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Electrochemical corrosion and hydrogen diffusivity in dual phase steel

Due to application in automotive industry, dual phase (DP) steels have received enormous attention over the last three decades. They show superior mechanical properties when compared to conventional high strength low alloyed (HSLA) steels, but their susceptibility to hydrogen embrittlement need to be explored in a greater extent. Therefore, in this study diffusion properties of hydrogen absorbed in steel were investigated in order to quantify the parameters of H-migration through complex microstructure of DP.

Electrochemical experiments have shown that exposure of DP steel in 2M H_2SO_4 under free corrosion potential at room temperature led to the evolution of hydrogen atoms in amount high enough for diffusion through the metal.

The values obtained for diffusivity and solubility of atomic hydrogen in DP steel suggest that permeability depends primarily on fine-grained microstructure of ferrite and martensite. Such heterogeneous polymorphic structure enables a high solubility of hydrogen within a network of numerous grain boundaries which act as reversible hydrogen traps. At ambient temperatures, these traps cannot retain hydrogen permanently and therefore the net result of trapping is low diffusion rate of hydrogen.

Key words: *DP steel, electrochemical corrosion, hydrogen diffusivity, ferrite, martensite*

1. INTRODUCTION

Dual-phase (DP) steels belong to a group of modern multi-phase steels (DP, TRIP, TWIP) characterized by ferrite matrix containing one or more phases (martensite, bainite and residual austenite) [1-3]. The coexistence of soft/hard phases and their interaction in working conditions allow both high strength and ductility to be achieved.

DP steels consisting of soft ferrite and hard martensite show superior mechanical properties compared to conventional HSLA steels. That has led the researchers to explore their suitability for different structural and constructional purposes [4-7]. Although a lot of papers were published regarding very good combination of mechanical properties in DP steels [8-13], further investigations are necessary to find the effect of phase constituents on the corrosion resistance properties [14,15]. The synergies of crystal structure of these materials with the hydrogen evolved and entrapped during corrosion is also a matter of a great concern and should be investigated in relation to the hydrogen embrittlement phenomena (HE) known as the most dangerous problem in HSLA steels exploitation [16-19].

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In view of the above, the present research is undertaken to understand the electrochemical behaviour of commercial DP steel immersed in 2M H_2SO_4 solution, as well as diffusion properties of H-atoms migrating in dual phase steel during spontaneous corrosion process.

2. EXPERIMENTAL

2.1. Material

Specimens were cut from the commercial DP-sheet produced with 3 mm in thickness by the compact strip production (CSP). This is an advanced manufacturing technology in the present iron and steel industry, which is widely adopted for hot strips production from a continuous cast slab in order to save energy and improve the productivity of steels [20]. Compared to the low carbon steel produced by conventional hot-rolling process, CSP is characterized by high strength and fine grain size. For the corrosion experiments the specimens of original thickness were used, while those in hydrogen permeation experiments were thinned mechanically from both sides to 1.5 mm.

2.2. Microstructural analyses

The microstructure of steel before and after hydrogenation was analysed by optical microscope Olympus GX 51. SEM images were recorded by detection of signals from the secondary electrons (SE) using Scanning Electron Microscope TESCAN

VEGA LSH (Czech Republic) equipped with energy dispersive x-ray spectrometer (Oxfords' Instruments INCA system with software and detector technology for EDS microanalysis).

2.3. Corrosion testing

Round specimens with surface of 0.384 cm2 were taken for electrochemical studies of corrosion. Prior to the experiment, each specimen was polished up to 600 emery paper followed by washing in distilled water and degreasing in ethanol. The experiments were conducted using PARSTAT 2273 potentiostat, interfaced with personal computer. Electrochemical polarization studies were performed in electrochemical cell in deaerated condition by N2-purging. The potential of the working electrode was measured against saturated calomel reference electrode (SCE) in the Luggin capillary placed close to the working electrode. Pt-mesh was used as a counter electrode. The potentiodynamic polarization studies were carried out at the open circuit potential (Eocp). The scan rate used was 5 mV/s. The corrosion rate was determined using Tafel's extrapolation method, as per ASTM standard. The Tafel's slope, cathodic (βc) and anodic (βa) and the corrosion current densities (icorr) were estimated from the Tafel plots. The corrosion rates were obtained from the corrosion current density using Faraday's law incorporated in Parstat software PowerCorrTM.

