

# Role of electrochemically diffusible hydrogen in the initial damage of low-alloyed pipeline steel

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## ABSTRACT

The electrochemical hydrogen charging of pipeline steel was studied in a model solution of groundwater under a galvanostatic regime which was close to conditions of free corrosion. This corresponds to the real conditions of steel hydrogenation during the operation of the pipeline. The specimens were hydrogen-charged at different times to achieve the different total concentrations of hydrogen in the steel. Using a special experimental procedure, the total hydrogen concentration as well as the concentration of diffusible hydrogen, and the concentration of residual hydrogen in the steel were determined. It was found that within hydrogen concentration range  $C_H \leq 0.227 \text{ ppm}$  all hydrogen in the steel is diffusible. Under  $C_H \geq 0.227 \text{ ppm}$  some amount of the hydrogen remains diffusible, but the residual hydrogen appears in the steel. Based on these results, it was supposed that two different effects of the electrochemical hydrogen on the steel microstructure can exist: for hydrogen concentration range  $C_H \leq 0.227 \text{ ppm}$  and for  $C_H \geq 0.227 \text{ ppm}$ . The study of the case where only a low concentration of diffusible hydrogen is present in the steel showed that after the action of the diffusible hydrogen the micro and macro porous defects (voids) appear in the steel leading to an increase in the overall defectiveness of the steel and the number of defects and their total area increase with the increase in the concentration of diffusible hydrogen. This defectiveness affects the strength and other mechanical properties of the pipeline steel.

**KEYWORDS:** pipeline steel, electrochemical hydrogen charging, hydrogen concentration, diffusible hydrogen, damaging of steel, void-like defects.

## 1. INTRODUCTION

The problems of electrochemical corrosion and the resulting hydrogenating of low-alloyed steels in the operation of underground pipelines are critical in terms of ensuring their reliable operation [1, 2]. Its solution requires targeted electrochemical studies in conditions close to the real operating conditions of pipelines. However, it should be noted that a significant number of recent publications [3-6] have been devoted to discussing the results of studies conducted using cathodic hydrogenation of steels at very high polarization currents. This process does not correspond to the hydrogenation of low-alloy steels in real operating conditions, where a free-corroding system exists due the action of groundwater on the pipeline. This circumstance was marked in the work of Li *et al.* [7].

In these conditions i.e., in deoxygenated, near-neutral pH solution, hydrogen atoms are generated on the steel surface by the electrochemical reduction of water molecules [8, 9]:



The adsorbed hydrogen atoms can subsequently be combined to  $H_2$  molecules by the chemical reaction:



or the electrochemical reaction;

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or can be absorbed by the steel:



Here it should be noted that [8, 9] the absorbed hydrogen atom concentration under the cathodic polarisation depends on the hydrogen atom recombination mechanisms. When the chemical reaction (2) dominates the hydrogen atom recombination, the applied cathodic polarisation enhances the generation of hydrogen atoms and thus the number of hydrogen atoms penetrating into the steel. The absorbed hydrogen atom concentration will increase continuously with the cathodic polarisation potential. In the case of electrochemical reaction (3) dominating the hydrogen atom recombination, the cathodic polarization promotes the generation of hydrogen atoms through reaction (1), and simultaneously, enhances the hydrogen atom recombination through reaction (3). Thus, the role of cathodic polarisation is to generate hydrogen atoms and also to recombine hydrogen atoms.

The negative role of the hydrogen factor on the properties of metallic structural materials is all-known and during recent years we can see an increased interest and intensification of studies dedicated to the impact of hydrogen on the characteristics of ductility, strength, fatigue behaviour, and resistance to fracture of the structural materials for pipeline infrastructure [10-12]. These studies are mainly focused on the phenomenon of hydrogen embrittlement and there is a lack of information about the initial effects of the hydrogen on the damage of the pipeline steels.

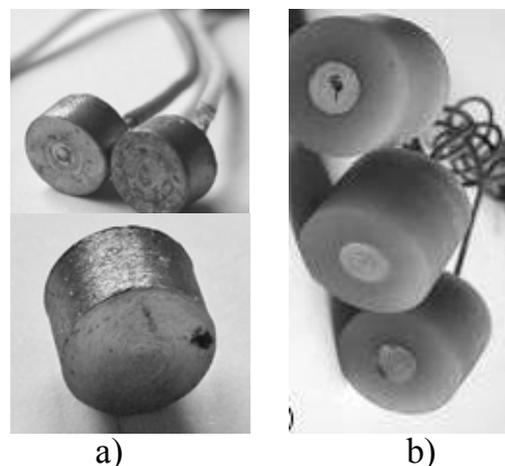
The novelty of the presented work consists in clarifying the role of electrochemically diffusible hydrogen in the initial damage of the low-alloyed pipeline steel. The residual hydrogen i.e. that is trapped in the imperfection of the material microstructure can be considered as one of the main reasons for hydrogen embrittlement [13, 14]. Therefore we focused on the situation where only low concentration diffusible hydrogen is present in the steel. The electrochemical hydrogen charging of steel was conducted in a model solution of groundwater under a galvanostatic regime which

was close to conditions of free corrosion. This corresponds to the real conditions of steel hydrogenation during the operation of the pipeline.

