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Hydrogen embrittlement in a 2101 lean Duplex Stainless Steel

Francesco Iacoviello*, Vittorio Di Cocco, Costanzo Bellini, Luca Sorrentino

Università di Cassino e del Lazio Meridionale, via G. Di Biasio 43, 03043 Cassino (FR), Italy

Abstract

Duplex Stainless Steels (DSSs) are an attractive class of materials characterized by a strong corrosion resistance in many aggressive environments. Thanks to the high mechanical performances, DSSs are widely used for many applications in petrochemical industry, chemical and nuclear plants, marine environment, desalination etc.

Among the DSSs critical aspects concerning the embrittlement process, it is possible to remember the steel sensitization and the hydrogen embrittlement.

The sensitization of the DSSs is due to the peculiar chemical composition of these grades which, at high temperature, are susceptible to carbide, nitrides and second phases precipitation processes mainly at grains boundary and in the ferritic grains. The hydrogen embrittlement process is strongly influenced by the duplex (austenitic-ferritic) microstructure and by the loading conditions.

In this work a rolled lean ferritic-austenitic DSS (2101) has been investigated in order to analyze the hydrogen embrittlement mechanisms by means of slow strain rate tensile tests, considering the steel after different heat treatments. The damaging micromechanisms have been investigated by means of the scanning electron microscope observations on the fracture surfaces.

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Keywords: Duplex Stainless Steel; Hydrogen embrittlement; Slow strain rate test.

1. Introduction

Duplex stainless steels (DSSs) offer a really interesting combination of high strength and really good resistance to chloride stress corrosion cracking (Gunn, 1997) with reasonable costs, especially if compared to the austenitic grades.

* Corresponding author. Tel.: +39-07762993681; fax: +39-07762993781.
E-mail address: iacoviello@unicas.it

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For these reasons, DSSs are widely used in many fields, ranging from pulp and paper industry to desalination plants, from nuclear industry to food industry applications, from storage tanks to bridges [Charles (2008) and (2015)].

Nomenclature

DSS	Duplex Stainless Steel
HE	Hydrogen Embrittlement
PREN	Pitting Resistance Equivalent Number (= %Cr + 3.3x(%Mo + 0.5x%W) + 16x%N)

Considering their pitting resistance, and using the PREN, different DDSs grades can be classified as follows:

- "lean" duplex grades (PREN ≤ 35): these alloys contain less alloying elements and are mainly used in architectural applications (e.g., bridges), when good, but not extreme, mechanical properties are necessary and the environment is not a critical parameter (e.g., atmospheric corrosion). Among these grades, it is possible to remember the 2101LDX grade (S32101) with 5% of Mn.
- "standard" (35<PREN≤40): the most used one is the DSS 2205 that is characterized by 22% Cr, 3% Mo, 5-6 % Ni content, with a YS value that is double that offered by the standard austenitic grades (e.g. AISI 304). This grade is also characterized by a really good resistance to general and localized corrosion attack in several environments (e.g., stress corrosion, crevice, pitting).
- "super" DSSs (40<PREN≤45): these grades are characterized by an improved localized corrosion resistance (pitting) and by higher Ni and Cr contents (Cr content exceeds 25%). A typical Super DSS is 2507 (S32750).
- "hyper" DSSs (PREN ≥ 45): recently optimized for extreme environments, among these grades can be classified SAF 3207 HD (UNS S33207) and SAF 2707 HD (UNS S32707).

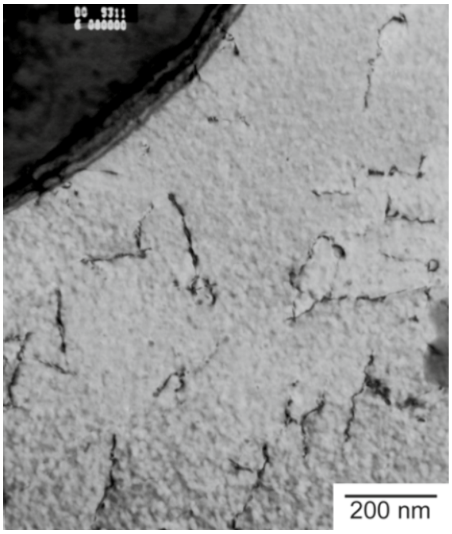

Fig. 1: 2101 DSS TEM analysis. Dislocations pinned by G phase particles in ferritic grain.