2.4. Hydrogen permeation

Electrochemical hydrogen permeation has been a well established experimental technique for more than forty years [21]. In the hydrogen permeation experiment two individual electrolytic cells are separated with a membrane made from the steel to be investigated. On the entrance side (cathodic compartment filled with 2M H_2SO_4 and deaerated) the hydrogen is produced spontaneously by corrosion reaction. The hydrogen is then adsorbed on the sample surface and atomically absorbed into the material of the membrane. A constant potential (+ 200 mV vs SCE) is applied to the output side (anodic compartment filled with 1M NaOH) using a potentiostat. The hydrogen which diffuses through the membrane is oxidized on this side and the resulting oxidation current is registered.

For the purposes of the electrochemical H-charging, the commercial DP strip was cut in the form of membrane with dimensions 80mm×50mm×1.5mm. Both sides of the steel membrane were ground up to 600 grit paper, and the detection side of steel membrane was electroplated with Ni in order to ensure the surface passivity and reliability of the hydrogen oxidation current [22]. After cleaning the specimen surface with ethanol, the steel membrane was mounted between two electrochemical cells. An area of 3.14 cm^2 was exposed to each electrolyte inside the cells.

All the measurements were done in triplicate, at room temperature (T = 20 °C).

3. RESULTS AND DISCUSSION

Table 1 and Figure 1 show the chemical composition and the microstructure of the tested steel, respectively. It can be seen that commercial DP strip is characterized by high purity since the content of carbon and sulfur is very low.

Table 1 - Chemical composition (mass. %) of DP steel

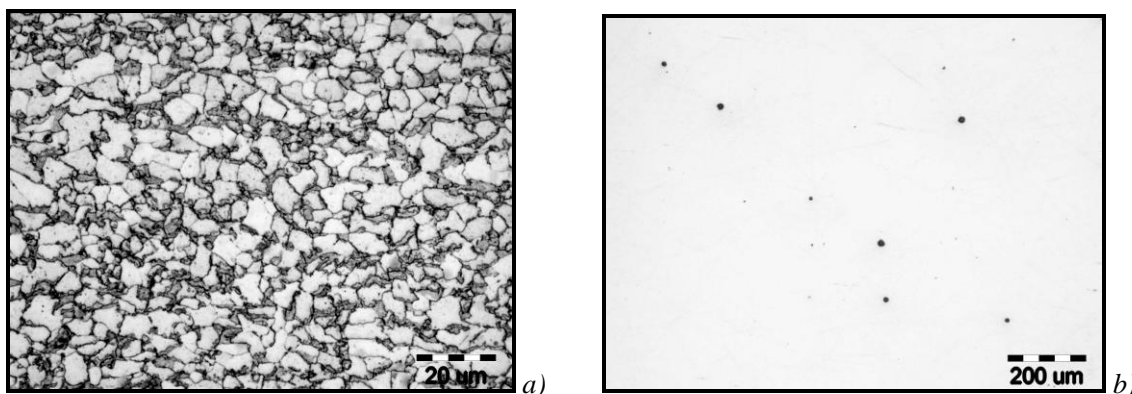| C	Mn	P	S	Si	Cu	Mo	Al	Cr	Ni	Sn	Nb	N
0.05	1.23	0.012	0.003	0.42	0.16	0.01	0.033	0.66	0.05	0.008	0.002	0.0085 ppm

Figure 1 - Optical micrograph of DP steel showing (a) the islands of martensite (dark phase) in ferrite matrix (light phase) and (b) globular particles of different size

Microstructure of as-received strip shown in Figure 1 reveals that the steel consists of fine and uniformly distributed polyhedral ferrite grains with diameter of about 5-15μm, and martensite islands (~10 %) embedded in a ferrite matrix. The presence of these two phases in contact with 2M H2SO4 significantly influenced the corrosion behaviour of DP steel during polarization studies and permeation experiments, as presented in Figure 2.

From experimentally obtained cathodic and anodic polarization curves in Figure 2a, corrosion potential and corrosion current have been derived using Tafel's linear extrapolation method. The data are shown in Table 2.
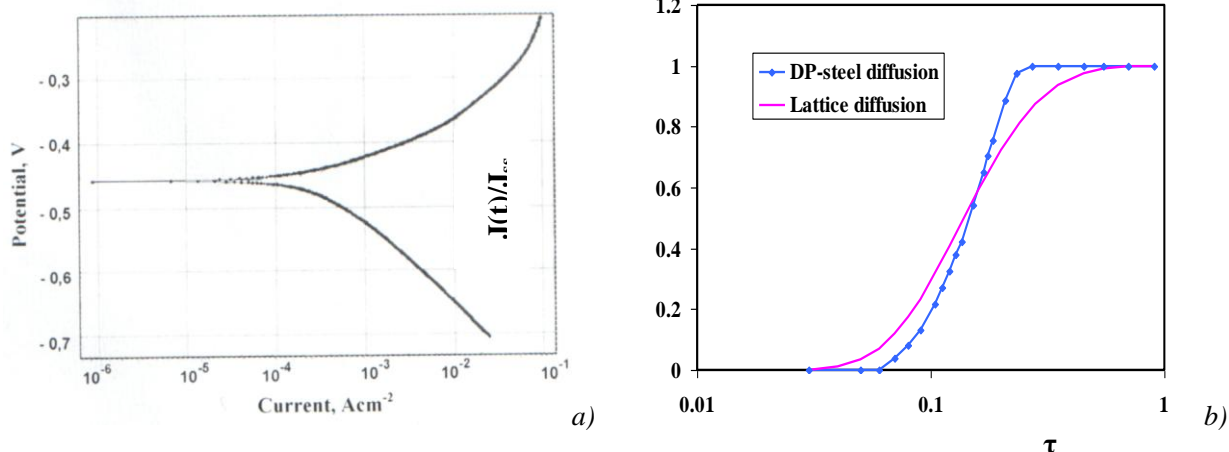