## 2. MATERIALS AND METHODS

The ferritic-pearlite pipeline steel with nominal chemical composition (in weight %): C = 0.17-0.24; Si = 0.17-0.37; Mn = 0.35-0.65; S<0.04; remainder Fe, was the object of present study. The disk specimens of diameter  $D = 8 \text{ mm}$  and thickness  $t = 4 \text{ mm}$  were used for evaluation of the hydrogen uptake of the steel under the hydrogen charging (Fig. 1).

The hydrogen charging of the specimens was carried out by the electrochemical method under cathodic polarisation. To simulate the hydrogen entry under real operating conditions of the buried pipeline, the following procedure was applied. The special deoxygenated, near-neutral pH NS4 solution [15], which is the model of underground water, was chosen as the electrolyte for the hydrogen charging of steel. The chemical composition of the NS4 solution is given in Table 1.



**Fig. 1.** Specimens for the study: a – with soldered conductors; b – in the plastic case.

**Table 1.** Chemical composition of NS4 solution (gram/litre) [15].

NaHCO <sub>3</sub>	KCl	CaCl <sub>2</sub>	MgCl <sub>2</sub> ·H <sub>2</sub> O
0.483	0.120	0.137	0.131



**Fig. 2.** Dynamic electrochemical laboratory VoltaLab40 (a) and hydrogen analyzer LECO DH603 (b).

Taking into account the situation of the freely corroding system that exists for the real pipeline [6, 7] the electrochemical hydrogen charging was carried out in the galvanostatic mode at a current density of cathodic polarization  $i_{cath} = 2 \mu A/cm^2$  that is close to the current density of free corrosion. This allowed ensuring a low intensity of hydrogen charging, which brings the simulated process as close as possible to the real conditions of hydrogen charging during the operation of pipelines.

The study was conducted using the dynamic electrochemical laboratory VoltaLab40 [16] and the standard three-electrode electrochemical cell (Fig. 2a).

For determination of the bulk hydrogen concentration in the specimens, the hydrogen analyzer LECO DH603 (Fig. 2b) was used which provides a fast and accurate measurement of the  $C_H$  values [17]. Also, using the functionality of this equipment we determined the total hydrogen concentration  $C_{H(total)}$  as well as the concentration of diffusible hydrogen  $C_{H(dif)}$ , and the concentration of residual hydrogen  $C_{H(res)}$ .

The procedure was as follows. For each series of hydrogen charging, we used two specimens simultaneously. The first one was immediately examined for determination of the total hydrogen concentration  $C_{H(total)}$ . The second one was exposed in vacuum for about 2 months. This action was aimed to extract the diffusible hydrogen from the metal ( $C_{H(dif)} \approx 0$ ). After that the residual hydrogen remained only in the steel and its concentration  $C_{H(res)}$  was determined. Assuming that:

$$C_{H(total)} = C_{H(dif)} + C_{H(res)} \quad (5)$$

the concentration of diffusible hydrogen  $C_{H(dif)}$  was evaluated as:

$$C_{H(dif)} = C_{H(total)} - C_{H(res)}. \quad (6)$$

The data on the residual  $C_{H(res)}$  and diffusible  $C_{H(dif)}$  hydrogen concentration in the specimens were used for the estimation of the event wherein the residual hydrogen appears in the specimens. The specimens which contain only diffusible hydrogen were examined by SEM using a scanning electron microscope EVO-40XVP [18].

