth of hydrogen estimated in chapter **3** did not exceed the 100 μ m even after 24 h of hydrogen charging in all cases. This has to be taken into account especially when commenting the mechanical stress response.

1. Fatigue phenomenon

1.1. The Wöhler curve

Generally speaking, fatigue refers to the response of a material when it is subjected to a cyclic loading. The ultimate consequence of repeated stresses may end the lifetime of the material by bringing its failure. The fatigue resistance of a material is defined by the numbers of cycles or reversals to produce the failure that depends on temperature, environment and mechanical conditions. A classical way to assess the fatigue resistance of a material is to submit a fatigue specimen under a stress amplitude while maintaining the other parameters constant (including the mean stress, the frequency) and to record the number of cycles at failure. The evolution of the stress amplitude versus the number of cycles to failure is known as Wöhler diagram (σ -N curve) as shown in Figure IV.1.



Figure IV.1 Wöhler diagram illustrating the stress amplitude versus the number of cycles to failure

The Wöhler diagram reveals three main domains:

- **LCF:** Low cycle fatigue, the stress levels are high enough to generate a macroscopic plastic deformation of the material, which results in short fatigue lives. The limit number of cycles admitted in this domain is restricted to 10⁵ cycles.

- **HCF:** High cycle fatigue, the stress levels are less than the yield stress and so the specimen is macroscopically deformed in the elastic domain, which results in longer fatigue lives up to 10⁵ cycles.

- **VHCF:** very high cycle fatigue where the fatigue life is longer than 10⁷ cycles. These tests are performed at higher frequency, in the order of several KHz to provoke the failure of the specimen in reasonable times.

One of the main differences between (LCF, HCF) and VHCF is the location of crack initiation, being respectively at the external surface and under the surface.

1.2. Low Cycle Fatigue

As mentioned previously, low cycle fatigue tests involve a macroscopic plastic deformation of the specimen. It is therefore recommended to perform (total or plastic) strain-controlled tests and to record the stress-strain evolution during a cycle which appears in the form of a hysteresis loop as shown in Figure IV.2.



Figure IV.2 Hysteresis loop

The cyclic response of the material is analysed in addition with the fatigue resistance. The analysis consists in collecting all the hysteresis loops during the entire test and measuring the evolution of the stress amplitude with the number of cycles.

Depending on the type of the material, the following responses can be obtained (see Figure IV.3):

- either the stress amplitude increases with cycling and then stabilizes: the material exhibits a cyclic hardening,
- either the stress amplitude decreases with cycling and then stabilizes: the material exhibits
- a cyclic softening,

- sometimes, the response is more complex since the material can hardens first and then softens or it can present a final cyclic hardening much later in the fatigue life.



Figure IV.3 Cyclic hardening and cyclic softening [91]

1.3. Advanced analysis of the hysteresis loop

When the mechanism of cyclic deformation is based on dislocations displacement, then it is possible to use the theory of Seeger [92]. According to this theory, the flow σ stress can be decomposed in two terms:

an athermal component σ_G and a thermal component σ^* : $\sigma = \sigma_G + \sigma^*(\dot{\varepsilon}_{pl},T)$

 σ_{G} , athermal stress or often called the internal stress and it is related to long range interactions (for instance the stress required to bow out and to overcome the elastic interaction with other dislocations).

 σ^* , thermal stress or also called the effective stress, results from short distance interactions that can affect the dislocation movement or the core of the dislocations. σ^* depends on the temperature and on strain rate.

In the eighties, Dickson's group has paid a lot of efforts to access to these components during fatigue. They developed the so-called "Handfield Dickson" (HD) method based on the analysis of the hysteresis loop as shown in Figure IV.4.



Figure IV.4 Assessment of the effective and internal stresses from a hysteresis loop

The HD technique attempts to approximate a stress dip to zero stress relaxation technique without performing the relaxation. It consists of determining the portion of the hysteresis loop whose slope most closely agrees with the (experimental) elastic modulus, taking the midpoint of this portion and then measuring the effective stress as equal to the difference between the preceding peak stress and the midpoint of this elastic region [93].

The thermal (σ^*) and athermal (σ_G) stress are calculated using these equations:

$$\sigma *= \frac{\sigma_{emax} - \sigma_{emin}}{2}$$
 (IV.1) $\sigma_{G} = \frac{\sigma_{emax} + \sigma_{emin}}{2}$ (IV.2)

Where, σ_{emax} is the maximum stress and σ_{emin} is the minimum stress in the elastic domain of the hysteresis loop.

This approach has been successfully employed on austenitic stainless steels to explain the role of nitrogen [29] and silicon [94] on the mechanisms of cyclic plasticity. It will be employed to enquire about the role of hydrogen on cyclic plasticity mechanism.

2. Experimental details

2.1. Specimen geometry and set up

Flat specimens were cut along the rolling direction by spark erosion according to ASTM E606. The specimens had a gauge length of 12 mm and a cross section of 6 x 0.5 mm^2 (see Figure IV.5).



Figure IV.5 Scheme of the fatigue specimen (the dimensions are given in mm)

It is necessary to prepare very carefully the gage part of fatigue specimens before doing any LCF test. The surface preparation aims to remove any surface defects which could propagate under cycling and initiate long crack. It also provides a very smooth surface for further analysis of the slip marks. The preparation procedure slightly differed between the hydrogen charged and uncharged specimen. First, the uncharged specimens were subjected to a mechanical

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polishing with SiC paper up to grade # 2400, then to a diamond paste up to 1 micron and finally to an electrolytic polishing in a solution of 80% acetic acid, 10% perchloric acid and 10% of distilled water at 25V. As mentioned in chapter **2** section **2.1.1**, both lateral surfaces of the flat specimens are subjected to a hydrogen charging. Thus, the two surfaces of the 5 h hydrogen charged specimens are directly electropolished after the hydrogen charging. While those of 24 h hydrogen charged specimens were subjected to a very slight polishing with 3 μ m and 1 μ m diamond paste following by an electrolytic polishing to remove the cracks formed during the cathodic charging.

LCF tests were conducted using an electromechanical Instron Schenck Trebel RMC10 machine under strain control using a strain gage extensometer stuck on the lateral part of the gauge length. To avoid the bending or the failure of the thin specimens (0.5 mm), we used an antibuckling system which has been approved in the lab for 350 μ m thick specimen used in the previous PhD work [94] (Figure IV.6).



Figure IV.6 Fatigue set up showing the anti-buckling system and the extensometer mounted on the specimen

For this purpose, the both surfaces of the gauge were covered by a blue tape to avoid any damage on the surface. LCF tests have been performed twice in order to confirm the results. Because the investigated materials had not the same mechanical strength, applying the same total strain did not result in the same plastic strain. Therefore, at first, it was needed to find

the total strain to be applied that provides an average plastic strain of the same order for each tested material (this will be described in details in section **2.2**).

2.2. Fatigue test parameters

LCF tests were conducted at room temperature using a fully push pull mode under strain control (strain ratio $R_{\epsilon} = \epsilon_{min}/\epsilon_{max} = -1$), a triangular waveform and a constant strain rate of 4 x 10⁻³ s⁻¹. At first, one specimen of each material has been sacrificed to find roughly the smallest total strain involving plasticity and to measure the corresponding plastic strain variation. It also aimed at having an overall look of the cyclic response of the annealed LDSS S32304. This consisted in cycling the specimen at a given total strain variation and then measuring the quasi-stabilized plastic strain variation which was in general reached after for 100 cycles. The specimen was also characterized to detect if the slip marks were present or not at the surface of the material.

Figure IV.7 summarizes the stress responses to strain cycling for the annealed LDSS S32304 subjected to five total strain variation increments.



Figure IV.7 Stress response to strain cycling of the annealed LDSS32304 subjected to increased strain variations for 100 cycles

A quasi-stable stress amplitude is recorded for the test at $\Delta \epsilon_t = 0.4\%$. Increasing the strain variation to $\Delta \epsilon_t = 0.6\%$ results in a strong increase of the stress amplitude which decreases with further cycling reflecting a cyclic softening. The further increases of the strain variations pointed out again the cyclic softening response of the annealed LDSS S32304. It is interesting

to note that the rate of softening was maximum for the test performed at $\Delta \epsilon_t = 0.8\%$ and then strongly decreases with the increased strain variations.

