Hydrogen trapping mechanism of different duplex stainless steels alloys

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ABSTRACT

Characteristics properties of duplex stainless steels (DSS) include excellent resistance to stress corrosion cracking, high strength and good weldability. The success of the duplex stainless steels in the industry has led to the development of an entire family of duplex alloys, such as the lean duplex stainless steel (LDS) and the super duplex stainless steel (SDSS), which vary in corrosion resistance depending on their alloy content. In this research we examine the austenite (γ) phase's stability (S) of each steel in the presence of hydrogen and its effect on hydrogen trapping mechanisms. It was found that the dominant phase transformation, as a result of hydrogen permeation in LDS, is $\gamma \rightarrow \varepsilon_H \rightarrow \alpha'$. After long aging times the ε_H-martensite lattice parameters continuously approached those of free ε-martensite or α'-martensite, which were formed by plastic deformation. It was shown using different methods that hydrogenated lean duplex stainless steel demonstrated higher amount of ε and α' martensite compared with those of super duplex stainless steel, due to the dominant phase transformation of $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ in the former.

A linear model of Lee and Lee was applied to calculate the trap activation energies of lean duplex and super duplex stainless steels. It was found that the lean duplex stainless steel presents $\sim$30% higher activation energy's values than the super duplex stainless steel, due to a less steady γ phase, which will eventually cause an increase in hydrogen diffusion. The relation between the microstructure and the hydrogen trapping of lean duplex stainless steel and super duplex stainless steel in the presence of hydrogen is discussed in detail.

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1. Introduction

The ferritic–austenitic duplex stainless steels (DSS) combining good strength with corrosion properties are under increasing development; these grades include the lean duplex stainless steel (LDS) and the super duplex stainless steel (SDSS). The LDS is a recently developed low alloyed duplex stainless steel. LDS alloys are being used in many architectural applications due to their high strength, good corrosion resistance and lower cost [1–8]. The LDS microstructure is very similar to that of the SDSS; it has a mixed crystal structure of ferrite (BCC, α) and austenite (FCC, γ), but its uniqueness is in the different quantity of the alloying elements, granting it better mechanical properties with a reduced cost. These alloys have the advantage of lower nickel content than austenitic alloys, while providing similar or better corrosion resistance in many environments. Therefore, they are candidates for undersea oil and gas applications such as flow lines [7–9]. The influence of hydrogen on the mechanical properties, known as hydrogen assisted cracking (HAC), and on the microstructure of DSS has been

significant for many years [1–3]; since only a small amount of hydrogen is enough to cause a serious degradation in the mechanical properties. Hydrogen has different effects on the α and γ phases. In addition, it is known that the stability of the γ phase, which can have a significant effect on the material's properties, is affected both by the steel composition and by the presence of hydrogen in solid solution [10–14]. In order to initiate a crack, a critical hydrogen concentration must be reached at potential crack sites. Since trapping affects the metal diffusivity, the crack initiation is dependent on the trap characteristics. It is known from earlier publications [15–17] that irreversible traps act only as sinks, however reversible traps, which can act both as sinks or sources, will have a major influence on the material's susceptibility to HAC. Since γ stability can affect both phase transition and hydrogen's diffusion, it will have a major effect on the steel's HAC characteristics and on the trap's activation energy for hydrogen. A 'good' trapping site for hydrogen has to possess an optimum combination of high binding energy to hydrogen and hydrogen capturing kinetics due to the dynamic nature of temperature and stress involved in the operated steel [17]. Therefore, the stability of the γ phase and the activation energy of traps will be measured and compared for the studied steels. In this research, the hydrogen

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trapping mechanism and hydrogen's influence on the microstructure of super duplex stainless steel, SAF 2507, and lean duplex stainless steel, LDX 2101, were examined and compared. This comparison will allow for a great understanding, if for example, a cost saving steel combining the same crystal structure of DSS will guarantee better hydrogen resistance.

2. Experimental procedure

2.1. Materials

The chemical compositions of super duplex stainless steel, SAF 2507, and lean duplex stainless steel, LDX 2101, are presented in Table 1. These steels were received in the fully annealed condition, as a 1 mm thick plate. In this study, the hydrogenation technique was electrochemical (cathodic) charging. The charging was performed at room temperature (RT) in a 0.5 N H_2SO_4 (sulfuric acid) water solution and 0.25 g l^{-1} of $NaAsO_2$ (sodium arsenide) with a constant current density of 50 mA cm^{-2} for different charging times. 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 ~10 μpa. In this work, the samples were heated from RT to 450 °C at constant heating rates of 2, 4 and 6 °C/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 elsewhere [18], allowed for the identification of different types of traps coexisting in the specimen. The total concentration of hydrogen that was absorbed into the samples and the amount of retained hydrogen after thermal desorption, were measured by vacuum extraction, using LECO RH-404 hydrogen determinator. The microstructure, phase composition and lattice parameter of the studied stainless steel were examined both – before and after hydrogenation by means of X-ray diffractometer (XRD), with Cu Kα radiation (λ = 1.54 Å) in the range of 30 < 2θ < 90. The charged specimens were aged at RT and examined at different time intervals in order to observe the different phase transformations during hydrogen desorption.