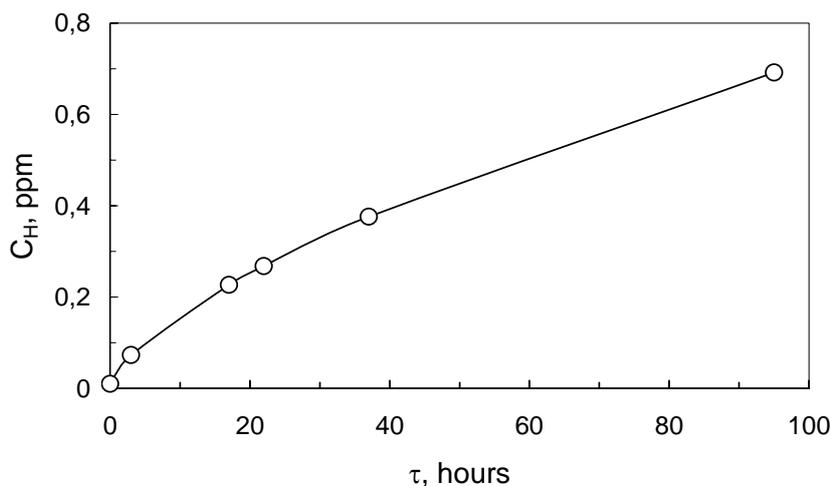
Here it should be noted that the SEM observation was aimed to study the bulk of the material after its hydrogenation. Therefore, the surface layer of the specimens with a thickness of about 1 mm was removed for excluding the surface effects potentially caused by the cathodic polarization during the hydrogen charging [19].

These studies aimed to compare the change in the microstructure of the steel under different diffusible hydrogen concentrations  $C_{H(dif)}$ . For obtaining the quantitative data on the effect of diffusible hydrogen on the microstructure defectiveness of pipeline steel, a special technique for computer analysis of the SEM images was applied [20, 21].

### 3. RESULTS AND DISCUSSION

The specimens were hydrogen-charged at different times to achieve the different total concentrations of hydrogen in the steel  $C_H$  (Fig. 3).

According to the proposed experimental procedure, the data about the diffusible  $C_{H(dif)}$  and the residual  $C_{H(res)}$  hydrogen concentrations depending on the  $C_H$  values were obtained (Table 2).



**Fig. 3.** Dependence of the  $C_H$  values on the time of the hydrogen charging  $\tau$  under cathodic polarization current density  $i_{cath} = 2 \mu A/cm^2$ .

**Table 2.** Data on the residual  $C_{H(res)}$ , diffusible  $C_{H(dif)}$ , and total hydrogen concentration  $C_H$  in low-alloyed steel depending on the time of the hydrogen charging  $\tau$  under cathodic polarization current density  $i_{cath} = 2 \mu A/cm^2$ .

$\tau$ , hours	$C_H$ , ppm	$C_{H(dif)}$ , ppm	$C_{H(res)}$ , ppm
0	0.010	0.010	0.010
3	0.073	0.063	0.010
17	0.227	0.217	0.010
22	0.268	0.236	0.032
37	0.376	0.252	0.124
95	0.692	0.412	0.280

It was found that within the hydrogen concentration range  $C_H \leq 0.227 \text{ ppm}$  all hydrogen in the steel is diffusible (Fig. 4). The point  $C_H \cong 0.227 \text{ ppm}$  can be considered specific because under  $C_H \geq 0.227 \text{ ppm}$  some amount of the hydrogen remains diffusible (Fig. 4, curve 1), but the residual hydrogen appears in the steel (Fig. 4, curve 2). Here we can see a significant increase in the  $C_{H(res)}$  values with a further increase in the total hydrogen concentration  $C_H$  in the material.

Based on these results, it was supposed that two different effects of the electrochemical hydrogen on the steel microstructure can exist [13, 22-24]: for hydrogen concentration range  $C_H \leq 0.227 \text{ ppm}$  and for  $C_H \geq 0.227 \text{ ppm}$ .

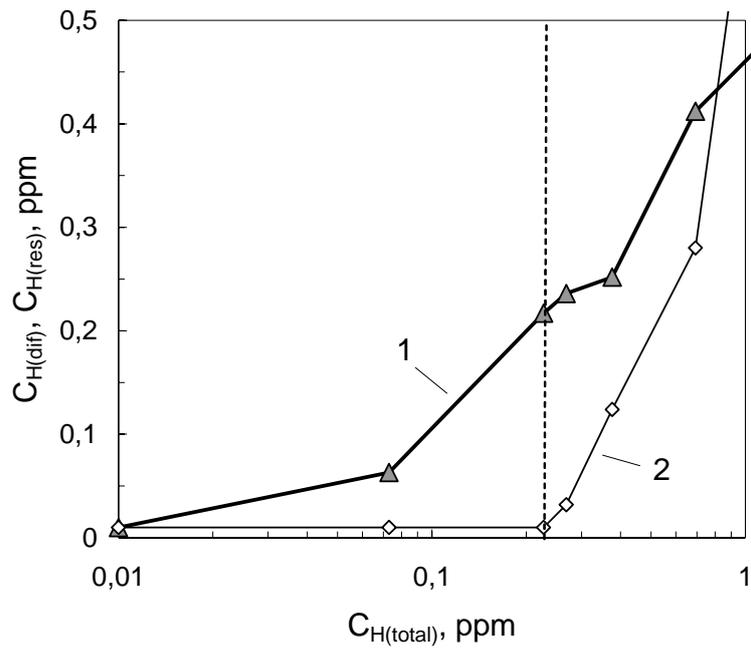
For a range of hydrogen concentrations  $C_H \geq 0.227 \text{ ppm}$ , the residual hydrogen is trapped in the defects of the material microstructure and this phenomenon can be considered as one of the main reasons for the hydrogen embrittlement of the material that is described in the literature [13, 14].

