THE INFLUENCE OF MICROSTRUCTURE ON HYDROGEN DIFFUSION IN DUAL PHASE STEEL

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Abstract
The permeation experiments in this study have shown that electrochemical corrosion of dual phase steel in 2M H_2SO_4 results in hydrogen evolution and absorption of H-atoms in the material. The consequence of hydrogen is special type of degradation known as hydrogen embrittlement (HE). High susceptibility to HE depends on different microconstituents acting as H-traps. The values of diffusion coefficient and H-solubility obtained in this study have shown that transport of diffusible hydrogen can be related to the traps present in DP steel. The metallographic and SEM analyses have revealed only small globular inclusions, acting as reversible traps in ferrite-martensite matrix.

Keywords: dual phases, hydrogen diffusion, microstructure, hydrogen embrittlement & traps

1   Introduction
Hydrogen is one of the most undesirable elements, which can absorb in metals and alloys during their production, processing or application. Absorption of atomic hydrogen in high strength low-alloyed steels causes significant loss of some mechanical properties such as deformation ability and stress intensity factor [1].

One of the most common damage caused by absorption of atomic hydrogen in metals is known as HIC-hydrogen induced cracking or HE-hydrogen embrittlement. Besides the change of mechanical properties of steel, HE causes also structural changes such as internal cracks, surface blisters, voids etc. [2].

It is known [3] that hydrogen sulphide and inorganic compounds of arsenic, antimony and selenium accelerate the hydrogen absorption. On the other hand, different discontinuities in material (dislocations, grain boundaries, non-metallic inclusions) act as hydrogen traps, so hydrogen is stronger bonded in metal at such places and shows lower diffusivity [4].

To predict the deterioration of material properties due to hydrogen acting, it is necessary to determine diffusion coefficient, hydrogen concentration and concentration of hydrogen traps. It can be achieved by different experimental methods [5], and one of the most common methods is hydrogen permeation method developed by Devanathan and Stachurski [6]. The principle of electrochemical hydrogenation is that during cathodic polarization of the metal membrane in a solution (acid or alkaline) hydrogen atoms evolved are collecting at the cathodic side of the sample, i.e. at the entry side of the electrolytic cell. The concentration gradient of hydrogen atoms provides their transport by the diffusion through the membrane. Hydrogen atoms which

have been passed through the steel membrane are oxidized to hydrogen ions in the anodic part of the cell.

As the demands for weight reduction and reduction of fuel consumption are further increased, new families of high strength steel, so called an advanced high strength steel have been developed. These new steel grades include DP (dual phase), TRIP (transformation induced plasticity), FB (ferrite-bainite), CP (complex phase) and TWIP (twinning induced plasticity) steels [7]. These multiphase steels possess high strength simultaneously with the increased deformation ability and possibility of high impact energy absorption [8].

They are produced by modern metallurgical technologies and their application is especially in area where decreasing of weight (constructions, automobiles) is necessary. The application of structural steels is closely connected with good combination of strength, ductility and simple production. The main goal of these steels is to get a high strength without deterioration of ductility. It can be achieved by the multiphase microstructure, due to combination of high strength in one phase with the high plasticity of another phase («microstructural engineering») [9].

Therefore, in this work the influence of microstructure on hydrogen diffusion of high strength low-alloyed dual phase structural steel was studied.

2   Materials and Experimental Procedure

The sample was prepared from the low-carbon high strength hot-rolled strip of dual phase DP steel (EN 10336) and marked as DP-A. In order to have insight in its quality the chemical composition of examined material and carbon equivalent CE (calculated according to International Institute for Welding-equation (1) are given in Table 1:

$$CE(IIW) = C + \frac{Mn}{6} + \frac{Cr + Mo + V}{5} + \frac{Cu + Ni}{15}$$ (1)

It can be seen from Table 1 that dual phase steel has low sulphur and phosphor content, which provides high purity and quality of examined steel material, because it minimizes the possibility of sulphides formation and other inclusions.

In order to investigate the tendency to hydrogen embrittlement, it is necessary to hydrogenate the samples. The penetration of hydrogen atoms through the steel materials can be accelerated by simple laboratory procedure of electrochemical examination of hydrogen diffusion in ferrous materials [6]. For permeation experiments the sample was cut from steel sheet of origin thickness into the membrane with dimensions ($5 \times 8 \times 0.165$) cm. Anodic (exit) side of sample was coated with nickel, so that the surface at the oxidation side of metallic membrane is passive or corrosion resistant. The coating with nickel was performed at ambient temperature through 55 minutes and with current density of 0.5 A/dm^2. Before every measurement the entry side of sample was grounded with emery paper to a 600 grit finish. After that the membrane was rinsed in distilled water and degreased in ethanol.

