Influence of microstructure in the hydrogen permeation in martensitic-ferritic stainless steel

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ABSTRACT

Martensitic-ferritic stainless steels (MFSS) have been proposed to fulfill an existing gap in material selection, caused by the limited corrosion performance of supermartensitic stainless steels and high costs of duplex stainless steels. This kind of steel basically presents a martensitic-ferritic matrix and, depending on heat treatment schedule, small amounts of retained austenite (γ_{ret}), chi-phase (χ), carbides and other deleterious phases can form. Since these microstructure features may affect corrosion behavior in different ways, the influence on hydrogen diffusion in a MFSS with different content of retained austenite (γ_{ret}) and chi-phase (χ) was investigated. Samples were submitted to electrochemical hydrogen permeation and thermal desorption spectroscopy (TDS) techniques. As a result, microstructures have shown different behaviors on hydrogen diffusion. The lower hydrogen apparent diffusion coefficient (D_{app}) was obtained for the sample called retained austenite (RA) with 7% of retained austenite, 20% of ferrite and 73% of martensite. The results of TDS showed that retained austenite plays a role as irreversible hydrogen trapping site.

Introduction

Metallic alloys which are used in oil and gas industry should be inspected and monitored, due the presence of H_2S which may cause premature failure of the equipment, because hydrogen entry in the steel. The steel exposure in the low pH and high H_2S concentration environments can absorb the atomic hydrogen produced by the cathodic reaction from H_2S and penetrate the metallic structure, promoting the Hydrogen Embrittlement (HE) phenomenon [1]. It is important to study the susceptibility of the material to the HE, thus, the materials for most oil and gas applications should be designed to be resistant to HE. For environments containing CO_2, stainless steels are an option widely used because besides having satisfactory mechanical properties they have higher general

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Nomenclature

MFSS	martensitic ferritic stainless steel
γ_{ret}	retained austenite
γ	austenite
χ	chi-phase
δ	ferrite
σ	standard deviation
M	martensite
D_{app}	apparent hydrogen diffusion coefficient
D_{appth}	theoretical apparent hydrogen diffusion coefficient
D_{appexp}	experimental apparent hydrogen diffusion coefficient
S_{app}	apparent hydrogen solubility
RA	retained austenite sample
Ea	activation energy
J_{∞}	maximum flux

corrosion resistance. Among them, supermartensitic stainless steels have been selected when slight amounts of sulfides are present and, consequently, resistance to HE is required.

Prior to understanding the problem of HE in stainless steels, it is important to assess how the transport of hydrogen takes place, how the diffusion is affected by the different microstructures typically found in this class of material and how hydrogen can travel using different paths inside the material according to the existing phases.

Defects in the steel lattice are traps for hydrogen atoms, being usually distinguished between reversible and irreversible trap sites which are determined by its activation energy (Ea). According to Pressouyre [2,3] if trapping energy exceeds 77 kJ mol^{-1} (0.79 eV), the trap is considered irreversible, which means the trap can absorb hydrogen until it becomes saturated and release it at a higher temperature. However, if the trapping energy is lower than 60 kJ mol^{-1} (0.62 eV), the trap is reversible, being able to release hydrogen at lower temperatures. Previous studies have shown that hydrogen may be trapped on dislocations, microvoids, interfaces between inclusions, particles, grain boundaries (e.g. segregation) and precipitates (e.g. particles of TiC) [2—5]. Szost et al. [6] report several types of reversible and irreversible traps, such as retained austenite which is irreversible in dual phase steel, and reversible in the high carbon steel.

The retained austenite which has a face-centered cubic crystal structure (fcc) may influence the hydrogen cracking resistance of the steel because of its ability to act as a hydrogen trap due to its low diffusivity. In general, the steel which presents this phase shows a lower diffusion coefficient and higher solubility based on its close packed lattice. In contrast, the ferritic phase which has a body-centered cubic crystal structure (bcc) enables a high diffusion rate and low solubility due to its open lattice structure. Martensite which has a body-centered tetragonal crystal structure (bct) is closer packed than bcc, and the hydrogen diffusion coefficient value is between ferrite and austenite [7]. The χ-phase is body centered cubic (bcc) and it is related to the detrimental effect on ductility, toughness and corrosion resistance. This phase can precipitate in the interface δ/δ, inside the ferrite grains

and the interface δ/γ [8]. It is also important to note that austenite found in martensitic or martensitic-ferritic stainless steels is inside the martensite structure as retained austenite. This austenite is quite different configuration of the austenite found in the duplex stainless steels.

The aim of this study is to investigate the influence of steel microstructure on the hydrogen diffusion in a MFSS. In this system, hydrogen permeation occurs in martensitic-ferritic matrix containing an amount of χ and γ_{ret}. Electrochemical hydrogen permeation and TDS tests were performed to evaluate the phenomenon of hydrogen diffusion in MFSS and correlate it with the microstructure, obtained by an especially designed heat treatment.

Experimental details

The composition of the steel used in this research is shown in Table 1. The specimens were extracted from seamless stainless steel tube water quenched after a solution treatment at 1000 °C for 30 min. In order to produce different microstructures, the specimens were tempered at different temperatures and times followed by water quenching, generating the samples listed in Table 2. The microstructure of each specimen was characterized using different techniques. The relative amount of martensite and ferrite was determined by image analysis using optical microscopy after etching with Lichtenegger-Blöch (LB) solution (20 g ammonium bisulfide, 0.5 g potassium bisulfate, 100 mL water) immersed for 15s [9]. Volume fraction of the retained austenite was determined by X-Ray diffraction (XRD) pattern recorded using a D8 ADVANCE X-ray machine (Cu Kα radiation with λ = 1.5406 Å). Phase transformation was investigated by using a scanning electron microscope (SEM), JEOL JSM 6460 with EDX Thermo/Noran System SIX Model 200 and Chi-phase was estimated by image analysis in optical microscopy after polishing.

In order to calculate the apparent hydrogen diffusion coefficient, electrochemical permeation tests were performed using a Devanathan-Starchucsk method [10]. An oxidation cell (detection side) was filled with NaOH 0.1 M and the potential used was obtained from open potentiometric circuit. A reduction cell (charging side) was filled with 3.5% NaCl solution with pH 4.0 (adjusted by CH$_3$COOH). A cathodic current (-20 mA) was applied on the charging side, and an anodic current was detected on the cell oxidation side [11]. Both currents were generated or detected by AUTOLAB PGSTAT100N potentiostat.

The apparent hydrogen diffusion coefficient (D_{app}) was calculated according to equation (1) [12].

$$D_{app} = 0.5 \frac{L^2}{\pi^2 t_b} \tag{1}$$

where D_{app} is the apparent diffusion coefficient, L is the thickness of the sample and t_b is the breakthrough time.

Table 1 — The chemical composition of investigated MFSS (wt%).

C	Cr	Ni	Mo	Mn	Si	S	P
0.012	14.00	5.00	3.00	0.32	0.20	0.002	0.014