3. Results and discussion

3.1. Hydrogen-induced phase transformation in lean duplex stainless steel (LDS)

In order to examine microstructural changes of hydrogen on LDS, XRD analysis was performed on charged samples for 72 h and aged for 1 month at RT. According to the XRD results in Fig. 1, when compared to the non-charged LDS, hydrogen cathodic charging resulted in a number of significant structural changes as the hydrogen diffused out of the specimen. Immediately after the hydrogenation process, the γ phase reflections exhibited significant broadening (smaller grain size) and a decrease in intensity; they were shifted to smaller 2θ values, meaning a larger lattice parameter. Simultaneously, the appearance of new phases including the rich hydrogen ε_H-martensite with hcp crystal structure and the γ*, an additional fcc phase with a 5% higher lattice parameter, are seen. The appearance of those new phases was seen in previous research on duplex stainless steel [3,19–21] and austenitic stainless steel [10,12,13,22]. Previously published works have identified the γ* phase as a hydrogen-enriched austenitic phase, which is derived from the initial γ-phase [10,12,23]. After 1 month aging at RT, the γ* reflections decrease and those of the γ phase increase in intensity and decreased in breadth; the γ line positions shifted to higher 2θ values, indicating a recovery in lattice expansion (decreasing lattice parameter compared with the as received sample), as shown in Fig. 1. During aging of the hydrogenated
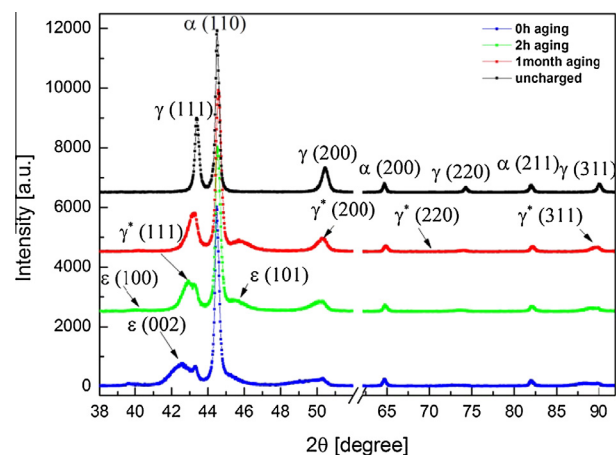

Fig. 1. XRD pattern of the uncharged and hydrogenated LDS for 72 h and aged for different time intervals.

specimens, the ε-martensite becomes stable, while the α phase reflections become broadened. This change can be explained by the ε → γ → α' phase's transition [3,10,12], as described in the present article. This means that part of the ε-martensite phase changes into α'-martensite with body centered tetragonal structure (BCT).

It is already shown from previous publications that the ε_H-martensite formation is due to compressive stresses at the surface, which happens as a result of hydrogen absorption. The formation of the α'-martensite is due to tensile stresses at the surface which occurs as a direct result of hydrogen desorption during the aging process [12,23]. These observations are supported by the OM micrographs showing the lath martensite appearance (Fig. 2b), indicating the stability of ε and α' martensite phases within LDS matrix after a long time at RT. These observations are compared with the non-charged LDS (Fig. 2a), showing the appearance of only two phases, α and γ. Moreover, the OM observation reveals the changes in α phase showing significant grain refinement (a decrease of 10 μm to ~5 μm).

3.2. Hydrogen-induced phase transformation in super duplex stainless steel (SDSS)

In order to compare the microstructural changes of hydrogen on LDS, XRD analysis was performed on SDSS with the same charging condition of LDS (72 h charging and aging for 1 month at RT). The comparison of the XRD spectra, Figs. 1 and 3, showed that the γ* and the ε_H-martensite phase's reflections in LDS demonstrate higher intensity (~80% higher), meaning greater stability of these phases in LDS. In order to estimate the ε-martensite quantities after 1 month aging in the studied steels, we conducted refinement of the XRD pattern using Rietveld method. Rietveld method is one of the most popular approaches to quantitative phase analysis in XRD, for it provides information about the quantity of the crystalline by a simple Gaussian model for the different intensities [24,25]. The quantitative analysis is based on the fact that intensity of different peaks on XRD depends on concentration of this phase in the studied material. According to the Rietveld method, the

Table 1
Chemical composition of the studied LDS and SDSS (wt%).

Sample	C	S	P	Mn	Si	Ni	Cr	Mo	N	Cu
LDX 2101	0.026	0.001	0.025	4.9	0.63	1.53	21.53	0.2	0.22	0.28
SAF 2507	0.025	0.004	0.022	0.411	0.288	6.745	24.012	4.63	0.3	0.072