Although DSSs offer a really interesting wide range of mechanical properties and general and localized corrosion resistance, they are prone to embrittle corresponding to different temperature ranges, with a kinetic that strongly depends on the chemical composition, with the higher alloyed grades that are characterized by the shorter incubation times. Three different critical temperatures ranges are usually identified:

- Between 300 and 600°C. This temperature range is characterized by the spinodal decomposition of ferrite into Cr-poor α and Cr-rich α' domains. Other precipitation processes would also occur. Among them, the main one is the Ni, Si, Mo-rich G phase precipitation (Guttmann, 1991). These particles are very small (usually from 1 to 10 nm, occasionally up to 50 nm, Fig. 1) and they precipitate, more or less uniformly, within the ferrite grains, depending on the steel chemical composition and their composition depends not only on the steel composition, but also on the ageing conditions. For instance, the overall concentration in G-forming elements increases from 40 to 60% if tempered at 350°C respectively for 1000 and 30000 hours (Guttmann, 1991 and Iacoviello, 2005). This critical temperature range determines the long-time service temperature, usually lower than 350°C (e.g., inlet temperature in some duplex stainless steels heat exchangers).

- Between 600 and 1050°C. This critical temperature range is characterized by the formation, mainly in ferritic grains at the α/α and α/γ grain boundaries, of a variety of secondary phases (e.g., σ phase), carbides (M_7C_3, $M_{23}C_6$) and nitrides (Cr_2N, π) with incubation times that are strongly affected by the chemical composition (e.g., Badi et al. 2008).
- Above 1050°C. Any temperature increase above 1050°C implies a ferrite volume fraction increase and a decrease in the partition coefficients of the alloying elements (e.g., Tehovnik et al. 2011).

In this work, the susceptibility to the hydrogen embrittlement of a lean DSS 2101 has been investigated, considering the heat treatments influence. Hydrogen embrittlement in steels is a complex phenomenon that involves mechanisms like hydrogen adsorption, absorption and desorption, diffusion, solubility and trapping (e.g., Iacoviello, 1998). All these phenomena are influenced by the steels microstructure, with the possibility of the presence of hydrogen diffusion short circuits (like surface, grains boundaries, mobile dislocations or phases with high hydrogen diffusivity) and of traps (low solubility phases, intermetallic phases etc) that can strongly influence the steel behavior and its mechanical properties. Focusing 2205 DSS (Iacoviello, 1997), it is evident that the microstructural transformations, obtained for the temperature ranges described above, are able to influence both the HE mechanisms and the hydrogen physical behavior, with evident trapping phenomena corresponding both to the lowest critical temperature range (475°C embrittlement) and to the highest critical temperature range (where the secondary phase, carbides and nitrides precipitation is obtained). An example of this influence is shown in Fig. 2, where the hydrogen quantity in a hydrogen charged 2205 DSS (after different tempering treatments for 3 hours) is measured by means of outgassing procedure at 600°C under vacuum.

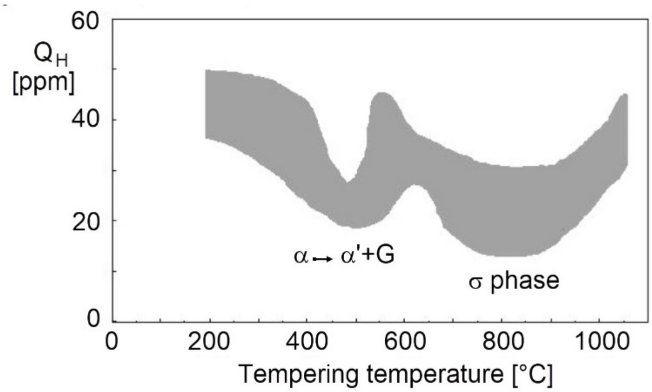

Fig. 2. 2205 DSS after different tempering heat treatments (3 hours). Hydrogen quantity measured by means of an outgassing procedure at 600°C under vacuum, Iacoviello 1997.

Considering all the physical, chemical, metallurgical and mechanical parameters that influence the hydrogen charging, diffusion, solubility and trapping in metals, many hydrogen embrittlement models are available, but no one is applicable to all the possible conditions. Among them, it is possible to remember (e.g., Barrera et al, 2018):

a) Models based on the hydrogen internal pressure, connected to the molecular hydrogen recombination corresponding to microvoids or interfaces.

b) Models based on the surface energy decreasing, due to the adsorbed hydrogen presence, with a consequent embrittlement increasing.

c) Models based on the cohesion decreasing: they propose that hydrogen decreases the interatomic cohesion at the crack tip (HID or HEDE, Hydrogen Induced Decohesion).

d) Models based on the interaction of hydrogen and plastic deformation: these models consider the complex interactions between hydrogen and dislocations during the plastic deformation. Considering ferrous alloys, two different behaviors are experimentally described:

- Hydrogen presence implies a decrease of the plasticity;
- Hydrogen-enhanced local plasticity (HELP).

e) Models based on the hydrides precipitation or fragile phases formation (e.g. formation of α’, cc, or ε, hc, martensitic phases in metastable austenitic stainless steels that could be hydrogen induced, HIPT, hydrogen-induced phase transformation).