The experimental device for monitoring of hydrogen diffusion through metallic membrane consists of cell for hydrogen charging (entry part) and oxidation cell (exit part) which are separated with thin steel plate (sample-working electrode), **Figure 1**. The entry side of sample is hydrogenated, so it is placed in contact with cell filled with 2M H$_2$SO$_4$ deaerated with nitrogen, while the anodic side is placed next to anodic (exit) part filled with 1M NaOH. In anodic part of the electrochemical assembly, saturated calomel electrode (SCE) as reference electrode and Pt-plate as counter electrode are placed. The potential of steel membrane in anodic (exit) cell is

maintained in the passivity area: + 200 mV vs. SCE. by PARSTAT Potentiostat/Galvanostat (Princeton Applied Research, USA) Model 2273. In the entry part of the experimental device the hydrogen evolution occurs, through corrosion reaction of steel with H_2SO_4. These H-atoms can form either hydrogen molecules leaving the solution in the form of gaseous hydrogen, or hydrogen atoms diffuse through the steel membrane reaching the anodic side. In anodic part no captured hydrogen at the exit side of membrane oxidizes in H^+-ions by the influence of applied potential. The current flow between the steel membrane (working electrode) and counter electrode (Pt-electrode) is registered in a PC and plotted as permeation current I/µA, which presents the measure for the amount of hydrogen that diffuses through the steel membrane.
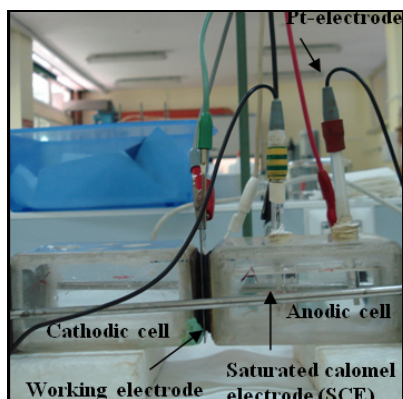

Fig.1 Apparatus for monitoring of hydrogen diffusion

Table 1 Chemical composition of examined dual phase steel DP-A (mass. %)

Type of steel	Dual phase
Sample	DP-A
C	0.073
Mn	1.85
Si	0.013
P	0.015
S	0.004
Al	0.047
N	0.0060
Cu	0.014
Nb	0.002
Ti	0.001
V	0.003
Cr	0.221
CE/%	0.43

For the purpose of metallographic investigations and microstructural characterization the steel sample was cut in the rolling direction and pressed by "SimpliMet®" machine for hot pressing of samples. After that, sample was grounded (emery paper No. 400, 500, 600 and 800 grit) and polished by the "Buehler" automatic device for grounding and polishing. Such prepared sample was observed by optical microscope with "Olympus GX 51" digital camera with system for automated picture analysis (AnalySIS® Materials Research Lab) to detect the inclusions. After that, the sample was etched by Nital (5 % HNO_3 in ethanol) to record its microstructure.

SEM analysis of registered inclusions and sample microstructure was carried out by scanning electron microscope "Tescan Vega LSH" (Czech Republic) equipped with "Bruker" EDS spectrometer.

3   Results and Discussion

On the basis of electrochemical diffusion measurements, taking in consideration registered hydrogen current at the exit side of membrane I/μA and working area A/cm^2, the permeation current density of atomic hydrogen i(t) was calculated according to following equation [10]:

$$i = \frac{I}{A} \qquad [\mu A cm^{-2}] \tag{2}$$

From diagram i = f (t) the steady-state permeation current density of atomic hydrogen i_{ss} and time t_{lag} (which presents a time to achieve a value of $0.63 i_{ss}$) were determined. From the obtained values and membrane thickness L, the diffusion coefficient D was calculated according to following equation [10]:

$$D = \frac{L^2}{6 \times t_{lag}} \qquad [cm^2 s^{-1}] \tag{3}$$

The amount of atomic hydrogen passing through the metal membrane per unit area in a steady-state condition was calculated according to Faraday's law:

$$n(H_2) = \frac{I \times t}{z \times F \times A} \qquad [mol\ cm^{-2}] \tag{4}$$

where I is the current (A), t is time (s), z is the number of exchanged electrons, F is Faraday's constant (96490 A s mol^{-1}) and A is the surface of steel membrane exposed to NaOH solution (3.14 cm^2).