Therefore we focused our further study on the range  $C_H \leq 0.227 \text{ ppm}$  where only low concentration diffusible hydrogen is present in the steel.

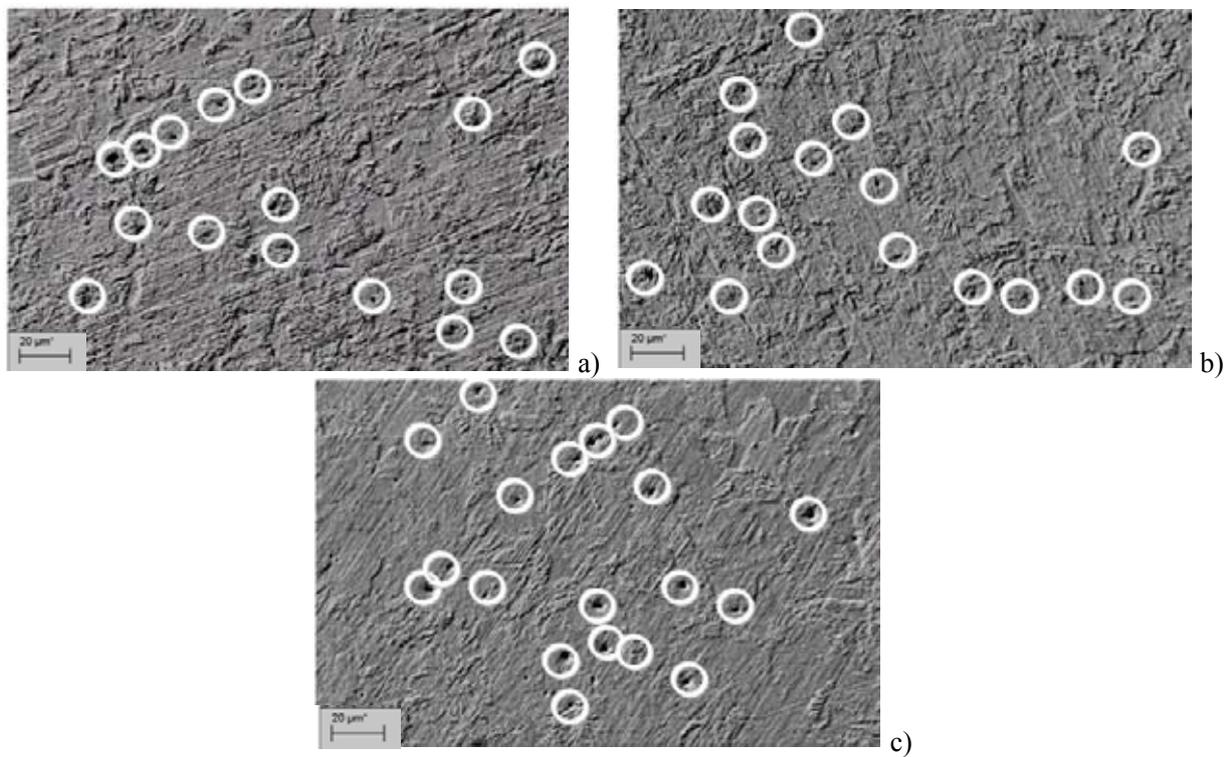
Three specimens with the hydrogen concentration  $C_H \cong 0.010 \text{ ppm}$ ,  $C_H \cong 0.073 \text{ ppm}$ , and  $C_H \cong 0.227 \text{ ppm}$  were examined by scanning electron microscopy (SEM). The obtained results showed (Fig. 5) that there are defects of the type of pores (voids) of different sizes for all examined specimens. These defects are dark in the SEM images and they are marked with white circles for clarity (Fig. 5).