2. Investigated alloy and experimental procedures

In this work, a rolled “lean” DSS 2101 has been investigated (chemical composition and tensile properties are shown in Tab. 1; microstructure is shown in Fig. 3).

Table 1. Investigated 2101 DSS chemical composition (wt%) and tensile properties.

21 Cr 1 Ni “lean” DSS; EN 1.4162.					
C	Mn	Cr	Ni	Mo	N
0.03	5.00	21.5	1.5	0.3	0.22
YS [MPa]	UTS [MPa]	A%			
483	700	38			

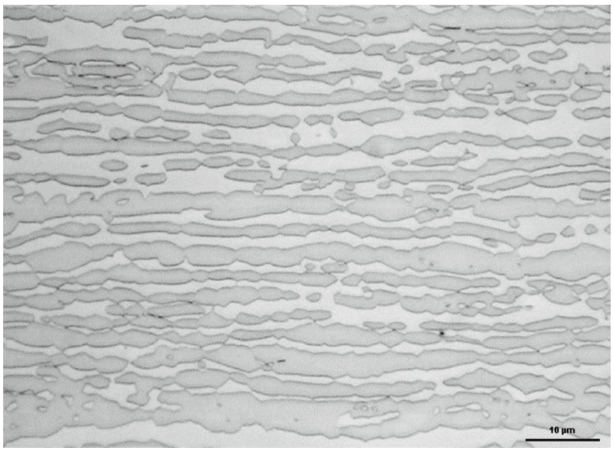

Fig. 3. Investigated 2101 DSS: microstructure (electrochemical etching NaOH 17.5%-15V-30''). Ferrite (darker grains) and austenite.

Tempering heat treatments have been performed on dog bone specimens (Fig. 4) between 350 and 800°C for 3 hours (in Argon). Some additional heat treatments have been performed with longer treatment times. In Fig. 5 and 6 it is possible to observe the microstructure modification after 1000 h at 475°C and after 100 h at 800°C, respectively.

Hydrogen charging has been performed in a 0.5M H_2SO_4 + 0.1M KSCN aqueous solution (- 700mV /SCE for 24 hours) and tensile tests have been performed under slow strain rate conditions, with a strain rate of 10^{-6} s^{-1} (three tests for each testing conditions).

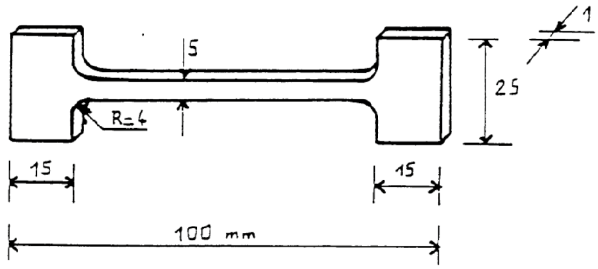

Fig. 4. Tensile test specimen.

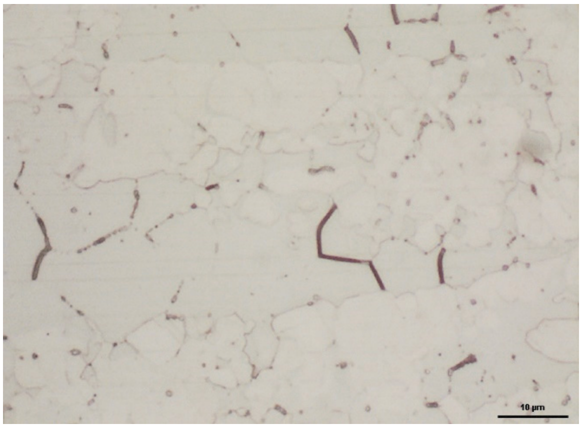

Fig.5. Investigated 2101 DSS (after 1000h at 475°C): microstructure (electrochemical etching oxalic acid aqueous solution, 6V-12"). G phase precipitation at ferritic grains boundaries implies susceptibility to a localized attack.