The volume of atomic hydrogen passing through the metal sample per unit area was calculated from the standard molar volume as follows:

$$V(H_2) = V^0(H_2) \times n(H_2) \quad [cm^3\ H_2\ cm^{-2}] \tag{5}$$

Atomic hydrogen permeation flux at the steady-state was obtained by the following equation [10]:

$$J_{ss} = \frac{I/A}{F} = \frac{i_{ss}}{F} \qquad [mol\ cm^{-2}\ s^{-1}] \tag{6}$$

From the above parameters the sub-surface concentration of atomic hydrogen in interstitial lattice sites on the charging side of the sample was given as [10]:

$$C_0 = \frac{J_{ss} \times L}{D} \qquad [molH\ cm^{-3}] \tag{7}$$

The number of reversible traps N_T, is calculated as [11]:

$$N_T = N_{Fe} \times \left(\frac{D_{Fe}}{D} - 1 \right) \times e^{-\frac{E_b}{RT}} \qquad [cm^{-3}] \tag{8}$$

where N_{Fe} is the number of reversible traps in α-Fe ($7.52 \cdot 10^{22}$ cm^{-3}), D_{Fe} is the lattice diffusion coefficient of atomic hydrogen without traps ($1.28 \cdot 10^{-4}$ cm^2 s^{-1}), D is the diffusion coefficient of examined material, E_b is the bond energy (0.3 eV), R is the universal gas constant and T is the temperature.

The diffusion parameters for the four permeation transients were calculated and showed in **Table 2**. The permeation current density of atomic hydrogen as a function of diffusion time and normalized flux of atomic hydrogen against normalized time are shown in **Figures 2** and **3**.

Table 2 Hydrogen diffusion parameters for examined DP-A steel

Permeation	1st	2nd	3rd	4th
i_{ss}/μAcm^{-2}	1.62	1.77	1.92	2.02
t_{lag}/s	16002	12666	11610	10560
$n(H_2)\times10^7$/molcm^{-2}	1.85	1.92	1.96	1.96
$V(H_2)\times10^3$/cm^{3}H$_2$cm^{-2}	4.15	4.29	4.39	4.39
$D\times10^7$/cm^{2}s^{-1}	2.84	3.58	3.91	4.30
$J_{ss}\times10^{11}$/molcm^{-2}s^{-1}	1.68	1.83	1.99	2.09
$C_0\times10^6$/molHcm^{-3}	9.76	8.43	8.40	8.02
$N_T\times10^{-25}$/cm^{-3}	3.38	2.68	2.45	2.23

From the values in Table 2 it can be noticed that diffusion parameters are three orders of magnitude lower than that in crystal lattice of α-Fe (D_{Fe} =1.28 $\cdot$ 10^{-4} cm^2 s^{-1}) [11]. It means that traps are present which slow down the transport of H-atoms through a membrane. The number of reversible traps in examined material was order of magnitude 10^{25}, which confirms the above mentioned fact. Namely, it is known that decreasing of D_{eff} and increasing of C_0 strongly depends on hydrogen trapping. The most frequently appearing traps are different defects in the material such as dislocations, grain boundaries, etc. [12].
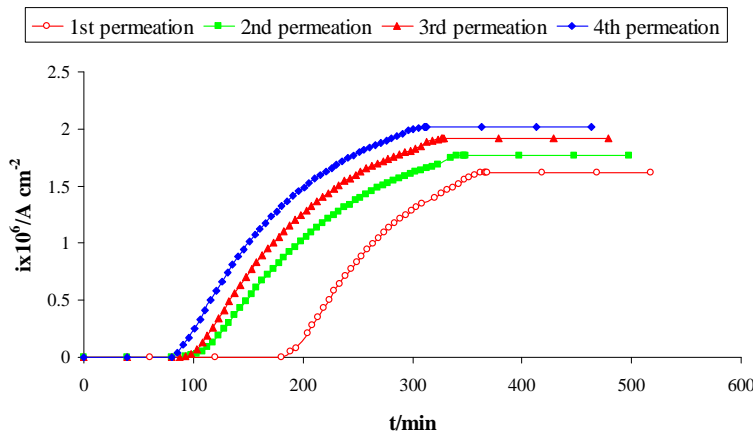

Fig.2 Time dependence of atomic hydrogen permeation current through membrane of DP-A steel

In Figures 2 and 3 the four curves are showed: the first curve presents hydrogen transport through the metal membrane which has never been in contact with corrosive medium, while the other permeation transients differ from the first because the membrane has already been in contact with medium and to some extent already hydrogenated.

