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Hydrogen Effect on Duplex Stainless Steels at very High Strain Rates

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Abstract

Due to their attractive combination of high strength along with great ductility, duplex stainless steels (DSS) are often being used as pressure vessels or underwater pipelines. The use of DSS in services combined hydrogen and mechanical load can lead to hydrogen embrittlement. The susceptibility to hydrogen embrittlement is directly related to the interaction between defects (traps) and hydrogen. Hydrogen effects are being studied by a thermal desorption spectrometry (TDS) process. In this research we determine the mechanical properties of DSS with hydrogen at high strain rates. Hydrogen trapping and its effect on the mechanical properties are discussed in details.

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1. Introduction

The elastic and plastic properties of hydrogen charged duplex stainless steel (DSS) at high strain rate and high pressure are important for the understanding of their durability at applications combining hydrogen and mechanical load. Measurements of elastic plastic properties at high strain rate in stainless steel alloys can be achieved by dynamic loading [1]. In this paper we compare between the effect of high strain rate (10^5 s^{-1}) and low strain rate (10^1

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7 s^{-1}) in order to add another milestone to the hydrogen embrittlement failure model [2]. We study on low strain rates via tensile machine and on high strain rate via plate impact experiments by dynamic loading.

In this work, dynamic loading is reported for duplex stainless steel (DSS) which combines austenitic and ferritic (BCC, α) phases. The effect of hydrogen in DSS under quasi-static loading has been investigated elsewhere [3], [4], yet its effect under dynamic loading was not studied and was previously covered by us in 2014 [5], [6]. Comparison between strain rates at different levels provide insights to the details of hydrogen behaviour at different deformation levels, in order to relate dynamic to static data.

Hydrogen behaviour at different deformation levels was studied by thermal desorption spectrometry (TDS). The potential failure mechanism and hydrogen diffusion related to it will be discussed in details.

2. Experimental procedure

2.1. Material properties

In this work we used the lean duplex stainless steel (LDS), LDX 2101. The microstructure of LDS consists of equiaxed grains with an average grain size of about $20 \mu\text{m}$ as was describes by us in previous studies [7]–[9]. Its chemical composition is Fe—0.026C—4.9Mn—21.53Cr—1.53Ni—0.2Mo—0.22N—0.63Si—0.001S—0.025P wt%. The hydrogen charging condition was gas-phase hydrogen charging at $300 \text{ }^\circ\text{C}$ and 60 MPa pressure for 3 hr. This charging procedure created a homogenous hydrogen content of 54 wt ppm along the samples' bulk. The microstructure of the gas-phase hydrogen charged LDS, published in different works by us [7]–[9], revealed the appearance of needle shaped sigma (σ) phase with the Fe(CrMo) composition. This phase plays an important role in the hydrogen embrittlement model.

2.2. Dynamic experiments

Dynamic experiments at strain rate of $\sim 10^5 \text{ s}^{-1}$ and dynamic pressure of $\sim 0.5\text{--}2 \text{ GPa}$ were conducted using 6 m long gas gun. The impact was performed by accelerating an LDS or Al impactor towards an LDS target. The target's surface is being illuminated by a coherent 532 nm Nd-Yag. The scattered light from the surface is collimated by mirrors and lens and returned to the VISAR [10]. After impact the targets are softly caught by a special made soft catching cell and are taking to microstructural observation.

2.3. Thermal desorption spectrometry (TDS)

The characteristics of hydrogen desorption were investigated by means of thermal desorption spectrometry (TDS). This technique involves accurate measurement of the desorption rate of hydrogen atoms, as solute or trapped in the material, while heating the sample a non- isothermal heating at a known rate under UHV $\sim 10 \mu\text{pa}$. In this work, the samples were heated from room temperature (RT) to $500 \text{ }^\circ\text{C}$ at constant heating rates of $2 \text{ }^\circ\text{C}/\text{min}$, $4 \text{ }^\circ\text{C}/\text{min}$ and $6 \text{ }^\circ\text{C}/\text{min}$. The mass spectrometer was operated under the fast multiple mode detection; the measured intensity channel was set to 2 amu in order to detect hydrogen desorption. The working procedure, as described by Lee and Lee [11], allowed for the identification of different types of traps coexisting in the specimen.

3. Results and discussion

3.1. Deformation response

Tensile testing at strain rate of $\sim 10^{-7} \text{ s}^{-1}$ was performed at RT on gas-phase hydrogen charged and non-charged LDS. The results are presented in Table 1. As already showed in previously work of us [9] hydrogen caused an increment in yield strength. This increment was calculated to be 20% higher in the gas-phase hydrogen charged sample compared with the non-charged sample.

Table 1. Quasi-static experimental results for LDS with and without H.