Figure 2 - Polarization curves of DP steel in H_2SO_4 (a); normalized hydrogen flux in DP steel (b)

Table 2 - Corrosion characteristics of DP steel in 2M H_2SO_4 solution

E_{corr} /mV vs SCE	I_{corr}/μAcm^{-2}	βa/mV	βc/mV	Corrosion rate/mma^{-1}
-455.6	736.7	56.7	122.8	8.55

Corrosion rate value is comparable to the one [23] for structural carbon steel in 1M H2SO4, and Tafel's coefficients βa and βa suggest that corrosion of tested dual-phase steel in acid solution is dominated by the hydrogen-ion reduction. When DP steel corrodes in H2SO4, the following reactions occur on the steel surface, with ferrite phase acting as anode:

Fe -2e→ Fe 2+   (anodic)

2H+ + 2e → H2   (cathodic).
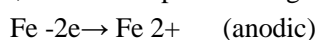
Very fine-grained structure of DP steel is characterized with number of the interfacial areas between ferrite (anode) and martensite (cathode) offering significant corrosion activity. Therefore, H-atoms evolved at the surface enter the metal and start their diffusion through the steel membrane. Because of the continuous oxidation of hydrogen at the output side and constant incoming flux of hydrogen from the input side of steel, the oxidation current is directly proportional to the amount of hydrogen penetrating through the membrane.

At a steady state, a constant concentration gradient through the DP-membrane is established. As a result, the evolution of hydrogen flux with time exhibits a sigmoid relationship shown in Figure 2b: the rate of hydrogen permeation rises after a certain break-through time and then approaches asymptotically to the steady state permeation rate. Normalized flux of hydrogen atoms through α-Fe is also presented in Figure 2b, for easier comparison with the theoretical (Fick's second law) lattice diffusion [22]. A permeation curves provide various informations on the hydrogen diffusion and trapping in the steel membrane, such as diffusivity (Dapp), permeability (Jss·L) and solubility (Sapp). Dapp represents the apparent lattice diffusivity of dissolved and reversibly trapped hydrogen, L is membrane thickness, Jss is H-flux in stationary state and the Sapp corresponds to the hydrogen in lattice and reversible traps. These values were calculated from the experimental curves and diffusion theory using tlag-method [22]. The data are listed in Table 3.

Table 3 - Hydrogen permeation data for DP steel

t_{lag}	i_{ss}	$J_{ss} \times 10^{11}$	$J_{ss} \times L \times 10^{11}$	$D_{app} \times 10^7$	$S_{app} \times 10^6$
s	μA cm^{-2}	mol cm^{-2} s^{-1}	mol cm^{-1} s^{-1}	cm^2 s^{-1}	mol H/cm^3
6600	2.07	2.15	0.32	5.68	5.66