Additional tests have also shown that the surface relief analysis did not show any modification in each phase of the annealed LDSS S32304 after 500 cycles applied at $\Delta \epsilon_t = 0.4\%$. In contrast, the cycling of a new specimen at $\Delta \epsilon_t = 0.5\%$ has triggered plastic marks in ferrite and austenite. From the associated hysteresis loop, the plastic strain variation was approximately $\Delta \epsilon_p \approx$ 0.07% (Figure IV.8).



In the following, the targeted plastic strain variation will be $\Delta \varepsilon_p \approx 0.07\%$ and the number of applied cycles N = 1500. The 1500 cycles were simply chosen to obtain a large plastic accumulated strain since the hardness of each phase is considered relatively high. In this study the σ -N (stress versus number of cycles) curves are plotted for the first 1000 cycles because the stress values remained approximately constant for the remaining 500 cycles.

The nomenclature adopted for the samples tested in air or after hydrogen charging is: LDSS-X-Air, LDSS-X-Hy where X represents the metallurgical state of the material (Annealed, CW or 475°C) and y represents the hydrogen charging time. For instance, LDSS-Annealed-H5 stands for the LDSS S32304, annealed and hydrogen charged for 5 hours.

3. Cyclic plasticity of LDSS-Annealed and LDSS-Annealed-H

3.1. Cyclic accommodation

Figure IV.9 summarizes the stress response to cycling under total strain range resulting in average plastic strain variation $\Delta \epsilon_p$ of 0.07% of LDSS-Annealed-Air, LDSS-Annealed-H5 and LDSS-Annealed-H24 as a function of the number of cycles.



Figure IV.9 Evolution of the tensile stress versus the number of cycles of the LDSS-Annealed-Air, LDSS-Annealed-H5 and LDSS-Annealed-H24 (average $\Delta \epsilon_p = 0.07\%$)

Aside from the stress value, one can see that the two hydrogen charged specimens exhibit the same shape of curve compared with the uncharged material (the LDSS-Annealed-Air). The latter sustains a stress amplitude value of about 425 MPa for 10 cycles then exhibits a significant decrease of the tensile stress for about 500 cycles which reflects its high tendency to soften. The marked cyclic softening is then followed by a quasi-stabilization of the stress. The early softening is typical of other DSS e.g. the 25Cr 7Ni 4Mo 0.26N steel [95] or the 25Cr 7Ni 4Mo 0.4N steel [29]. We can notice the significant effect of hydrogen on the stress amplitude if the LDSS-Annealed is hydrogen charged for 24 hours. A sharp increase of the stress amplitude is recorded at the beginning of cycling and remains always higher along the test. A very slight softening can also be observed with a very moderate rate. Apparently charging for 5 h would have led to the conclusion that it does not produce any effect if one had considered only the first cycle of loading. But the next cycles show that it is not the case

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since the stress amplitude remains quasi constant for 100 cycles and then starts decreasing and then stabilizes after 500 cycles. The difference between the maximum value recorded during the test and the stabilized stress is however much higher for the uncharged steel (about 60 MPa) than for the 5 h hydrogen charged specimen (about 30 MPa).

3.2. Surface relief characterization in LDSS-Annealed-Air

An overall observation by SEM of the gauge part of the specimen after cycling is shown in Figure IV.10.a. Higher magnification images of the slip marks are then given in Figure IV.10.b and Figure IV.10.c for ferrite and austenite respectively.



Figure IV.10 SEM-SE images of the annealed LDSS S32304 after 1500 cycles at $\Delta \epsilon_p = 0.07\%$ (a) overview, (b) extrusions in ferrite and (c) slip lines in austenite

The slip marks or slip bands appeared as slip steps and extrusions on the surface of each phase. These observations confirmed the contribution of both phases of the LDSS S32304 in the accommodation of the cyclic deformation as it has been emphasized in the DSS 2507 with 0.26 wt% of nitrogen [95]. The extrusion shapes appear similar to those published on other DSS but cyclically deformed in other conditions. It is noticeable that the fatigue extrusions formed in both phases of the annealed LDSS even though the applied strain range was rather low and the number of cycles rather small. When formed in the ferritic phase, the extrusions appear rather well developed and curvilinear or of the cord-like shape (Figure IV.10.b). Extrusions in the austenite were finer than those of ferrite, straight and inclined with the loading axis (Figure IV.10.c). The morphology of the slip bands in austenite grains suggests a planar slip mode.

3.3. Modification of the surface relief of LDSS-Annealed by hydrogen addition

Observations of the surface relief were carried out by AFM to obtain both qualitative and quantitative information on the slip marks network. The observations confirmed plasticity marks at the surface of both phases of the hydrogen charged annealed LDSS after the cyclic loading.

The fatigue specimens cathodically charged for 5 h and 24 h with hydrogen (LDSS-Annealed-H5, LDSS-Annealed-H24) show a significant plastic deformation activity inside the austenite grains (Figure IV.11).



Figure IV.11 AFM amplitude signal error image of slip marks in austenite of (a) LDSS-Annealed-Air, (b) LDSS-Annealed-H5 and (c) LDSS-Annealed-H24 after 1500 cycles at $\Delta \epsilon_p = 0.07\%$

The austenite surface was mostly covered by slip steps instead of extrusions. Moreover, activation of a second slip system was frequently observed in the hydrogenated austenite (Figure IV.11.b). An increase in the slip planarity beside the smoothness of the slip lines has been detected in austenite after the hydrogen addition.

Meanwhile, the morphology of the slip bands in ferrite grains remains the same after 5 h of hydrogen charging (Figure IV.12.b). In contrast, the hydrogen charging for 24 h affects the plastic marks in ferrite, the slip lines appear finer than those in LDSS-Annealed-Air and LDSS-Annealed-H5 (Figure IV.12.c).



Figure IV.12 AFM height images of slip marks in ferrite of (a) LDSS-Annealed-Air, (b) LDSS-Annealed-H5 and (c) LDSS-Annealed-H24 after 1500 cycles at $\Delta \epsilon_p = 0.07\%$

3.4. Modification of slip lines features in LDSS-Annealed after hydrogen addition

Table IV.1 compares the slip line features of the LDSS uncharged and charged with hydrogen measured in 10 zones of 10 x 10 $\,\mu m^2$ from AFM analysis.

Table IV.1 Mean values of SBH and SBS of the slip marks measured by AFM after fatigue test of the uncharged
and hydrogen charged LDSS S32304

	LDSS-Annealed-Air		LDSS-Annea	aled-H5	LDSS-Annealed-H24	
	Ferrite	Austenite	Ferrite	Austenite	Ferrite	Austenite
SBH (nm)	[15-30]	[5-30]	[5-28]	[2-8]	[5-18] & [4-8]	[2-8]
SBS (µm)	[0.9-3]	[0.7-3]	[0.7-2]	[0.2-1]	[0.5-1]	[0.2-1]

It shows a significant decrease in the values of SBH (slip bands height) and SBS (slip band spacing) in ferrite after only 24 h of hydrogen charging. While, no significant change is noted in the ferrite slip bands after 5 h of hydrogen addition. However, austenite is much more sensitive to the addition of hydrogen. An important decrease is noted in SBH and SBS values of austenite phase in both cases of LDSS-Annealed-H5 and LDSS-Annealed-H24. SBH in austenite decreases from [5-30] nm (LDSS-Annealed-Air) to [2-8] nm (LDSS-Annealed-H5 or H24). Likewise, SBS in austenite phase decreases from [0.7-3] μ m in LDSS-Annealed-H5 and LDSS-Annealed-H5 and SBS and SBH in austenite after 5 h and 24 h of hydrogen charging.

Our SBH and SBS measurements in austenite phase go in an opposite way to the published results on the 316L austenitic steel with large grains in the study of Ménard et al. [45]. But

they mentioned a decrease in the SBH and SBS values for the fined grains of the same steel. The authors attributed the observed changes to the grain size effect that influences the dislocation quantity produced during the deformation that interacts with hydrogen.

3.5. Analysis of dislocation structures in LDSS-Annealed after hydrogen addition

To better understand the effect of hydrogen on austenite grains, it is needed to investigate the microstructure responsible for the accommodation of cyclic plasticity. This has been approached with ECCI analysis only on the LDSS-Annealed-Air and LDSS-Annealed-H24. This selection of hydrogen charging duration appears relevant on the basis of AFM measurements. Indeed, 5 h of charging appeared to affect only the plasticity of austenite and 24 h appeared to affect that of ferrite while the austenite presented similar modifications as that after 5 h of charging.

