Effects of hydrogen-charging on the properties of S235JR steel

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Abstract. The paper presents the test results of the S235JR steel susceptibility to damage under the influence of hydrogen. The test of mechanical properties was performed on the basis of a static stretch test of non-hydrogenated samples and after cathodic polarization. Electrochemical measurements for the assessment of corrosion resistance of non-hydrogenated and hydrogenated steels were carried out using open circuit potential measurement and registering of potentiodynamic polarization curves in a three-electrode measuring system. Hydrogenation was carried out for between 3 and 24 hours in a solution of 0.1 N sulfuric acid (VI) with the addition of 2 mg/dm^3 of arsenic oxide (III) at an electric current density of 10 mA/cm^2. The hydrogen content in the steel before and after saturation with hydrogen was determined using the analyzer. Fracture samples after tensile test were observed using scanning electron microscope. The results of the research showed that as the hydrogen concentration in the examined steel increased (the lengthening of the saturation time), the deterioration of its mechanical and electrochemical properties occurred.

1 Introduction

Hydrogen penetration into the construction material occurs both at product's manufacturing stage and during its exploitation. In the welding zone, hydrogen can come from several sources, i.e. from moisture, water vapour, degradation of cellulose products from the electrode cover, protective gas and also from the grease present on the surface of the welded material or electrode [17]. In the marine environment, a biofilm containing anaerobes may be the source of hydrogen which reduce sulphates to sulphides and hydrogen sulphide.

The concentration of hydrogen in metals and alloys contributes not only to changes in their mechanical, physical and electrochemical properties, but also to the change in the performance properties of constructions or devices made of them. The level of property changes depends on factors that characterize the state of the alloy, its stress state, the level of deformation associated with it, and the time of being subjected to the surrounding environment's influence.

The effect of hydrogen in steels and alloys is a complex phenomenon. The level of mechanical properties degradation is the basic criterion for material destruction. Slow Strain Rate Test (SSRT) with obtained narrowing changes as its result is particularly informative, or, to a slightly lesser degree, the length changes [1,2]. Structural criteria are also used in assessing the hydrogen degradation level. The presence of trapped hydrogen in defects in the microstructure affects the change of materials' fracture mechanisms [3]. Differences in hydrogen concentration are not only reflected on the surface of the breakthroughs after the tensile test [4,5] but also in deterioration of corrosion properties [6-8]. In addition, recent research has shown that the method of quantitative assessment of breakthroughs can be used in assessing the hydrogen degradation level of alloys [9].

There are many research results of hydrogen degradation in various materials (steels, alloys) [10-13], which can be found in reference books. The authors of these works have evaluated the destruction of materials based on only one criterion, i.e. mechanical or structural properties. It should also be noted that there are not many works presenting the results of research on hydrogen influence on steel degradation which take the change in mechanical properties along with corrosion resistance into account.

The S235 steel belongs to unalloyed structural steels. It is widely used for welded, load-bearing and dynamically loaded constructions [14]. Due to operating conditions, this type of steel may undergo hydrogen degradation during the production of welded constructions (in the form of cold cracks) or in the process of utilizing the structure (in the form of hydrogen induced cracks HIC).

Since there is little information about the hydrogen degradation of unalloyed structural steels and about the assessment of their degradation according to mechanical properties criterion including corrosion resistance level, these issues have become the subject of the undertaken research. The results obtained may be useful to researchers interested in the hydrogen degradation of iron alloys. What is more, they can be used by engineers

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who are involved in the process of designing materials resistant to hydrogen degradation, and to help improve the efficiency of choosing the material during designing process.

2 Research material and methodology

2.1 Material

S235JR steel in the form of 2.0 mm thick metal sheet was used (Table 1).

Table 1. The chemical composition of the tested S235JR steel (Fe rest).

Steel	Chemical elements [wt.%]							
	C	Mn	Si	P	S	Cu	Cr	Ni
PN-EN 10025-2	0.17	1.40	-	0.025	0.025	0.55	-	-
Spectra analysis	0.13	0.98	0.01	0.013	0.015	0.02	0.03	0.02

The analysis of the chemical composition was conducted using an optical spectrometer. Table 1 lists the content requirements for S235JR steel according to PN-EN 10025-2 [14] and the average content of the elements in the check chemical analysis of the tested S235JR steel.

2.2 Hydrogenation of samples and determination of hydrogen content

Hydrogenation of rectangular specimens of 10 x 10 x 2 was carried out in a solution of 0.1 N H_2SO_4 with the addition of arsenic oxide (III) (2 mg/dm^3). An electric current density of 10 mA/cm^2 was used for between 3 and 24 hours. The cathodic polarization conditions were chosen in such a way as to ensure the same hydrogen concentration across the sample.