From the hydrogen transients in Figure 2b, it is obvious that break-through time required for H-atoms to reach the exit site of DP-membrane is longer than that in α-iron. However, the diffusion coefficient D becomes about 100 time lower (Table 3) in comparison with the value for lattice diffusivity in α-Fe (DFe = 6.2 × 10-5 cm2 s-1) [24]. It is known [25] that the decrease in diffusivity and increase in solubility of hydrogen in steel strongly depend on trapping of H by various defects like dislocation, grain boundaries, matrix-particle interface etc. SEM/EDS analyses performed on the tensile fracture surfaces of DP steel have shown (Figure 3) the presence of characteristic inclusion particles with Ca, Al and O as the main constitutive elements.
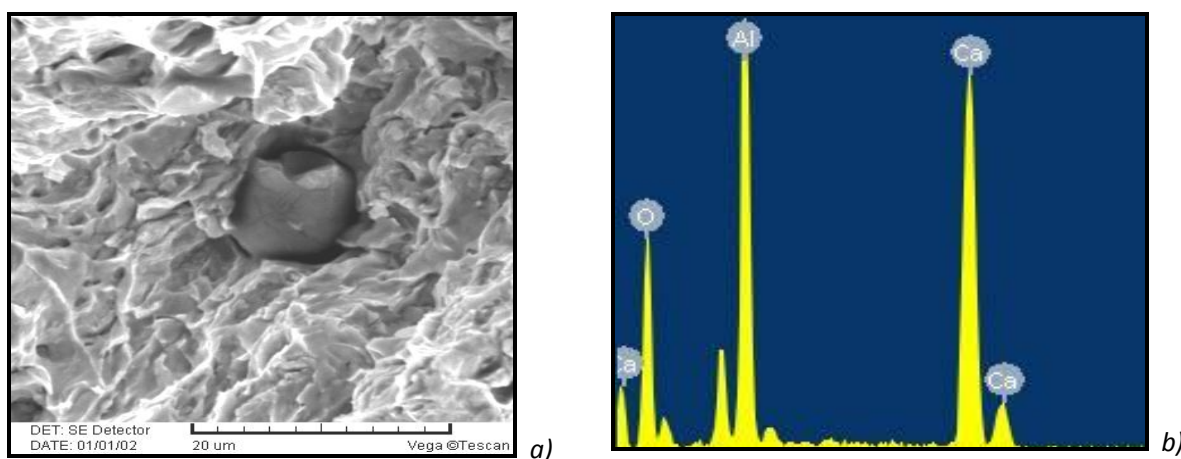

Figure 3 - SEM micrograph and EDS spectrum of inclusion particle on the tensile fracture surface of tested DP steel

It is obvious that particles identified are Ca, Al-oxides registered also by optical metallography. Their random distribution and globular shapes are presented in Figure 1b.

Hydrogen atoms trapped by such strong traps are released only if heated to very high temperatures and do not contribute to diffusivity at ambient temperature.

Hence, most of the traps present in DP steel would be of low binding energy like grain boundaries and dislocations. Very fine ferrite-martensite structure of DP-strip provides extremely high density of such traps, especially that of grain boundaries. At ambient temperatures, these traps cannot retain hydrogen permanently and therefore the net result of trapping is the decrease in diffusion rate of hydrogen, which in turn results in an apparent increase in the solubility.

4. CONCLUSION

- Electrochemical corrosion of dual-phase steel in 2M H2SO4 solution is dominated by the hydrogen-ion reduction and results in Fe-ion release.

- The exposure of DP steel to the electrolyte solution under free corrosion lead to the evolution of hydrogen atoms which enter the crystal lattice.

- The lower permeability and diffusivity of atomic hydrogen in DP steel compared to α-Fe is the consequence of heterogeneous polymorphic structure with different traps in which H-atoms may be captured.

- Most of the traps present in DP steel are of low binding energy like grain boundaries and dislocations although some globular Ca, Al-oxides, known as strong traps are detected in DP steel.

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IZVOD

ELEKTROHEMIJSKA KOROZIJA I DIFUZIJA VODONIKA U DVOJNOJ FAZI ČELIKA

Zbog primjene u automobilskoj industriji, dvofazni čelici (DP) pobudili su tijekom protekle tri dekade izuzetno zanimanje. U usporedbi s konvencionalnim visokočvrstim niskolegiranim čelicima (HSLA) imaju superiorna mehanička svojstva, ali njihovu sklonost krhkosti potaknutoj vodikom (HE) treba posebno ispitati. Stoga su u ovom radu proučavana difuzijska svojstva vodika apsorbiranog u čeliku, s ciljem da se odrede parametri karakteristični za H- migraciju kroz kompleksnu mikrostrukturu DP-a.

Elektrokemijski eksperimenti pokazali su da tijekom kontakta DP čelika s otopinom 2M H_2SO_4 u uvjetima spontane korozije pri sobnoj temperaturi nastaju vodikovi atomi u količini koja je dovoljna za difuziju u metalu.

Vrijednosti izračunate za topljivost i difuziju atomarnog vodika u DP čeliku sugeriraju da permeabilnost prvenstveno ovisi o izrazito sitnoznatoj mikrostrukturi ferita i martenzita. Takva heterogena polimorfna struktura omogućava dobru topljivost vodika zahvaljujući brojnim granicama zrna koje djeluju kao reverzibilne zamke za vodik. Pri sobnim temperaturama ovakve zamke ne mogu vodik trajno zadržati, ali ga usporavaju tako da je brzina difuzije smanjena.

Ključne riječi: *DP-čelik, elektrokemijska korozija, difuzija vodika, ferit, martenzit*