Figures IV.13.a and Figure IV.13.c taken from the austenite of LDSS-Annealed-Air show planar arrangements of dislocations and the presence of many stacking faults respectively. The austenite of the charged material LDSS-Annealed-H24 features the same deformation microstructures, i.e., stacking faults in a nearly equivalent amount and planar arrangements but with a higher density as shown in Figure IV.13.b and Figure IV.13.d. The density of slip planes where dislocations are confined is in good agreement with the high number of slip marks expressed by SBS in LDSS-Annealed-H24.



Figure IV.13 SEM-ECCI images of austenite in (a), (c) LDSS-Annealed-Air and (b), (d) LDSS-Annealed-H24, indicating the stacking faults by the white arrows, after 1500 cycles of fatigue at $\Delta \varepsilon_p = 0.07\%$

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SEM-ECCI images of the ferrite in LDSS-Annealed-Air and LDSS-Annealed-H24 are shown in Figure IV.14.a and Figure IV.14.b respectively. The dislocations are remained confined also in their slip planes, homogenously distributed without any arrangement in substructures as walls or cells. There is no significant difference between the uncharged and 24 h hydrogen charged material except the slightly higher dislocation density in the latter.



Figure IV.14 SEM-ECCI images of ferrite in (a) LDSS-Annealed-Air and (b) LDSS-Annealed-H24 after 1500 cycles of fatigue at $\Delta \varepsilon_p$ = 0.07%. The white arrows indicate the dislocations

3.6. Discussion

Combining the microhardness values of the ferrite phase before and after the cathodic charging with the values of SBH and SBS allows drawing some conclusions on the hydrogen location according to the cathodic charging duration. After 5 h of hydrogen charging, the increase of microhardness in the austenite of the LDSS Annealed from $HV_{0.025} = 259 \pm 7$ to $HV_{0.025} = 279 \pm 13$ just before the LCF test attests the presence of hydrogen in the austenite phase. In ferrite, the microhardness remained stable, $HV_{0.025}$ of ferrite in LDSS-Annealed-Air is 236 \pm 5 and in LDSS-Annealed-H5 is 242 \pm 8. Here, the presence of hydrogen cannot be denied but we can assume that the concentration of hydrogen presented in this phase is insufficient to modify the plasticity of ferrite.

After 24 h of hydrogen charging, the microhardness values evolve in both phases. The microhardness of hydrogenated austenite after 24 h is $Hv_{0.25} = 284 \pm 16$ and that of ferrite is $HV_{0.025} = 274 \pm 18$ just before the LCF test. Thus, the increase in hydrogen charging time has probably forced hydrogen to strongly enrich the ferrite. These results suppose that during the 24 h of hydrogen charging, hydrogen is more present in austenite during the first hours and, then it continues diffusing to enrich later on the both phases. The former assumption, partition and introduction sequence of hydrogen in the two phases of the LDSS S32304

suggested by the microhardness tests, fits well with the analysis of the surface relief analysis after fatigue test. After 5 h of charging, the very minor changes in SBS and SBH in ferrite and the noticeable ones in austenite reflect that the hydrogen content in austenite was likely enough to affect its plasticity in contrast with that in ferrite phase. Increasing the charging time from 5 h to 24 h did not change the slip bands features of austenite but obviously affected those of ferrite. The slip marks are less spaced and less developed which supports now that the presence of hydrogen in ferrite is more important and it was sufficient to affect its plasticity.

Moreover, our observations are consistent with the work of Claeys et al. [52], where they noticed an increase in dislocation density and in sources activation in ferrite of the DSS 2205 after introducing a high hydrogen concentration in the material.

A closer look of the relief in the ferrite has shown narrow slip bands accompanied with microcracks only in LDSS-Annealed-H24 compared to LDSS-Annealed-Air (Figure IV.15).



Figure IV.15 SEM images of ferrite in (a) LDSS-Annealed-Air and (b) LDSS-Annealed-H24 showing the microcracks inside the slip bands of hydrogenated ferrite after 1500 cycles of fatigue at $\Delta \varepsilon_p = 0.07\%$

It is often found in the literature that hydrogen addition reduces the stacking fault energy (SFE) [45,53] which can be visible from the smoothness of the austenite slip lines and the slip planarity mode. This was not found in our case since the latter features did not obviously change. In addition, the investigated LDSS-Annealed-Air showed stacking faults (SFs) after fatigue and the amount was not so much modified by the hydrogen addition. This is a good indication to confirm the low value of the stacking fault energy of austenite phase (SFE $\simeq 11$ mJ.m⁻²) as mentioned in chapter **2** section **1.1** which can explain the pre-existing of SFs before

fatigue. Even if SFs are in a higher amount after fatigue, they are not the main way in the accommodation of the cyclic plasticity.

Regarding the dislocation structures, the type of their arrangements was not modified by the introduction of hydrogen. In austenite, planar arrays were observed in the uncharged and the hydrogen charged material as well. In the ferrite phase, the dislocations remain isolated in their slip planes without any structuration. However, the micrographs clearly suggest that in austenite, hydrogen has promoted the activation of new dislocations sources, triggered secondary slip and activated other grains. The increase in dislocation multiplication in a super duplex stainless steel caused by hydrogen charging has been reported previously by Liang et al. [96]. They measured by neutron diffraction an increase in dislocation density with one order of magnitude in the austenite. In a qualitative way, a clear change in dislocation density was observed before and after cycling in both phases. However, there is no big difference in the dislocation density in ferrite and austenite between the 5 h charged specimen and the 24 h charged specimen material.

From the analysis of the hysteresis loops, the effective stresses have been measured and they are reported as a function of the number of cycles N (Figure IV.16). Paying attention on the effective stress is relevant in the present work since Oliveira et al. [97] demonstrated an important influence of hydrogen on the effective stress that due to short-range interaction in a 316L austenitic steel at low plastic strain amplitude (0.2%). They reported a large influence of hydrogen on the long-range interaction (internal stress component) at higher plastic strain amplitude (0.7%). For this reason, only the effective stress will be taken into account to explain the effect of hydrogen on the steel since the material is cyclically strained at low plastic strain. It can be seen that the effective stresses measured in the hydrogen charged materials are much higher than in the uncharged one (Figure IV.16). For the latter, the evolution of the effective stress together with the tensile stress tends to strongly decrease after the first hundred cycles. For the 5 h and 24 h hydrogen cathodic charging durations, the effective stress remains at a higher level of that in the uncharged material throughout the cycling. We must be very wise with the interpretation of the effective stress measured in a bi-phased materials since the measured value comes from the average response of each phase. In the present case, we believe that the difference between the uncharged and the 5 h charged material arises eventually from the austenite phase.



Figure IV.16 Evolution of the effective stress and tensile peak stress with the number of cycles at $\Delta \varepsilon_{p}$ = 0.07% in the LDSS-Annealed-Air, LDSS-Annealed-H5 and LDSS-Annealed-H24

In order to have a more quantitative image of the variations in the dislocation densities, KAM measurements were performed before and after fatigue in the LDSS- Annealed-H24 material. The KAM value was higher in both phases at the end of the test (KAM = 0.145° in ferrite and 0.2° in austenite) than before fatigue (KAM = 0.102° in ferrite and 0.088° in austenite). This suggests that the rate of dislocation production is higher than the rate of annihilation.