The presence of pores in non-charged specimens, i.e. under  $C_H \cong 0.010 \text{ ppm}$  (Fig. 5a) can be explained by the natural defectiveness of low-alloyed steel, which is inherent to all engineering structural materials. However, as can be seen visually (Fig. 5b and 5c), the presence of diffusible hydrogen at a low concentration in the material ( $C_H \cong 0.073 \text{ ppm}$  and  $C_H \cong 0.227 \text{ ppm}$ ) increases its defectiveness.

Based on the obtained images, we performed a quantitative analysis of the change in the defectiveness of the microstructure of steel due to the influence of hydrogen (Table 3, Fig. 6). It was found that the diffusible hydrogen causes the



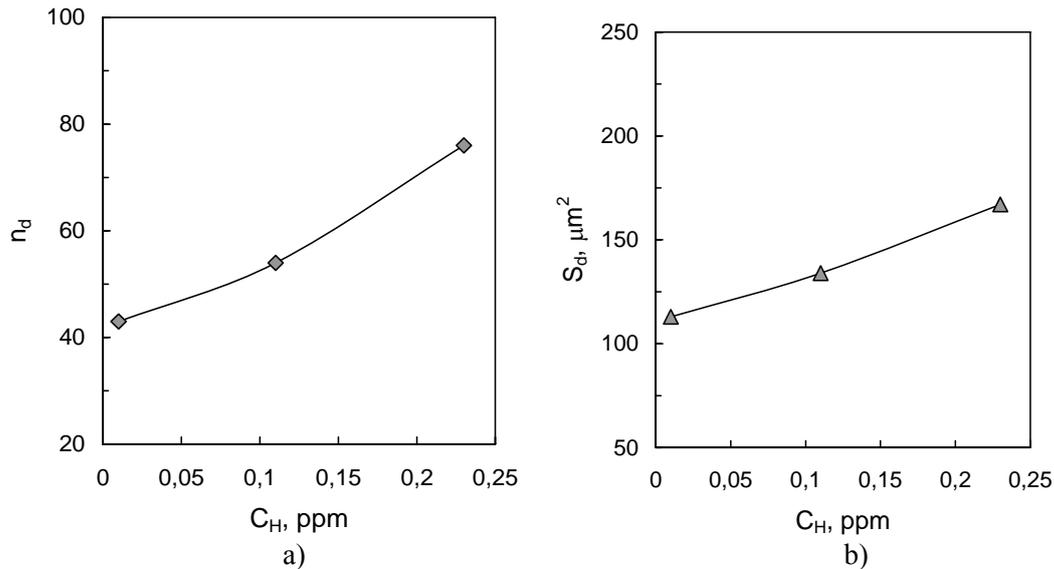
**Fig. 4.** Dependence of the diffusible hydrogen concentration  $C_{H(\text{dif})}$  (1) and the residual hydrogen concentration  $C_{H(\text{res})}$  (2) on its total concentration  $C_H$  in low-alloyed steel.



**Fig. 5.** SEM-images of the defectiveness of steel: a -  $C_H \cong 0.010 \text{ ppm}$ ; b -  $C_H \cong 0.073 \text{ ppm}$ ; c -  $C_H \cong 0.227 \text{ ppm}$  ( $\times 500$ ). The area of observation was equal to  $41300 \mu\text{m}^2$ .

**Table 3.** Data on the effect of hydrogen on the microstructure defectiveness of low-alloyed steel.

$C_H, ppm$	Area of observation $S, \mu m^2$	Number of defects, $n_d$	Total square of defects $S_d, \mu m^2$
0.01	41300	43	113
0.11	41300	54	134
0.23	41300	76	167

**Fig. 6.** Number of defects  $n_d$  (a) detected in specimens and their total area  $S_d$  (b) as the function of the diffusible hydrogen concentration  $C_H$ .

increase of the microstructure defectiveness and the number of porous micro-defects increases by about 1.8 times in comparison to the initial defect number in steel, which leads to an increase in the total area of defects by 1.5 times.

Taking into account the above-presented, it can be supposed that the action of diffusible hydrogen is to generate the micro and macro porous defects (voids) in the material, which leads to an increase in the overall defectiveness of the steel. Such defects can appear even at the nano level. Evidence of this is the image of the microstructure of the sample obtained by transmission electron microscopy (TEM), which is shown in Fig. 7. Here we can see porous defects of several nanometres in size, which are marked with white circles for clarity.