The amount of hydrogen in the samples of the tested steel before and after polarization was determined using the LECO ONH836 analyzer. The hydrogen content of the steel was determined in ppm. The hydrogen content in steel was measured on three samples at delivery state and after saturation with hydrogen. In order to limit the risk of hydrogen desorption in the alloy until measuring its concentration in the material, the samples were stored in liquid nitrogen.

2.3 Study of mechanical properties

A tensile test was used to evaluate the susceptibility of the examined steel by using flat samples with an initial measuring length of 50 mm and a cross section of 2 x 12.55 mm in accordance with PN-EN ISO 6892-1 [15]. The test specimens were wet ground with sandpaper, gradation of 240 to 1200, and then degreased with acetone. The tests were performed on the ZWICK/ROELL endurance machine with a deformation rate of 0.00003 s^{-1}. Due to the significant effect of the hydrogen desorption process from the alloy on the obtained results of mechanical properties (change of hydrogen concentration), the tensile tests were carried out immediately after the hydrogenation was completed. Measurements were made at 21÷23ºC. Each study was carried out on 3 samples with characterizing the state of the material without hydrogen and after hydrogenation.

The assessment of the hydrogen damage of steel was made on the basis of the so-called hydrogen embrittlement index HEI. The HEI index is determined by the percentage change of the determined parameter after the sample is saturated with hydrogen in relation to this parameter before saturation [3,16].

The higher the value of the HEI index, the greater the susceptibility of steel to hydrogen degradation.

$$HEI = \left|\frac{X_H - X_{wH}}{X_{wH}}\right| \cdot 100\% \quad (1)$$

where:
X_H - value of the parameter in the presence of hydrogen,
X_{wH} - value of the parameter without hydrogen.

2.4 Microscopic observations

The microstructure of the investigated S235JR steel was evaluated on metallographic polished sections digested with 3% Nital using the Hitachi S-3400N scanning electron microscope. After the tensile test, the assessment of hydrogen influence on the change in the nature of the fracture was conducted. Contamination from samples was removed in an ultrasonic scrubber using acetone. Fracture samples were observed on the Hitachi S-3400N scanning electron microscope.

2.5 Electrochemical research

Electrochemical measurements for assessing the corrosion resistance of non-hydrogenated and cathodic polarized steel were conducted using open circuit potential measurement (E_0) and registering the potentiodynamic polarization curves in a three-electrode measuring system. The measuring system consisted of a measuring vessel, an AMEL PSW01 System 5000 potentiometer and a computer with "CorrWare" software. The auxiliary electrode was made of platinum, while the calomel saturated electrode (NEK) was used as the reference electrode. A 3% aqueous NaCl solution at 23ºC was used for the study. Depending on the type of the test, the work electrode (WE) was respectively non-hydrogenated and hydrogenated steel samples of approximately 50 mm^2 surface. The test specimens were ground with waterpaper of 1200 grit and then thoroughly rinsed with distilled water, avoiding greasing the ground surfaces. The ground samples were purified in ethyl

alcohol using ultrasonic washer, rinsed with distilled water and dried with blotting paper. The samples prepared in such a way, depending on the type of the test, were placed directly in the electrochemical vessel or in the electrolyser to saturate with hydrogen. Before conducting polarization measurements of non-hydrogenated and hydrogenated samples, the measurements of the open circuit (E_{OCP}) were carried out to determine the value of the initial corrosion potential (E_{corr}). Once the open circuit potential has stabilized, they were polarized at a potential scanning rate dE/dt = 1 mV/s in the area of ±300 mV from the open circuit potential value (E_{OCP}). The corrosion current density (I_{corr}), corrosion potential (E_{corr}) and polarization resistance (R_p) were determined using the Stern method.

3 Results and discussion

3.1 Microstructure of steel

The Hitachi S-3400N electron microscope studies show that the microstructure of the S235JR steel is composed of ferrite and perlite grains (Fig. 1).

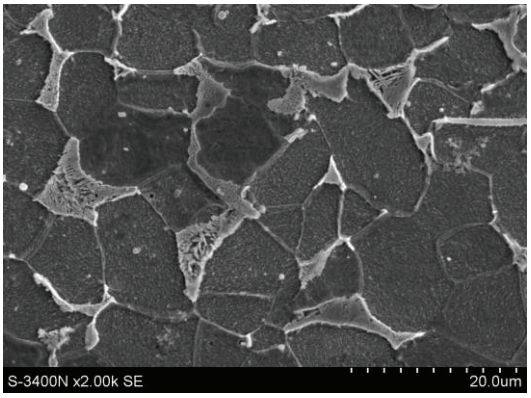


Fig. 1. S235JR steel structure.