3.7. Highlights

Taking into consideration all these analyses, as far as **austenite of the LDSS 32304 (annealed)** is concerned, the role of hydrogen on the cyclic plasticity validates some of the characteristics of HELP mechanism:

- The increased number of activated dislocations sources and the promoted dislocation nucleation in the presence of hydrogen in austenite indicate a decrease in the critical shear stress in a same way as proposed by Claeys et al. [52], Nibur et al. [40] and Murakami et al.[81].
- The distances between the planes where dislocations are stacked and the increased proximity between dislocations suggest that hydrogen has produced a shielding effect on the elastic stress field of dislocations and thus reduced the repulsive forces between dislocations. Together this increases the dislocations mobility

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However, the results of the present PhD study reveal some specific points related to the material and the loading conditions, here the cyclic plasticity, which do not match completely with the HELP theory:

- The increased mobility is may be also a result of dislocation annihilation events promoted by hydrogen, that is an indirect effect of hydrogen. Indeed, in low SFE materials, cross slip is not generally admitted or less probable to occur which disfavour dislocation annihilation. In the present hydrogen-containing austenite, despite a low SFE and a planar slip, the interaction distance between dislocations on two parallel slip planes is strongly reduced and may approach the critical distance of annihilation. Therefore, annihilation events are very likely to occur as a result of the back-and-forth displacement of dislocations
- The HELP mechanism is often associated with a softening of the material. This is particularly true for a monotonic loading. In the present study, the stress response to strain cycling with the number of cycles does not exhibit the strong softening as it occurred in the uncharged material. The observed quasi-stabilisation of the stress or the weak cyclic softening reflects the competition production rate of dislocation and annihilation rate of dislocations. This tends to conclude that dislocation nucleation is much favoured than dislocation displacement in presence of hydrogen.
- Finally, the reduced mobility of dislocations, just above suggested, is supported by the value of the effective stress. As well, this may also be amplified by the loading condition.
 During fatigue, and in case of annihilation process, a high amount of point defects is produced which can contribute to the increase of the effective stress.

Concerning the **ferrite of LDSS S32304 (annealed)**, the HELP mechanism does not reflect the effect of hydrogen on the mechanical response even though it is claimed in some (scarce) papers, e.g., [98] From our observations focused on the LDSS-Annealed-H24, the following conclusions can be drawn:

- Hydrogen hardens ferrite by a possible effect of hydrogen atoms-dislocations interactions
- Hydrogen has restricted the mobility of dislocations in ferrite as indicated by the SBH values

The effective stresses are weaker in the LDSS-Annealed-H24 than in the LDSS-Annealed-H5 due to the significant effect of hydrogen on ferrite which could suggest that hydrogen decreases the difference in mobility of screw and edge dislocations.

4. Cyclic plasticity of LDSS-CW-Air and LDSS-CW-H

The objective of this part is to investigate if hydrogen introduced in an enriched pre-existing dislocation layer of the LDSS 32304 behaves in a similar way of the non-cold worked material under cyclic loading. Remember that the flat specimens (500 μ m of thickness) of the so-called LDSS-CW consist of 200 μ m external the cold worked layer beside the 300 μ m annealed state the material. Since the hydrogen concentration provided from 5 h of hydrogen charging did not affect the ferrite in LDSS-Annealed, we decided to charge directly the LDSS-CW with 24 h of hydrogen. To point out the action of hydrogen charging, microhardness measurements were performed in the two phases of LDSS-CW-H24 before fatigue. Both phases exhibited a high microhardness after cathodic charging. The microhardness of austenite increased from HV_{0.025} = 302 ± 14 to 367 ± 17 and that of ferrite increased from 274 ± 13 to 296 ± 14 after hydrogen addition.

4.1. Cyclic accommodation

The cyclic accommodation of the LDSS-CW charged and uncharged of hydrogen with regards to the number of cycles is illustrated in Figure IV.17. In both cases, the cyclic response is characterized by an initial hardening during the first 10 cycles and then by a continuous cyclic softening. We can notice that the LDSS-CW-Air and LDSS-CW-H24 exhibit the same behaviour but the tensile stress is slightly higher for the hydrogenated material. The highest difference appears during the first cycle of LCF test where the tensile stress is 489 MPa for LDSS-CW-H24 and 471 MPa for LDSS-CW-Air. Then the difference progressively vanishes but the tensile stress values of the hydrogenated material remain always higher than those of the cold worked as the number of cycles increased. It can be concluded that the 200 µm of cold worked layer has impacted the strength of the 500 µm thick specimen. The increase in the stress values of the LDSS-CW-H24 in comparison with the LDSS-CW-air reflects the effect of hydrogen in the cold worked layer of one side of the fatigue specimen and in the annealed layer of the opposite side.



Figure IV.17 Evolution of tensile stress versus the number of cycles of LDSS-CW-Air and LDSS-CW-H24 at $\Delta \epsilon_p$ = 0.07%)

4.2. Surface relief characterization in LDSS-CW-Air and LDSS-CW-H24

The slip bands morphology of austenite and ferrite in the uncharged LDSS-Cold worked specimen (LDSS-CW-Air) is very similar to that obtained in LDSS-Annealed-Air. Straight slip lines reflecting a planar slip mode have been identified in austenite whereas curvilinear slip bands have been found in ferrite. The number of zones featuring of slip bands was significantly higher in ferrite than in austenite as illustrated by the AFM images of Figure IV.18. This suggests a more active participation of ferrite in the accommodation of the plastic deformation of the LDSS-CW-Air compared to LDSS-Annealed-Air.



Figure IV.18 AFM amplitude signal error images showing the slip marks in ferrite of LDSS-CW-Air after 1500 cycles of fatigue at $\Delta \epsilon_p$ = 0.07%

The austenite in LDSS-CW-H24 exhibited the same modifications presented in austenite of LDSS-Annealed-H5 and LDSS-Annealed-H24. Slip steps have been frequently noted in austenite grains with the activation of a second slip system (Figure IV.19). The smoothness of slip bands was well defined accompanied with a decrease in slip lines features to reach the same values of those obtained in austenite of LDSS-Annealed-H5 and LDSS-Annealed-H24; SBH and SBS reached [2-8] nm and [0.4-1] μ m respectively. For ferrite, slip bands were not observed with AFM.



Figure IV.19 (a) AFM height image of austenite in LDSS-CW-Air showing the slip marks and (b) AFM amplitude signal error of austenite in LDSS-CW-H24 showing the fine slip lines accompanied with a second slip system after 1500 cycles of fatigue at $\Delta \varepsilon_p = 0.07\%$

4.3. Modification of slip lines features in LDSS-CW after hydrogen addition

The height of the slip bands and their spacing were measured as for the annealed materials in 10 zones of $10 \times 10 \ \mu m^2$ approximately. Their values are listed in Table 2.

	LDSS-Annealed-Air		LDSS-C\	V-Air	LDSS-CW-H24	
	Ferrite	Austenite	Ferrite	Austenite	Ferrite	Austenite
SBH (nm)	[15-30]	[5-30]	[80-160] & [20-50]	[25-90] & [12-30]	-	[2-8]
SBS (µm)	[0.9-3]	[0.7-3]	[0.9-1.5]	[0.7-2]	-	[0.4-1]

Table IV.2 Mean values of SBH and SBS of the slip marks measured by AFM after fatigue of the uncharged orhydrogen charged cold worked LDSS S32304

Comparing to the LDSS-Annealed-Air, the slip band are higher as well in the austenite as in the ferrite of the cold worked material: the values of SBH_{γ} are [25-90] nm and [12-30] nm in LDSS-

CW-Air while they were [5-30] nm in the LDSS-Annealed-Air, and the SBH_{α} values were varied between [80-160] nm and [20-50] nm instead of [15-30] nm in LDSS-Annealed-Air. The slip bands spacing in austenite is the same as in the annealed material where SBS_{γ} found in the LDSS-CW-Air was [0.7-2] μ m. While SBS_{α} in LDSS-CW-Air was slightly lower than that in the annealed material, it was ranged between [0.9-1.5] μ m.

4.4. Analysis of dislocations structure of LDSS-CW after hydrogen addition

ECCI images show an increase in dislocation activity in austenite of LDSS-CW-H24 (Figure IV.20.b) compared to LDSS-CW-Air (Figure IV.20.a). Consequently, new emerging dislocation sources started to be activated due to the presence of hydrogen. Figure IV.20.c and IV.20.d show the presence of SFs surrounded by dislocations regardless the addition of hydrogen which indicates that the SFs generation is not related to the hydrogen charging. These observations are similar to the ones obtained for austenite in LDSS-Annealed-Air and LDSS-Annealed-H24. It seems that the dislocation gliding becomes more dominant than the formation of SFs in the hydrogenated austenite.