For a more detailed understanding of the influence of hydrogen on the formation of macro, micro, and nano defects in the microstructure of low-alloyed

steels, X-ray diffraction studies were performed using an automated diffractometer DRON-3. Processing of diffraction spectra was performed using the software package DHN\_PDS. The Laue method was used to determine the microstructural parameters of the specimens and the dislocation density [25].

Evaluation of the influence of diffusible hydrogen concentration in the steel on its microstructure was performed based on changes in two main parameters: the dislocation density  $\rho$  and the relative microdeformation of the crystal lattice  $\varepsilon$ .

The received data showed as follows. The values of  $\rho$  and  $\varepsilon$  decrease with an increase in the diffusible hydrogen concentration  $C_H$  (Table 4, Fig. 8). For a possible explanation of this fact, we built on the suggestion that the diffusible hydrogen can induce the internal microstresses in the material which increase with increase in the hydrogen concentration  $C_H$  [26]. In this case, the presence

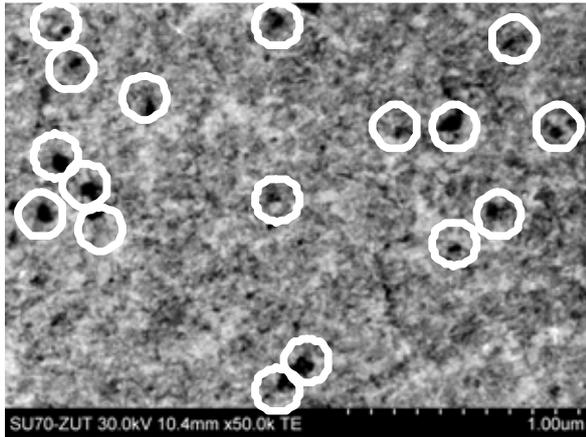


Fig. 7. TEM image of the specimen's microstructure under the hydrogen concentration  $C_H \approx 0.227$  ppm in the metal.

**Table 4.** Density of dislocations  $\rho$  and relative microdeformation of the crystal lattice  $\varepsilon$  in low-alloyed steel after its failure depending on the hydrogen concentration  $C_H$  in the metal.

$C_H, \text{ppm}$	$\rho \cdot 10^{-12}, \text{cm}^{-2}$	$\varepsilon, \%$
0.01	0.13	0.030
0.11	0.12	0.030
0.23	0.04	0.015

of diffusible hydrogen can promote the coalescence of dislocations and their density  $\rho$  decreases [13]. The process of the dislocations coalescence causes the initiation and creation of nano voids (Fig. 7) and then micro and macro voids in the steel (Fig. 5). At the same time, the coalescence of dislocations and creation of the void-like defects leads to a certain relaxation of microstresses, and thus to a decrease in the microdeformation of the crystal lattice  $\varepsilon$ .

If we link the trends in the parameters  $\rho$  and  $\varepsilon$  with the defectiveness of low-alloyed steel caused by the action of diffusible hydrogen of different concentrations, we obtain their correlation with the total area of defects  $S_d$  in the material (Fig. 9).

Thus, the effect of diffusible hydrogen on the microstructure of low-alloyed steel consists in the generation of porous defects at nano, micro, and macro levels that affect the deforming ability of the material and consequently can reduce its strength and resistance to fracture.

#### 4. CONCLUSIONS

The electrochemical hydrogen charging of pipeline steel was studied in a model solution of groundwater under a galvanostatic regime which was close to