It can be seen from the Figure 2 that hydrogen absorbed in DP-steel at first permeation transient needs 180 minutes to diffuse to the opposite side of the membrane. When all traps are filled,

steady-state flux of atomic hydrogen is established at the exit side of membrane, which can be seen as J_{ss} after 368 minutes. Every following permeation transient needs less time to reach the opposite side of the membrane, because only the reversible traps are slowing down the hydrogen transport [10]. Namely, hydrogen atoms in irreversible traps are tightly bonded and they can be driven out from the material only at temperatures 305-750 °C. Hydrogen atoms in reversible traps are weakly bonded and they can move by diffusion for a long time through a crystal lattice until they reach the other side of membrane [12, 13]. Such hydrogen is called diffusible hydrogen. The hydrogen trapped in reversible traps can be driven out from sample already at room temperature and completely at temperature interval 112-270 °C. Diffusible hydrogen is dangerous because it can move through a crystal lattice for a long time until it finds a suitable place, but it also can move from one place to another and cause an additional stress in a crystal lattice and consequently the delayed fracture.
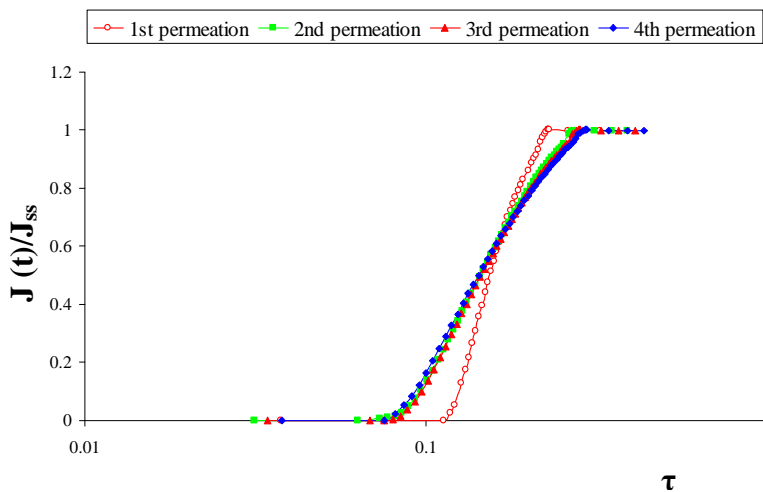

Fig.3 Normalized time dependency of normalized flux of atomic hydrogen for DP-A steel
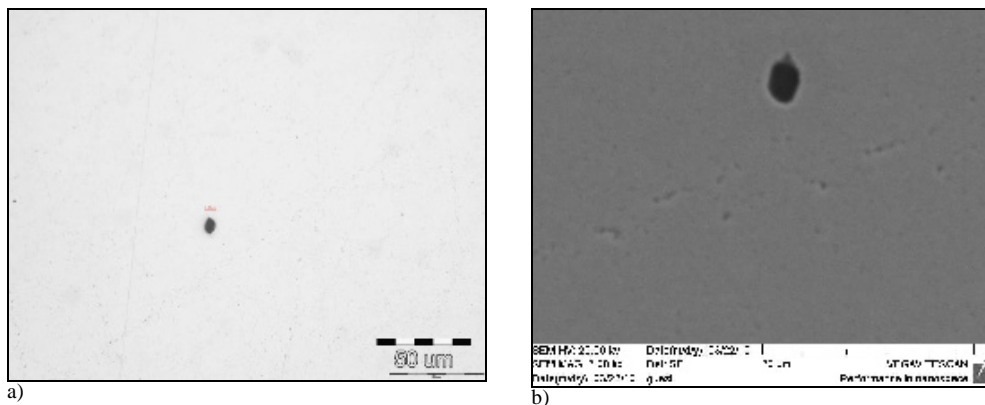

Fig.4 a) Optical micrograph of globular inclusion in DP-A steel, b) SEM micrograph of globular inclusion in DP-A steel