Figure IV.20 ECCI images of austenite in (a), (c) LDSS-CW-Air and (b), (d) LDSS-CW-H24 after LCF test after 1500 cycles of fatigue at $\Delta \varepsilon_p = 0.07\%$ (white arrows point out the SFs)

As mentioned above, the AFM observation did not reveal any slip marks in ferrite of the LDSS-CW-H24. Nevertheless, attention was paid to conclude that no plastic activity has occurred in the ferrite of the hydrogenated cold worked material. At first, it was very easy to image the slip marks in the ferrite grains of LDSS-CW-Air as shown in Figure IV.21.a. While the hydrogen addition on the LDSS-CW seems to suppress the slip markings in ferrite (Figure IV.21.b). A closer look in the hydrogenated ferrite of LDSS-CW-H24 using ECCI approach shows an increase in dislocation density compared to that of LDSS-CW-Air (Figure IV.21.c and IV.21.d).



Figure IV.21 SEM images showing (a) the slip bands in ferrite in LDSS-CW-Air and (b) the non-observed slip marks in ferrite of LDSS-CW-H24. ECCI images showing (c) the extrusion surrounded by dislocations in LDSS-CW-Air and (d) increase in dislocation density in LDSS-CW-H24; images taken after 1500 cycles at $\Delta \varepsilon_p = 0.07\%$

4.5. Discussion

Even in the cold worked material, hydrogen was able to enter in both phases enriched in preexisting dislocations before fatigue. The absence of slip bands in ferrite of the LDSS-CW- H24 after fatigue can be due to the hinder of dislocations by hydrogen or also to the interaction between austenite and ferrite, and more precisely to the plastic deformation accommodated by the hydrogenated austenite. The estimation of the effective stress was therefore undertaken in the same way as for the annealed material (see Figure IV.22).



Figure IV.22 The effective stress evolution of LDSS-CW-Air and LDSS-CW-H24 during the LCF test at $\Delta \varepsilon_p = 0.07\%$ It shows a slight increase in the effective stress values in LDSS-CW-H24 compared to those of LDSS-CW-Air. The austenite of LDSS-CW-H24 was featuring the same slip markings pattern as that obtained in hydrogenated austenite in LDSS-Annealed-H5 and LDSS-Annealed-H24. Hence, we can suggest that hydrogen has increased the difference in the accommodation of cyclic plasticity between the cold worked austenite and cold worked ferrite.

Once hydrogen is introduced in the LDSS-CW, the plastic deformation becomes mostly accommodated by austenite. And in ferrite, the dislocation motion is quasi-inhibited or occurs on very short distance and explain the high values of the effective stresses at the beginning of cycling. The impossibility of accommodating the cyclic plasticity by the hydrogenated ferrite leads to concentrate the strain in the hydrogenated austenite. During the first cycles, the latter contains pre-existing dislocations which are pinned by the presence of hydrogen atoms and exhibit difficulties to move. But as the cycles progress, the effective stresses decrease which means that the dislocations are now released from their pinning points and can move easily in austenite as previously explained in the study of Murakami et al. [7].

4.6. Highlights

Concerning the influence of the pre-existing dislocations at the surface of LDSS S32304 before hydrogen charging and cyclically loading, the main conclusions are:

- Hydrogen in the cold worked austenite of LDSS S32304 pins the pre-existing dislocations
- Dislocations depinning from hydrogen atoms occurs in austenite upon cyclic loading especially during the last cycles while dislocations remain pinned in ferrite
- Planar slip mode is observed in austenite with dislocation nucleation markedly promoted by hydrogen while ferrite behaves in an inactive way in the presence of hydrogen
- In the austenite phase, the plastic activity becomes very intense due to the depinning of dislocations from hydrogen atoms and due to deformation transfer from ferrite to austenite
- Finally, the cold working produces a striking effect on the plastic response of LDSS
 S32304 in the uncharged condition.

5. Cyclic plasticity of LDSS-475°C-Air and LDSS-475°C-H

As previously mentioned, the goal of the aging treatment at 475 °C in our study is to change the metallurgical state of the LDSS S32304, especially the ferrite phase, without resulting in an embrittlement of the steel. In **chapter 3**, section **6.2**. the analysed fracture surfaces of a 475 °C aged tensile specimen for 25 h only showed indeed a ductile fracture mode.

5.1. Cyclic accommodation of LDSS-475°C-Air

Figure IV.23 summarizes the stress response to cycling under total strain range resulting in average plastic strain variation $\Delta \varepsilon_p$ of 0.07% of the LDSS-Annealed before and after 475 °C aging as a function of the number of cycles.



Figure IV.23 Evolution of tensile stress versus the number of cycles of LDSS-Annealed-Air and LDSS-475 °C-Air during fatigue at $\Delta \epsilon_p = 0.07\%$

Comparing to the LDSS-Annealed-Air, the aging alone unsurprisingly leads to a change in the cyclic stress response with higher stress values as it has been emphasized in duplex BöA911 thermally aged at 475 °C in the PhD work of D. Salazar [24]. The aged LDSS-475 °C-Air starts with a quasi-stable response for 50 cycles (between 476 MPa and 480 MPa) linked to the increase of the microhardness of ferrite (from $HV_{0.025} = 236 \pm 5$ to 270 ± 6 after the aging treatment), then exhibits a cyclic hardening after 100 cycles to stabilize for the rest of the test.

5.2. Surface relief characterization in LDSS-475°C

The comparison of the surface modifications of the LDSS-Annealed-Air and LDSS-475°C-Air is displayed in Figure IV.24. The curvilinear slip bands observed in ferrite of LDSS-Annealed-Air (Figure IV.24.a) became straight after the aging treatment as shown in Figure IV.24.b. The AFM micrograph of austenite in LDSS-475 °C shows similar slip bands morphology to that observed in LDSS-Annealed-Air (Figure IV.24.c), the only difference is that they are bit wider as shown in Figure IV.24.d. It can be suspected that the chromium redistribution resulted from the spinodal decomposition created a wide path to let the dislocations move easily between the clusters.



Figure IV.24 AFM height images of slip bands in ferrite of (a) LDSS-Annealed-Air, (b) LDSS-475°C-Air and austenite in (c) LDSS-Annealed-Air, (d) LDSS-475°C-Air after 1500 cycles at $\Delta \varepsilon_p = 0.07\%$

5.3. Surface relief characterization of LDSS-475°C-H24

To evaluate the effect of hydrogen charging on aged specimens, a first attempt consisted in charging with hydrogen the fatigue specimen for 24 h since the plastic deformation has been observed in both phases using this condition for the two tested materials above. After fatigue at $\Delta \varepsilon_p = 0.07\%$, optical microscopy observations of the fatigue specimen charged in hydrogen show a large crack surrounded by dense slip bands in the middle of the gauge specimen (Figure IV.25).



Figure IV.25 Optical micrograph showing a large fatigue crack in the middle of the specimen formed during LCF test at $\Delta \varepsilon_p = 0.07\%$

The large crack has occurred during the cyclic test. It seems that 24 h of hydrogen charging for the thermally aged material is too severe on the mechanical behaviour of the material. The reason behind this failure is probably the very large loss ductility of the material. For this purpose, a shorter hydrogen charging duration (5 h) has been chosen to detect the influence of hydrogen on the plastic deformation of the thermally aged LDSS and to better understand the cause of the failure observed in LDSS-475°C-H24.

5.4. Cyclic accommodation of LDSS-475°C-H5

To point out the combined effect of aging treatment and hydrogen charging on the LDSS, the evolution of the tensile peak stress versus the number of cycles is plotted in Figure IV.26.



Figure IV.26 Evolution of tensile stress versus the number of cycles of LDSS-475°C-Air and LDSS-475°C-H5 during fatigue at $\Delta \varepsilon_p = 0.07\%$

The introduction of hydrogen leads to a strong increase of the tensile stress from the beginning of cycling where 584 MPa is recorded for LDSS-475°C-H5 and 484 MPa for LDSS-475°C-Air at the first cycle. Hydrogen addition resulted in a stable response of the material with the increase of cycles number with maintaining a higher stress level than of that in LDSS-475°C-Air.

5.5. Surface relief characterization in LDSS-475°C-H5

The introduction of hydrogen into the LDSS-475°C modifies the partition of plasticity. After cyclic loading, SEM observations revealed plastic deformation marks essentially in austenite phase of LDSS-475°C-H5 (Figure IV.27). No plastic markings have been detected in ferrite of the LDSS-475°C-H5 using SEM. Even AFM approach confirmed that no slip lines have covered the surface of the hydrogenated ferrite in the thermally aged material.