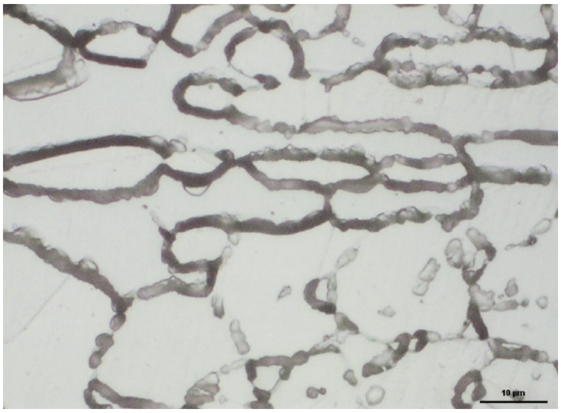

Fig.6. Investigated 2101 DSS (after 10h at 800°C): microstructure (electrochemical etching oxalic acid aqueous solution, 6V-60"). Carbides precipitation at α/α and α/γ grains boundaries.

3. Experimental results and discussion

Focusing on the influence of the heat treatment and of the hydrogen charging on the steel ductility, experimental results are summarized in Fig. 7 (mean values; results are characterized by a high repeatability). For all the investigated tempering temperature, it is possible to underline that hydrogen is quite evident. Considering a HE parameter defined as:

$$HE = \frac{\varepsilon_{withoutH} - \varepsilon_{withH}}{\varepsilon_{withoutH}}$$

it is possible to show the heat treatment conditions that correspond to the most developed hydrogen embrittlement phenomenon (Fig. 8). According to the experimental results, the lower HE values are obtained in the as-rolled conditions, and for the tempering temperature of 450°C and 550°C (Fig. 8, red arrows). The Light Optical Microscope (LOM) macroscopical analysis of the lateral surfaces of the hydrogen charged specimens allows identifying the presence of many secondary cracks (Fig. 9). These secondary cracks are not present in the uncharged specimens, for all the investigated heat treatments.

Lower HE values correspond to a reduced evidence of the HE on the fracture surface morphology. Instead, the Scanning Electron Microscope (SEM) analysis of the fracture surface of specimens with higher HE values shows the presence of secondary intergranular cracks (e.g., Fig. 10, heat treatment temperature = 600°C).

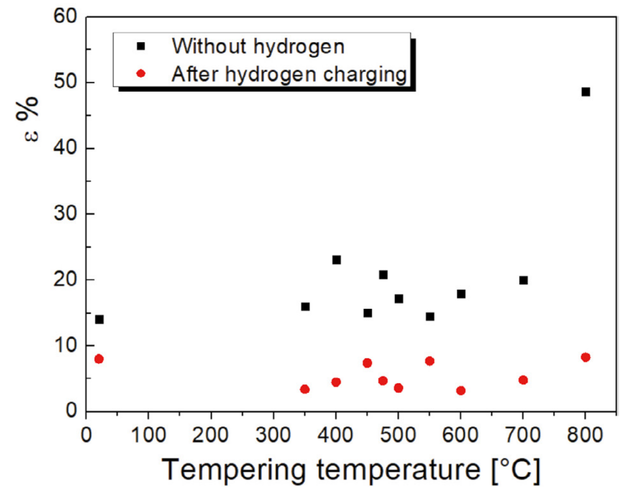

Fig. 7. 2101 DSS. Microstructure and hydrogen influence on the steel ductility.

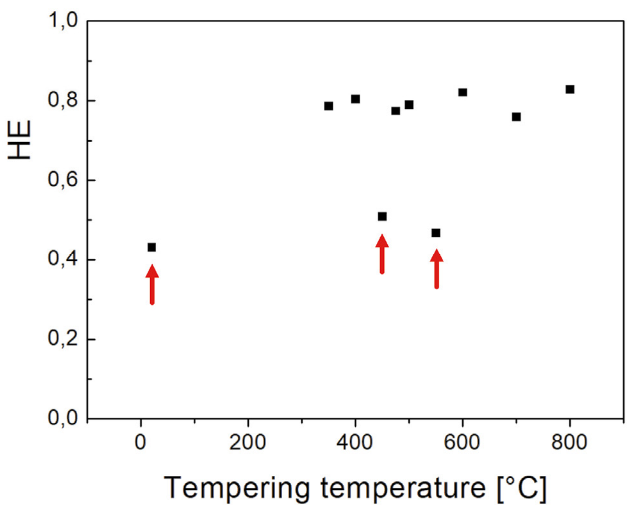

Fig. 8. 2101 DSS. HE parameter evolution with the tempering temperature.