Sample	$\sigma_y \pm 0.02$ [GPa]
w/o H, 10^{-7} s^{-1}	0.32
with H, 10^{-7} s^{-1}	0.40

Dynamic experiments at strain rate of $\sim 10^5 \text{ s}^{-1}$, Fig. 1, did not show any change between non-charged and hydrogen charged sample; the dynamic yield strength remained the same. Therefore, it can be said that only when hydrogen has enough time for diffusion, as in the case of lower strain rate experiments, solid solution hardening will occur. This hardening can be related to the pinning of dislocations by the attached solute atoms [2].

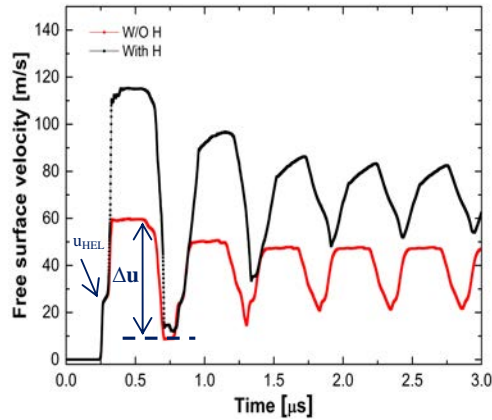


Fig. 1. Simulations results of the free surface velocity of LDS with and without hydrogen at dynamic pressures 1-2 GPa.

The deformation behavior at high strain rate was investigated by calculating the elastic-plastic transition also known as Hugoniot elastic limit (HEL) [1]. The dynamic yield stress under uniaxial strain loading was extracted from HEL, according to the follow relation [12]:

$$\sigma_{HEL} = \frac{\rho_0 c_l U_{HEL}}{2} \tag{1}$$

$$\sigma_y = \frac{(1 - 2\nu)\sigma_{HEL}}{(1 - \nu)} \tag{2}$$

where c_l is the longitudinal sound velocity, ρ_0 is the initial density, u_{HEL} is the free surface velocity at the precursor front and ν is the Poisson's ratio which was taken as 0.33.

In all the experiments the presence of hydrogen did not affect the HEL, Fig. 1. These results are summarized in Table 2.

Table 2. Dynamic experimental results for LDS with and without H.

Sample	Dynamic pressure [GPa]	$\sigma_{HEL} \pm 0.05$ [GPa]	$\sigma_y \pm 0.02$ [GPa]
w/o H	1	0.75	0.38
with H	2	0.75	0.38

In order to better understand these findings the impacted targets were softly caught and collected for metallurgical analysis, Fig. 2. The micrographs in Fig. 2 indicate on two insights: the first relates to spall incomplete,

meaning that the cracks did not coalesce into a whole rupture. The second relates to the idea that hydrogen seems to propagate crack motion. This finding clearly presents the hydrogen embrittlement phenomenon and indicates on the same behaviour of hydrogen crack propagation at low and high strain rate (10^{-7} s^{-1} and 10^5 s^{-1} at $\sim 0.5 \text{ GPa}$).

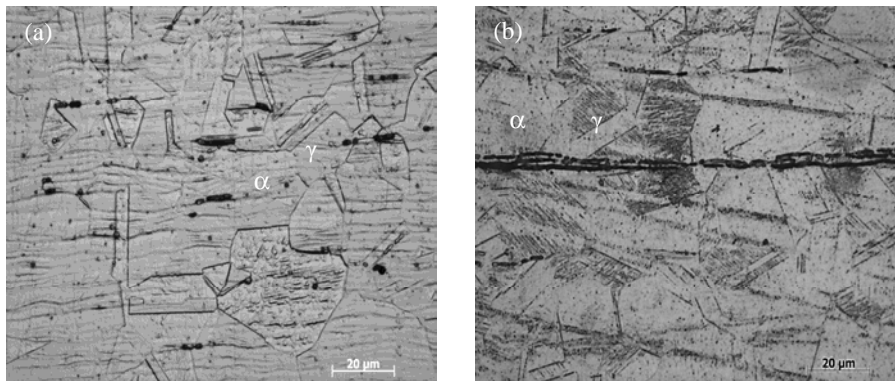


Fig. 2. OM analysis of the impacted cross-section targets: (a) non-charged LDS and (b) gas-phase hydrogen charged LDS.

3.2. Hydrogen trapping mechanism

Hydrogen trapping mechanism of gas-phase hydrogen charged LDS samples non-deformed and deformed were studied by means of TDS analysis. The deformed samples include gas-phase hydrogen charged LDS after (10^{-7} s^{-1}) tensile loading (quasi-static loaded) and after dynamic (10^5 s^{-1}) loading (dynamic loaded). By applying Lee and Lee's model [11], the activation energy for hydrogen release (E_a) may be calculated from the slope of $\ln(\dot{\varphi} / T_c^2)$ versus $1/T_c$, where T_c is the critical temperature for desorption and $\dot{\varphi}$ is the heating rate. According to their model an E_a equal to or higher than 60 kJ/mol will be ascribed as an irreversible trap, else it will be ascribed as a reversible trap. This notion is highly important since only diffusible hydrogen through lattice sites or hydrogen residing at traps with the lowest activation energy contributes to a metal's embrittlement [13]. In order to evaluate the trap's activation energies, three different heating rates in the range of 2-6 °C/min were applied to the samples. Fig. 3 presents TDS spectra of different gas-phase hydrogenated LDS samples non loaded, quasi-static loaded and dynamic loaded; the summary of TDS' results are presented in Table 3.