Figure IV.27 SEM images illustrating slip lines in only austenite phase in LDSS-475°C-H5 by white squares and the absence of slip marks in ferrite phase after 1500 cycles at $\Delta \epsilon_{p}$ = 0.07%

Imaging the slip marks in the austenite of LDSS-475°C-H5 by AFM reveals the presence of protrusions containing individual extrusions. A protrusion is a macro slip mark consisting in an agglomeration of extrusions and intrusions (Figure IV.28).



Figure IV.28 AFM height image illustrating the protrusions in austenite of LDSS-475C-H5 after 1500 cycles $\Delta \epsilon_{p}$ = 0.07%

5.6. Modification of slip lines features in LDSS-475°C-Air and LDSS-475°C-H5

Concerning the slip markings characteristics in the three studied materials, Table IV.3 compares the slip line features measured in 10 zones of 10 x 10 μ m² of LDSS-Annealed-Air, LDSS-475°C-Air and LDSS-475°C-H5.

Table IV.3 Mean values of SBH and SBS of the slip marks measured by AFM after fatigue of the LDSS-Annealed-
Air and uncharged or 5h hydrogen charged aged LDSS S32304

	LDSS-Annealed-Air		LDSS-475°C - Air		LDSS-475°C - H5		
	Ferrite	Austenite	Ferrite	Austenite	Ferrite	Austenite	
SBH (nm)	[15-30]	[5-30]	[6-22]	[7-30]	_	[10-90] & [15-30] & [8-15]	
SBS (μm)	[0.9-3]	[0.7-3]	[0.3-1]	[0.5-2]	_	[0.7-2.5] & [0.2-0.6]	

The slip band features in ferrite were slightly affected by the aging treatment where SBH_{α} values found are [6-22] nm and SBS_{α} varied between [0.3-1] μ m. This means that 25 h of aging treatment has indeed modified the microstructure of ferrite as pointed out by the increased in micro-hardness values. Regarding the austenite phase in LDSS-475°C-Air, their slip bands features remained almost unchanged, SBH_{γ} [7-30] nm and SBS_{γ} [0.5-2] μ m compared to those of austenite in LDSS-Annealed-Air.

Furthermore, the height of the slip lines in the hydrogenated austenite was very high, SBH $_{\gamma}$ reached [10-90] nm, [15-30] nm and [8-15] nm than that obtained in the hydrogenated austenite of the annealed or cold worked LDSS, where it exhibited [2-8] nm. The spacing

between the slip bands inside the bundle of extrusions decreased to reach a range between $[0.2-0.6] \mu m$. While, the SBS between each bundle of extrusions remains almost unchanged $[0.7-2.5] \mu m$.

5.7. Analysis of dislocations structure in LDSS-475°C-Air and LDSS-475°C-H5

The partition of plasticity was also investigated from the dislocation distribution by ECCI. The closer observation of the microstructure of austenite shows that hydrogen induced the slip activity in austenite. Figure IV.29.b shows a higher amount of slip traces concentrated in the hydrogenated austenite grains compared to those in austenite of LDSS-475°C-Air (Figure IV.29.a) due to an activation of new dislocation sources induced by the presence of hydrogen. Moreover, Figures IV.29.c and d display the presence of stacking faults (SFs) in austenite in both LDSS-475°C-Air and LDSS-475°C-H5. These observations are similar to those obtained in the austenite charged or uncharged with hydrogen of LDSS-Annealed and cold worked.



Figure IV.29 ECCI images of austenite in (a), (c) LDSS-475°C-Air and in (b), (d) LDSS-475°C-H5 after 1500 cycles at $\Delta \varepsilon_p = 0.07\%$

The ECCI analysis also confirms no localisation of cyclic plasticity into slip marks in the ferrite of LDSS-475°C-H5. In both LDSS-475°C-Air and LDSS-475°C-H5, the dislocations are well distributed in their slip plane. Figures IV.30.a and b show the distribution of dislocations beside

extrusions inside the ferrite of LDSS-475 $^{\circ}$ C-Air. However, the comparison between Figures IV.30.a, IV.30.b and IV.30.c seems to point out a nearly same dislocation density in ferrite of LDSS-475 $^{\circ}$ C-H5.



Figure IV.30 ECCI images of LDSS-475°C-Air in (a) and (b) showing the extrusions and dislocations pattern, and LDSS-475°C-H5 in (c) illustrating dislocation distribution after 1500 cycles at $\Delta \epsilon_p = 0.07\%$

5.8. Discussion

The microhardness measurements performed on LDSS-475°C-H5 showed an increase in both phases comparing to those in LDSS-475°C-Air. The microhardness of ferrite increased from 270 \pm 6 to 292 \pm 8 and that of austenite raised from 259 \pm 7 to 291 \pm 12 after the hydrogen addition for 5 h. Here, the evolution of the microhardness is clearly observed in both phases while it was only occurred in austenite of LDSS-Annealed-H5. This result suggests that the "clusters of chromium" formed in ferrite after 475 °C attracted more hydrogen atoms and so act as trapping sites. In other words, aged ferrite became more susceptible to trap more hydrogen than that in the annealed material after a short hydrogen charging time.

An attention to the evolution of the effective stresses is required to clarify the role of "chromium clusters" in the thermally aged material tested in the air and with the presence of hydrogen. Figure IV.31 highlights the calculated effective stress versus the number of cycles
of LCF test. As noticed, LDSS-475°C-Air exhibits higher effective values than the LDSS-Annealed-Air. Moreover, the effect of aging treatment is more noticeable on the effective stress which is slightly increased by hydrogen addition. It is also noticeable that the effective stresses in the 475°C aged material remain quasi constant or decrease very slightly during cycling.



Figure IV.31 Evolution of effective stress versus the number of cycles of LDSS-Annealed-Air, LDSS-475°C-Air and LDSS-475°C-H5

The aging treatment has produced the expected effect, a moderate hardening of the ferrite of the LDSS S32304 that allows its plastic deformation. Therefore, the spinodal decomposition occurred in ferrite and "chromium clusters" have formed. The H-D method is very easy to be referred because the aging affects the entire bulk of the material so that it can be considered as homogeneous at the specimen scale. The aging treatment modifies only the ferrite microstructure since austenite did not show any additional modification after the aging treatment: morphology, SBH and SBS of their slip bands and even its microhardness remained unchanged. The "clusters of chromium" are like small domains that can pin dislocations and impede their motion on short range distance as indicated by the high effective stresses. Then, in the further cycles, the dislocations are unanchored and part of them still encounter these obstacles while another part can move easily in "clean" tracks between the clusters. This can explain the straight shape of slip bands observed in the thermally aged ferrite together with the measurement of high effective stresses during the cycling.

Regarding the hydrogen charging, the effect of hydrogen was highly remarked in both phases by the increase of their microhardness measurements and moreover hydrogen can be more present at the surface than the bulk of the specimen as we showed in chapter **3** section **7.2**. This makes a major difficulty for the understanding of the effect of hydrogen on the microstructure of each phase by the H-D method. Indeed, the hysteresis loop from which the effective stress is estimated reflects the average behaviour of the specimen. Nevertheless, hydrogen shows a strengthening effect on the effective stresses compared to those of LDSS-Annealed-Air. The increase in stress values can result from hydrogen possibly located at dislocations which prevent them from gliding (short-range obstacles). Hydrogen can be present also at grain boundaries or ferrite/austenite interphases. Therefore, the possible trapping of hydrogen at various sites complicates the understanding of its effect on each phase. For the aged ferrite, hydrogen has disfavoured plastic deformation since no slip marks or deformation localisation have been detected by AFM or ECCI. We can suspect that the "clusters of chromium" have attracted hydrogen e.g., act as hydrogen trapping sites which strengthen the anchorage of dislocations and prevent their gliding. For the aged austenite, hydrogen promotes nucleation and displacement of dislocations that appeared in form of protrusions and have SBH_{γ} and SBS_{γ} values much higher than those in austenite of LDSS-Annealed-H5 and LDSS-CW-H5. This tends to support a noticeable effect of the hydrogenated ferrite on austenite. Furthermore, hydrogen is probably present in lower content in the aged austenite compared to that in LDSS-Annealed-H5 and LDSS-CW-H5 because of the presence of new hydrogen trapping sites in ferrite (clusters of chromium).