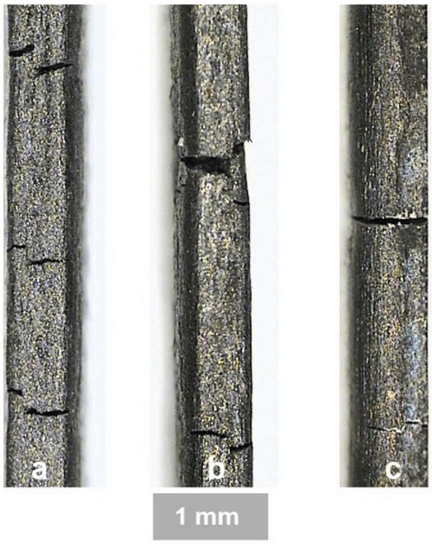

Fig. 9. Light Optical Microscope observation of the hydrogen charged 2101 DSS (three different heat treatments: a) rolled; b) 450°C 3-h; c) 600°C-3h).

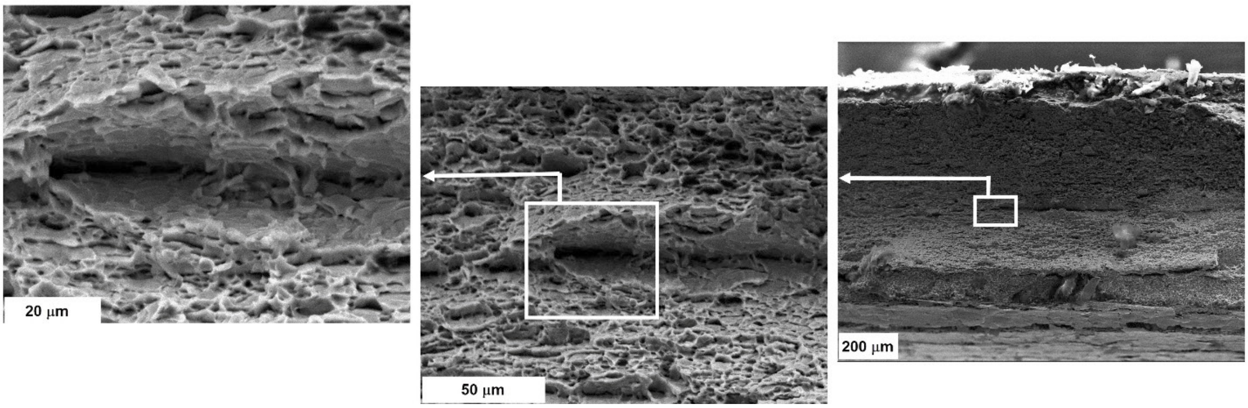

Fig. 10. 2101 DSS (heat treatment: 600°C-3 h; hydrogen charged). SEM fracture surface analysis. Different magnifications.

Due to its peculiar chemical composition, 2101 DSS is characterized by different critical temperature ranges if compared to the standard or super DSS (Outokumpo datasheet, 2018), especially corresponding to the highest critical range, with a "nose" at about 700°C instead of about 800-850°C. Although the observed macroscopical and microscopical damaging mechanisms (cracks observed on the specimens lateral surfaces and secondary intergranular cracks observed on the fracture surfaces, respectively) on the hydrogen charged specimens seem to be not influenced by the microstructure modifications, the different secondary phases, carbides, nitrides and the ferrite decomposition in σ phase and austenite influence the ferritic grains mechanical properties and their susceptibility to be hydrogen embrittled.

Conclusions

Duplex Stainless Steels are prone to be hydrogen embrittled in many different environments and electrochemical conditions. In this work, the susceptibility of a "lean" 2101 duplex stainless steel to be hydrogen embrittled has been investigated considering the influence of the different secondary phases, carbides and nitrides that can be obtained after a tempering heat temperature (between 350°C and 800°C). According to the experimental results, the following conclusions can be summarized:

- 2101 DSS is prone to be hydrogen embrittled for all the investigated tempering temperatures
- Although the macroscopical and microscopical damaging mechanisms are always the same for all the investigated tempering temperatures, the quantification of the HE by means of a parameter based on the ductility shows some tempering conditions with a lower hydrogen embrittlement
- For all the conditions with the highest embrittlement, the HE parameter based on the ductility seems to be roughly constant and does not seem to be influenced by the microstructure modifications due to the tempering heat treatment.

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