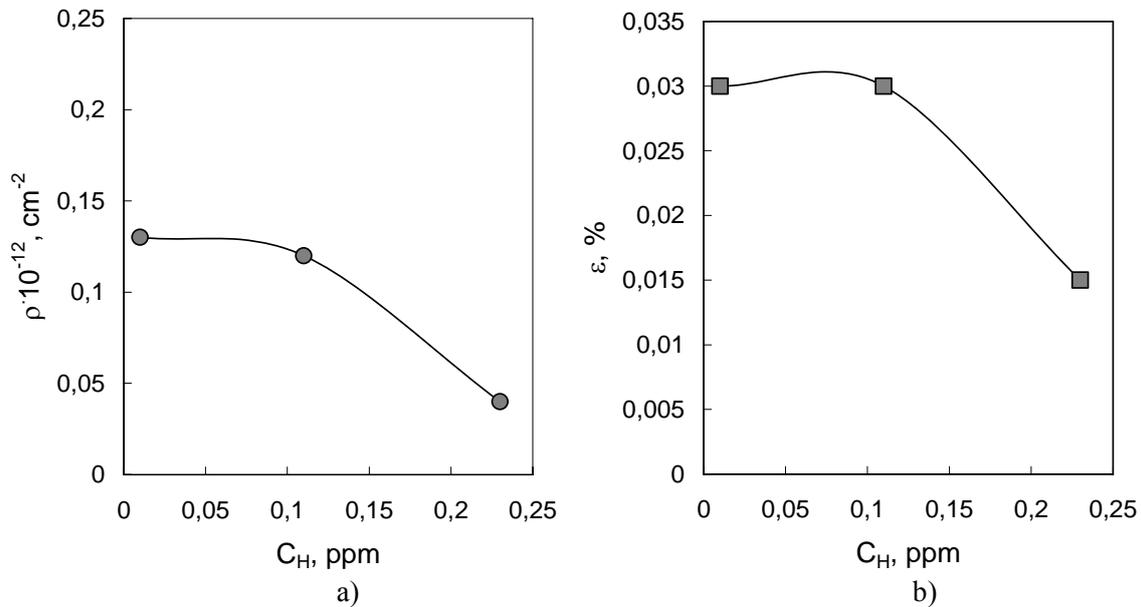
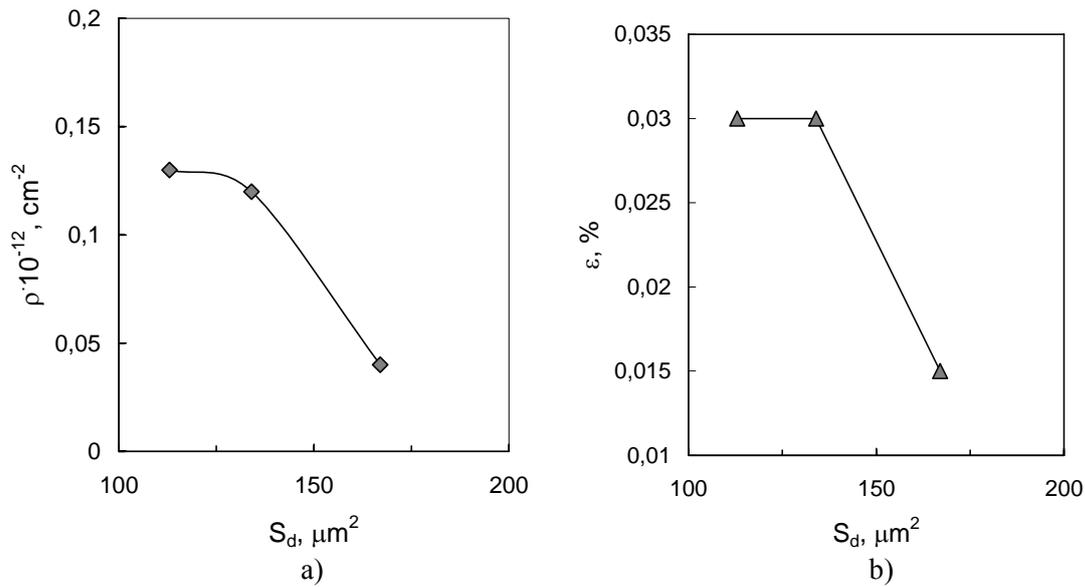


Fig. 8. Density of dislocations  $\rho$  (a) and relative microdeformation of the crystal lattice  $\varepsilon$  (b) in low-alloyed steel after its failure depending on the hydrogen concentration  $C_H$  in the metal.



**Fig. 9.** Density of dislocations  $\rho$  (a) and relative microdeformation of the crystal lattice  $\varepsilon$  (b) of low-alloyed steel depending on the total area of defects  $S_d$  in the metal.

conditions of free corrosion. This corresponds to the real conditions of steel hydrogenation during the operation of the pipeline.

The specimens were hydrogen-charged at different times to achieve the different total concentrations of hydrogen in the steel. Using a special experimental procedure, the total hydrogen concentration  $C_H$  as well as the concentration of diffusible hydrogen  $C_{H(dif)}$ , and the concentration of residual hydrogen  $C_{H(res)}$  in the steel were determined.

It was found that within the hydrogen concentration range  $C_H \leq 0.227 \text{ ppm}$  all hydrogen in the steel is diffusible. Under  $C_H \geq 0.227 \text{ ppm}$  some amount of the hydrogen remains diffusible, but the residual hydrogen appears in the steel. Based on these results, it was supposed that two different effects of the electrochemical hydrogen on the steel microstructure can exist: for hydrogen concentration range  $C_H \leq 0.227 \text{ ppm}$  and for  $C_H \geq 0.227 \text{ ppm}$ .