5.9. Highlights

Concerning the combined effect of hydrogen and spinodal decomposition on the cyclic plasticity of the LDSS S32304, it can be concluded that:

- 25 hours of aging at 475°C is enough to modify the metallurgical state of ferrite by a spinodal decomposition.
- The combined effect of aging treatment and hydrogen charging produced a sharp increase in the cyclic stress response.

- Both phases can accommodate the cyclic deformation in the uncharged material while it is restricted mainly to austenite after hydrogen charging.
- The "chromium clusters" act as trapping sites for hydrogen
- Aged ferrite presents "easy glide" tracks for dislocation displacement and areas enriched in chromium cluster obstacles.
- In the aged austenite, hydrogen promotes nucleation and displacement of dislocations appeared as protrusions at the surface of austenite.

Conclusion

First, before hydrogen charging, the contribution of austenite and ferrite to the plastic deformation was highlighted in the "monolithic" materials, annealed and thermally aged LDSS. On the other hand, the "hybride" material LDSS-CW containing 200 μ m of cold worked layer (rich in dislocations), the partition of plasticity was slightly modified where a more active participation of ferrite in the plastic deformation accommodation has been noticed.

Once hydrogen is introduced in LDSS-Annealed, the plastic deformation becomes mostly accommodated by austenite regardless the hydrogen charging duration. The nucleation and activation of new dislocations sources inside austenite grains were evidenced which indicates a decrease of the critical shear stress. However, the 5 h of hydrogen charging was insufficient to distrupt the plastic activity of ferrite but the increasing of hydrogen charging for 24 h forced hydrogen to be more efficient to affect the plasticity of ferrite as revealed by an increase in its hardness. The significant effect of hydrogen in the latter condition has restricted the mobility of dislocations.

The presence of hydrogen in LDSS-CW modified the accommodation of cyclic plasticity between the cold worked austenite and cold worked ferrite. Despite the higher dislocation density present in the cold worked material, the overall plastic deformation behaviour of the hydrogenated austenite was very similar to that of austenite in LDSS-Annealed-H5 and LDSS-Annealed-H24. While, the hydrogenated ferrite remained inactive in LDSS-CW contrarily to what observed in ferrite of LDSS-Annealed-H24. The impossibility in accommodating the cyclic plasticity in ferrite of LDSS-CW-H24 is attributed to the pinning effect of hydrogen on the pre-existing dislocations.

The 25 h of aging treatment at 475°C changed the metallurgical state of the material especially the ferrite phase as a result of the spinodal decomposition. The "chromium clusters" resulted from the spinodal decomposition inside ferrite modified the dislocation displacements by creating "clean" track for their gliding. The combined effect of aging treatment and hydrogen charging has manily restricted the plastic accommodation to austenite phase. Ferrite became more sensitive to hydrogen in the aged material because of the presence of "chromium clusters" that acted as trapping sites for hydrogen. We can suspect that the hinder of dislocations by the "chromium clusters" was the reason behind the failure observed in LDSS-475°C-H24.

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Indeed, the hydrogen concentrated in a layer of 100 μ m or less in each studied material has clearly impacted the mechanical behaviour of the entire steel which led to modify the plastic accommodation of austenite and ferrite.

Graphical abstract

Effect of hydrogen on each metallurgical state of LDSS S32304

LDSS S32304 annealed after 5 h of cathodic hydrogen charging and 1500



LDSS S32304 annealed after 24 h of cathodic hydrogen charging and 1500 cycles at $\Delta \epsilon_p$ = 0.07%



Effect of hydrogen on LDSS S32304 cold worked after 24 h of cathodic hydrogen charging and 1500 cycles at $\Delta \epsilon_p$ = 0.07%



LDSS S32304 thermally aged at 475 °C for 25 h after 5 h of cathodic hydrogen charging and 1500 cycles at $\Delta \epsilon_p$ = 0.07%



- **1** Hydrogen charging of LDSS-475°C for 5 h \rightarrow increase of the microhardness of austenite and ferrite (HV_y = 259 ± 7 \rightarrow HV_y = 300 ± 12, HV_a = 270 ± 6 \rightarrow HV_a = 313 ± 12)
- **2** After 4 h of holding time \rightarrow decrease of the microhardness of austenite (HV_{γ} = 291 ± 12) \rightarrow decrease of the microhardness of ferrite (HV_{α} = 292 ± 8)





Conclusions and perspectives

The goal of the present PhD project was to contribute on the understanding of the sensitivity of the metallurgical state of a lean duplex stainless steel (LDSS) to hydrogen embrittlement. For that, our efforts have been focused on a LDSS produced in an industrial line and our research experiments have been directly performed on the as received conditions. The material was the LDSS S32304 delivered in the form of a plate 5 mm in final thickness.

The studied lean duplex stainless steel (LDSS) was formed of a ferritic matrix embedding austenitic islands in a proportion of 55% and 45% respectively. As a result of the fabrication process, the skin of the LDSS plates was cold worked to 200 μ m of depth of both sides of the normal direction (ND). This was easily estimated from microhardness measurements and microscopy techniques (TEM, ECCI and KAM). Therefore, the delivered material has in fact a "sandwich" structure. The bulk of the material is considered as the annealed part of the plates and the external surfaces as the cold worked layers. In other words, the delivered LDSS plates are formed of two different metallurgical states, for this reason we took advantage to separate the steel into two different materials: cold worked and annealed. A third metallurgical state was obtained by thermally aging the annealed LDSS at 475 °C for a short duration of 25 h only. Because the specimen for mechanical testing had a thickness higher than 200 µm, the specimens of the three metallurgical states investigated differ in their degree of homogeneity. The annealed and thermally aged specimens are considered as monolithic materials since the surface and the bulk have same characteristics. While for the called "cold worked specimens", they are considered as hybrid since 200 µm of thickness is cold worked and the rest of the specimen (300 μ m) form the bulk or the annealed part of the steel.

For the introduction of hydrogen, the cathodic charging was employed by using a solution of $0.5 \text{ M H}_2\text{SO}_4$ and $0.2 \text{ g/L As}_2\text{O}_3$. At first, the current density ($i_c = -10 \text{ mA/cm}^2$) and the charging time (5 h and 24 h) were determined in order to introduce hydrogen without provoking strong degradation of the material.

The depth of the material affected by the hydrogen penetration was estimated by performing tensile tests up to failure followed by fractographic analysis. It was found that the annealed material exhibited fully ductile fracture while the charged specimen presented a dual fracture

mode consisting of a brittle fracture at the surfaces of the specimen and a ductile fracture in the center of the specimen. The three metallurgical states showed a difference in the depth penetration of hydrogen in terms of the size of brittle zone which did not exceed the 100 μ m after 24 h of hydrogen charging. It turns out that all the hydrogen charged steels can be considered as sandwich materials because the core of each specimen remained unaffected by hydrogen after 5 h or 24 h of charging. Since the change in the metallurgical state of the LDSS affected the hydrogen depth, it was interesting to study the effect of hydrogen on the activity and the partition of plasticity of each phase in each case.

A low cycle fatigue test under controlled total strain was employed to acquire enough plastic deformation without resulting in a strong damage of the specimen as it could occur under monotonic loading, cyclic plasticity tests were preferred under total strain control. The fatigue tests conducted on each sample showed for the uncharged specimens, a hardening cyclic stress response for the first cycles followed by a softening behavior for the LDSS-Annealed and the LDSS-CW. While the aging treatment leads to a hardening cyclic response throughout the cycles. Once hydrogen is introduced into the material, the cyclic response in the three metallurgical states exhibited higher stress values with a quasi-stable behavior. Regarding the surface morphologies, for the uncharged specimens, a difference appeared in the fatigue slip marking in the ferrite phase where they developed straight slip lines in the thermally aged LDSS instead of curvilinear as in LDSS-Annealed and LDSS-CW. In the three metallurgical states, austenite was more sensitive to hydrogen addition, where an important plastic deformation activity has been pointed out. Indeed, ECCI images of the dislocations have shown that hydrogen promoted the nucleation of dislocation sources which at the same time resulted in interactions of a large number of emitted dislocations that affected their mobility.