However, differences in calculated diffusion parameters between the first and the other permeation transients weren't very big, which leads to conclusion that examined DP-steel is not

characterized with a great number of irreversible traps. Namely, although the first permeation transient needs longer time (Figures 2 and 3), which indicates to presence of irreversible traps, the steeper curve of the first permeation transient indicates to a small number of irreversible traps (Figure 3) [10]. Observations by optical microscope and scanning electron microscope prove these constatation (**Figures 4-6**).
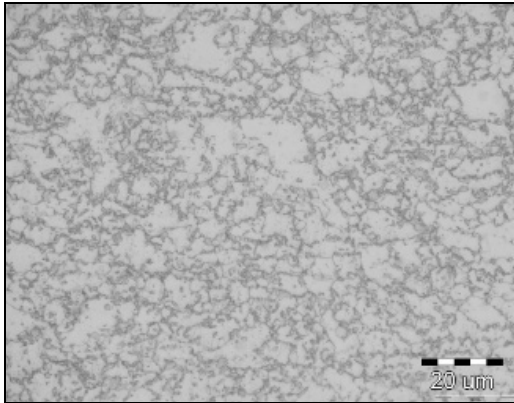

Fig.5 Optical micrograph of microstructure of DP-A steel etched by Nital

Since examined dual phase steel has very low carbon and sulphur content, irreversible traps such as carbides and inclusions are not expected [12, 13, 14]. Accordingly, SEM analysis of dual phase steel revealed a very small number of globular inclusions with dimensions from 2-7 μm (Figure 4), while elongated MnS-inclusions haven't been registered.
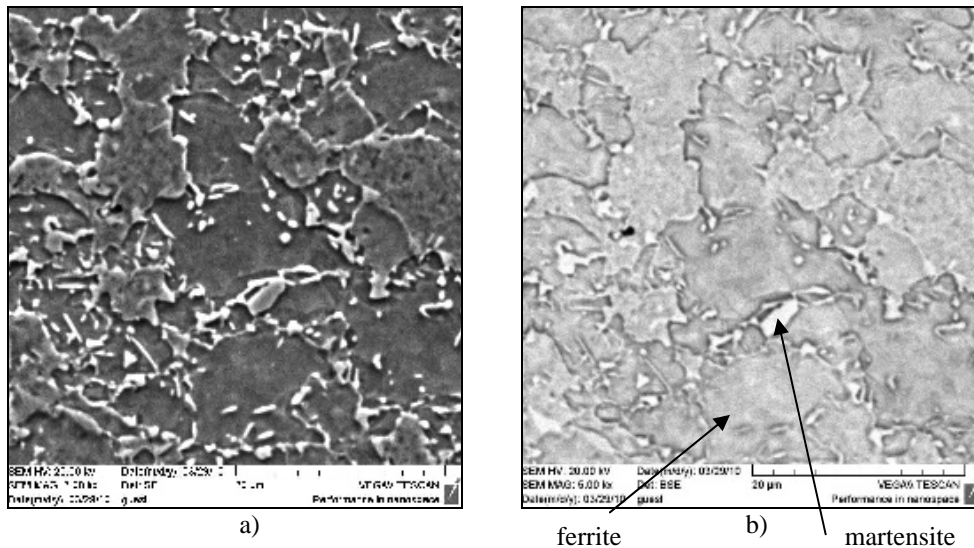

a)   b)

ferrite   martensite

Fig.6 Microstructure of DP-A steel etched by Nital: a) SEM micrograph and b) BSE micrograph

However, by analysing the fine-grained microstructure of examined ferrite-martensite DP steel (grain size No. 13, Figures 5 and 6), it can be concluded that reversible traps dominating

diffusible hydrogen behaviour are dislocations and grain boundaries. Namely, high density of dislocations and numerous grain boundaries provide longer paths of atomic hydrogen through a crystal lattice and slower hydrogen penetration to the opposite side of membrane.

4   Conclusions

By the electrochemical method of hydrogen permeation diffusion, the diffusion parameters of high strength dual phase DP steel were determined and the following was concluded:

Diffusible hydrogen accumulated in the reversible traps (C_0) contributes to the lower value of the diffusion coefficient (D).

The low diffusion coefficient of atomic hydrogen in DP steel indicates the presence of a great number of traps in comparison to α-Fe.

Reversible traps dominate in the structure, what can be seen from the difference in diffusion parameters between the first permeation transient and the following ones (D, C_0, N_T).

A few globular inclusions revealed by the metallographic and SEM analysis confirm that irreversible traps are not present in a significant number.

By analysing the fine-grained microstructure of examined ferrite-martensite DP steel, it can be concluded that reversible traps dominating diffusible hydrogen behaviour are dislocations and grain boundaries.

Acknowledgements

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