The study of the case  $C_H \leq 0.227 \text{ ppm}$  where only a low concentration of diffusible hydrogen is present in the steel showed as follows:

- after the action of the diffusible hydrogen the micro and macro porous defects (voids) appear

in the steel that lead to an increase in the overall defectiveness of the steel;

- the number of defects and their total area increases with the increase in the concentration of diffusible hydrogen  $C_{H(dif)}$ ;
- the dislocation density  $\rho$  and the relative microdeformation of the crystal lattice  $\varepsilon$  decrease with the increase in the diffusible hydrogen concentration. This can be considered as the confirmation that the diffusible hydrogen can promote the coalescence of dislocations as the primary source of steel defectiveness.

The defectiveness of pipeline steel caused by the electrochemically diffusible hydrogen affects the strength and other mechanical properties of the pipeline steel.

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#### CONFLICT OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**REFERENCES**

1. Nykyforchyn, H. 2021, Degradation Assessment and Failure Prevention of Pipeline Systems (Eds. G. Bolzon, G. Gabetta, H. Nykyforchyn), Springer Nature, 15.
2. Shipilov, S. A. and May, I. L. 2006, Eng. Fail. Anal., 13(7), 1159.
3. Hardie, D., Charles, E. A. and Lopez, A. H. 2006, Cor. Sci., 48, 4378.
4. Torres-Islas, A., Salinas-Bravo, V. M., Albarran, J. L. and Gonzalez-Rodriguez, J. G. 2005, Int. J. Hydrogen Energy, 30, 1317.
5. Zhang, T., Chu, W. Y., Gao, K. W. and Qiao, L. J. 2003, Mat. Sci. Eng. A, 347, 291.
6. Cheng, Y. F. 2007, Int. J. Hydrogen Energy, 32, 1269.
7. Li, M. C. and Cheng, Y. F. 2007, Electrochimica Acta, 52, 8111.
8. Cheng, Y. F. and Niu, L. 2007, Electrochemistry Communications, 9, 558.
9. Cheng, Y. F. 2007, Electrochimica Acta, 52, 2661.
10. Chen, Z. F., Chu, W. P., Wang, H. J., Li, Y., Wang, W., Meng, W. M. and Li, Y. X. 2022, Ocean Eng., 247, 110731.
11. Chen, Z., Chen, Y., Wang, W., Lu, K., Yang, H. and Zhu, W. 2020, Int. J. Hydrogen Energy, 45, 23142.
12. Keshtegar, B. and el Amine Ben Seghier, M. 2018, Eng. Fail. Anal., 89, 177.
13. Lynch, S. P. 2003, Hydrog. Eff. Mater. Behav. Corros. Deform. Interact (Eds. R. H. J. N. R. Moody, A. W. Thompson, R. E. Ricker and G. W. Was), 449.
14. Isfandbod, M. and Martínez-Pañeda, E. 2021, Int. J. Plast., 144, 103044.
15. Capelle, J., Gilgert, J., Dmytrakh, I. and Pluinage, G. 2008, Int. J. Hydrogen Energy, 33(24), 7630.
16. VoltaLab 40 (PGZ301 & VoltaMaster 4). Dynamic Electrochemical Laboratory. Instruction. – Radiometer Analytical, 2009.
17. LECO DH603. Manual, LECO Corporation, 2019.
18. ZEISS, Scanning Electron Microscope ZEISS SIGMA 300, Carl Zeiss SMT Ltd, Cambridge (England).
19. Dmytrakh, I. M., Akid, R. and Miller, K. J. 1997, Brit. Corr. J., 32(2), 138.
20. Kosarevych, R. Ya., Student, O. Z., Svirsk'a, L. M., Rusyn, B. P. and Nykyforchyn, H. M. 2013, Mater. Sci., 48, 474.
21. Kosarevych, R. J., Rusyn, B. P., Korniy, V. V. and Kerod, T. I. 2015, Cybernetics and Systems Analysis, 51, 704.
22. Nygren, K. E., Nagao, A., Wang, S., Sofronis, P. and Robertson, I. M. 2021, Acta Mater., 213, 116957.
23. Wasim, M., Djukic, M. B. and Ngo, T. D. 2021, Eng. Fail. Anal., 123, 105312.
24. Tehranchi, A. and Curtin, W. A. 2019, Eng. Fract. Mech., 216, 106502.
25. Laue method. Dictionary of Gems and Gemology. 2009 (Ed. M. Manutchehr-Danai) Springer, Berlin, Heidelberg.
26. Stashchuk, M. and Dorosh, M. 2017, Int. J. Hydrogen Energy, 42, 6394.