Moreover, the increase in dislocations number and the reduction of slip bands spacing observed in the hydrogenated austenite of the three metallurgical states pointed out the shielding effect of hydrogen that related to HELP mechanism. But the increase of effective stresses values tends to suggest a reduction in dislocations mobility which is in contrast with HELP. Therefore, the results do not converge completely into HELP mechanism. Regarding the ferrite phase, 5 h of hydrogen charging was insufficient to harden ferrite (microhardness value remained the same before and after charging) or to affect the plastic deformation of ferrite in the annealed state. The ferrite in the annealed state or after 5 h of hydrogen charging exhibited a high degree of deformation as indicated by the developed slip bands. Increasing

CONCLUSIONS AND PERSPECTIVES

the hydrogen charging until 24 h showed a slight modification in the plastic deformation behavior of ferrite phase. On the other hand, the higher dislocation density in the cold worked material or the formation of "chromium clusters" in ferrite resulted from aging treatment contributed to the increase of the sensitivity of ferrite to hydrogen. In fact, the hydrogenated cold worked ferrite showed a restriction in their slip markings but the hardening effect of hydrogen on ferrite was clearly remarked from the increase of its microhardness. Hydrogen was also present in the thermally aged ferrite after 5 h of hydrogen charging and its hardening effect was revealed by the increase of microhardness value unlike the 5 h hydrogen charged annealed material.

Compared to the annealed sate, the higher dislocation density in cold worked ferrite enhanced the trapping of more hydrogen atoms as suggested by the absence of slip markings and the smaller brittle zone obtained after 5 h and 24 h of hydrogen charging. The thin layer of cold worked seemed to be beneficial for the material because its presence at the surface of an annealed steel could shield the bulk by preventing the penetration of hydrogen over long distances and therefore delayed the hydrogen embrittlement of the steel. Otherwise, the "chromium clusters" showed a strong hydrogen capture ability and prevented the plastic deformation of ferrite but the long hydrogen charging duration (24 h) of a fatigue specimen led to a sudden failure. Therefore, these trapping sites are too severe ferrite more sensitive to hydrogen embrittlement (HE) and cannot be considered as beneficial specially for the long hydrogen charging duration.

From our results, we can conclude that trying to find how hydrogen affects the dislocation mobility has to be approached in regards to the metallurgical environment and how this environment evolves. This can help to extend or adapt existing models of HE to the present situation. For instance, hydrogen can indeed increase the mobility of dislocations, but the latter being so mobile, they become at their turn an obstacle to displacement

Finally, the diffusion path of hydrogen showed a strong dependency on the metallurgical state of each phase which can be tortuous by creating new traps besides the pre-existing ones, interfaces and length of austenitic islands. In addition, the bi-constituent microstructure of LDSS complicates the understanding of the hydrogen permeability. The morphological texture of the DSS as well as the numerous interfaces seem to influence the hydrogen partition and penetration in the bulk of the material. Therefore, a first extension of the present work would be a study of the effect of orientation of austenitic islands on hydrogen penetration. Performing an electrochemical permeation by changing the hydrogen penetration side of LDSS S32304 from normal direction to the rolling direction would be helpful to clarify the effect of hydrogen on the complex textured morphology of the LDSS. Moreover, it could be interesting to perform a heat treatment on the LDSS by changing the volume fraction of each phase and further studying the permeability of hydrogen in the steel.

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Abstract

The particularity of duplex stainless steels (DSS) is the simultaneous presence of two different phases, ferrite and austenite, that offers an excellent combination of good corrosion resistance and high mechanical properties. In some applications where harsh environments are present e.g., hydrogen and high temperatures, DSS are prone to hydrogen embrittlement (HE) and 475°C embrittlement. The metallurgical differences of ferrite and austenite represent a real challenge for the understanding of hydrogen effect on their mechanical behavior towards the damage and fracture of the material. Thus, the present work aims to understand the effect of hydrogen in a lean duplex stainless steel at the microstructural scale by taking into consideration three different metallurgical states of the material: annealed, cold worked and thermally aged at 475°C. To achieve this goal, the propensity of hydrogen to diffuse into the bulk of the material in regards with the microstructure has been studied, then the accommodation of plastic deformation of each phase for each metallurgical state has been investigated. The depth of hydrogen penetration was assessed from tensile tests and fracture surfaces analyses by Scanning Electron Microscopy (SEM). For the study of hydrogen-plasticity interactions, cyclic loading has been supported in order to accumulate large plastic strain avoiding thus instability or cracking of the steel. The slip markings were investigated by Atomic Force Microscopy (AFM) and SEM. The dislocation structures were then deeply featured using Electron Channeling Contrast Image (ECCI). The brittle fracture surfaces of austenite and ferrite phases were clearly identified after 5 h of hydrogen cathodic charging. The depth of hydrogen penetration is strongly depended on the metallurgical state, the most important depth was obtained for the annealed LDSS. The plastic deformation activity of austenite became very intense in all the three metallurgical states after hydrogen addition. Hydrogen promoted the nucleation of dislocation sources which at the same time resulted in interactions of a large number of emitted dislocations that affected their mobility. The presence of hydrogen has restricted the plastic markings evolution of ferrite specially in the cold worked and thermally aged state due to the pinning effect of hydrogen on the dislocation cores. Ferrite became more sensitive to hydrogen in the aged material because of the presence of "chromium clusters" that acted as trapping sites for hydrogen.

The presence of a thin cold worked layer at the surface of the annealed LDSS appears to prevent the penetration of hydrogen over long distances in the bulk of the steel.

Keywords: AFM, Plastic deformation, Stainless steel, Fatigue slip marks

Résumé

La particularité des aciers inoxydables duplex (DSS) est la présence simultanée de deux phases différentes, la ferrite et l'austénite, qui offre une excellente combinaison d'une haute résistance à la corrosion et de bonnes propriétés mécaniques. Dans certaines applications et sous des conditions sévères comme la présence d'hydrogène et les hautes températures, les DSS sont exposés à la fragilisation par hydrogène (HE) et à la fragilisation par vieillissement à 475°C. Les différents états métallurgiques de la ferrite et de l'austénite constituent une véritable difficulté pour la compréhension de l'effet de l'hydrogène sur leur comportement mécanique en termes de rupture de l'acier. Le présent travail vise à comprendre l'effet de l'hydrogène sur le comportement d'un acier inoxydable lean duplex à l'échelle microstructurale en considérant trois états métallurgiques différents : recuit, écroui et vieilli à 475°C. Pour atteindre cet objectif, la propension de l'hydrogène à diffuser dans le matériau en fonction de sa microstructure a été étudiée, puis l'accommodation de la déformation plastique de chaque phase pour chaque état métallurgique. La profondeur de l'hydrogène a été déterminée à partir d'essais de traction et l'étude des faciès de rupture par Microscopie Électronique à Balayage (MEB). Concernant l'interaction hydrogène-plasticité, le matériau a été soumis à une sollicitation cyclique afin d'accumuler une déformation plastique importante dans le matériau sans induire une instabilité ou une fissuration de l'acier. Les marques de glissement ont été caractérisées par Microscopie à Force Atomique (AFM) et MEB, les structures de dislocations détectées en utilisant l'Imagerie de Contraste par Canalisation d'Électrons (ECCI). Les faciès fragiles de l'austénite et de la ferrite ont été clairement distingués après 5 heures de chargement cathodique en hydrogène. La taille de la zone fragile dépend fortement de l'état métallurgique du matériau, elle était plus importante pour l'acier avec un état recuit. Pour les trois états métallurgiques étudiés, une déformation plastique plus importante est observée au niveau de l'austénite après l'addition de l'hydrogène. La nucléation de nouvelles sources de dislocations provenant de la présence d'hydrogène semble favoriser l'interaction entre les dislocations émises qui peuvent à leur tour affecter la mobilité des dislocations. La présence d'hydrogène a limité la déformation plastique de la ferrite, en particulier pour les états écroui et vieilli à 475°C. L'effet de l'hydrogène peut en effet bloquer le mouvement des dislocations. La ferrite devient plus sensible à la fragilisation par l'hydrogène après vieillissement thermique par l'existence de clusters riches en Cr qui servent de piégeage à hydrogène. De plus, la présence d'une fine couche écrouie à la surface de l'acier recuit empêche la pénétration de l'hydrogène à longues distances dans la structure de celuici.

Mots clés : AFM, déformation plastique, Acier inoxydable, Lignes de glissement