Table 3. Calculated activation energies for: non-loaded, quasi-static loaded and dynamic loaded.

Non-loaded		Quasi-static loaded		Dynamic loaded	
Temp ± 1 [°c]	Ea ± 0.5 [kJ/mol]	Temp ± 1 [°c]	Ea ± 0.5 [kJ/mol]	Temp ± 1 [°c]	Ea ± 0.5 [kJ/mol]
75-90	20.0	65-92	19.0	67-107	20.0
143-160	39.0	117-140	22.0	122-160	30.0
300-340	67.0	210-300	40.0	314-353	72.0

The great differences in activation energies are seen in the quasi-static loaded sample, Fig. 3 b and Table 3. These values are classified as reversible trapping sites, since they are lower than 60 kJ/mol. The reason for the great changes between quasi-static loaded and dynamic loaded are due to hydrogen diffusion time and distance which was longer in the quasi-static loaded sample. Diffusion's calculations performed by us in other work [9] predicted 4 times higher diffusion distance for hydrogen in the quasi-static loaded sample compared with dynamic loaded. The desorption activation energy of the non-loaded sample and dynamic loaded presented one value which is higher than 60 kJ/mol. This value is 50% higher than the quasi-static loaded sample and was ascribed as irreversible trapping site. The irreversible trapping sites were ascribed to σ phase formation and their wide range (67-72 kJ/mol) were ascribed to σ 's phase density and hydrogen content in it. At this dynamic pressure $\sim 0.5 \text{ GPa}$ the dislocation velocity was not fast enough to break-away from hydrogen [2], and hydrogen was still able to escape. This occurrence

enabled hydrogen to escape from deeper potential trapping site to less deep. This explanation is supported by the microstructural observations after dynamic experiments, Fig. 2b [9], which showed massive cracking for dynamic loaded sample compared with non-loaded sample, Fig 2a. These results support hydrogen embrittlement at high strain rate (10^{-5} s^{-1} at 0.5 GPa). The dynamic loaded hydrogenated sample showed intense cracking due to hydrogen's ability to escape from trapping site and promote cracking. This phenomenon is supported by other works which confirm that the susceptibility to hydrogen will depend on the competition between reversible and irreversible traps [13].

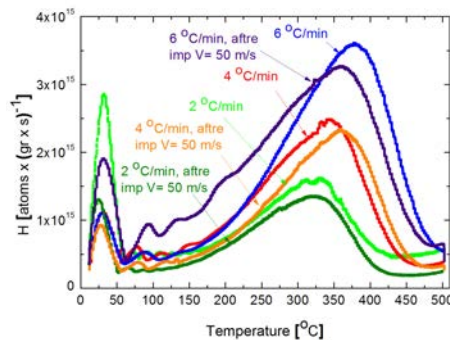


Fig. 3. Hydrogen desorption rate as a function of temperature, TDS spectra of non-loaded and dynamic loaded.

4. Summary and conclusions

This study examines the effect of low and high strain rates (10^{-7} s^{-1} and 10^5 s^{-1} , respectively) on hydrogen charged and non-charged LDS. Quasi-static experiments showed an increment of $\sim 20\%$ in yield strength which was related to the experiment deformation rate; higher deformation rate will not allow for enough time for hydrogen diffusion. This statement is well pronounced at dynamic experiments which did not show any effect of hydrogen on dynamic yield strength, σ_y .

The hydrogen trapping energies of the quasi-static loaded ($\sim 10^{-7} \text{ s}^{-1}$) sample were $\sim 40\%$ lower than the non-loaded LDS sample and $\sim 45\%$ lower than the dynamic loaded sample. At quasi-static loading, hydrogen had enough time to escape from the irreversible trapping site- σ phase, created during gas-phase hydrogen charging. The differences between the activations energies of the rest of the samples were belonged to σ phase density and deformation response which is responsible for hydrogen trapping. The greater deformation which was formed at dynamic experiments caused hydrogen to be trapped deeper in trapping sites (high energy trapping sites). Hydrogen embrittlement model is also seen and valid in the dynamic loaded sample and indicates on the same behaviour of hydrogen at low and high strain rate (10^{-7} s^{-1} and 10^5 s^{-1} at ~ 0.5 GPa).

Acknowledgements

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