3.2 The amount of hydrogen in steel under different cathodic polarization conditions

Fig. 2 shows the results of the measurements of hydrogen content in the steel samples tested before and after saturation with hydrogen.

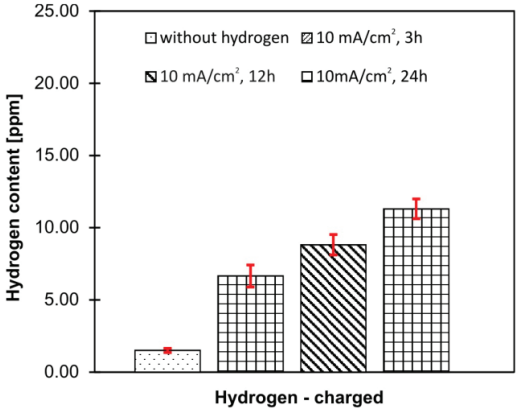


Fig. 2. Hydrogen content in the researched S235JR steel.

From the analysis of the data in Fig. 2, it was observed that with the increase of cathodic polarization time, the concentration of absorbed hydrogen in the steel increased. In the samples of non-polarized steel, the hydrogen content was 1.50 ppm.

3.3 The effect of hydrogenation conditions on mechanical and electrochemical properties

The following parameters were used to evaluate the effect of hydrogen on the mechanical properties of the tested S235JR steel: percentage elongation (A), percentage reduction (Z), tensile strength (R_m) and the yield strength ($R_{p0.2}$). The stress-elongation curves of the steel samples before and after the hydrogenation are shown in Fig. 3. Table 2 summarizes the results of the strength and plastic properties tested in the tensile test.

Based on the experimental results (Table 3) from relation (1), the degree of hydrogen damage was determined taking into account the percent reduction of area of non-hydrogenated and hydrogenated samples. The results are shown in Fig. 4.

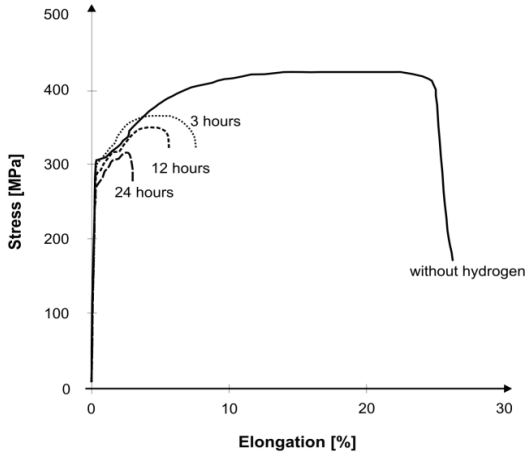


Fig. 3. S235JR steel stress-elongation curves before and after hydrogenation.

The analysis of the data in Table 3 shows that the change in the cathodic polarization conditions of S235JR steel has a different effect on the change of its mechanical properties, i.e. strength and plasticity. The analysis of the mechanical properties of the post-hydrogenated steel showed a decrease in the yield point from 324 MPa (the sample stretched in air without hydrogen interaction) to 281 MPa after cathodic polarization lasting 24 hours. The tensile strength of steel was reduced from 425 MPa (without hydrogen interaction) to 320 MPa with hydrogen content of 11.30 ppm. The analysis of the stress-elongation curves (Fig. 3) of steel showed that hydrogen saturation contributes to reducing its percentage elongation. After 3 hours of cathodic polarization, the percentage elongation of steel has decreased about 3 times (from 26.4% to 8.9%), and 4 times after the polarization period has been extended to 12 hours. The steel percent reduction of area decreased from 45% to 19.6% at the hydrogen content of 6.66 ppm

and about 11 times at the hydrogen content of 13.30 ppm. HEI's index ranged from 56% to 86% and increased along with the polarization time (Fig. 4).

surface of S235JR steel after hydrogenation showed a change in the fracture character. The samples of steel prior to hydrogenation were macroscopically ductile (Fig. 5). The samples of steel subjected to 3 hours of

Table 2. Mechanical properties of S235JR tested before and after hydrogenation.

Sample	$R_{p0,2}$ [MPa]	R_m [MPa]	A_{50mm} [%]	Z [%]	HEI [%]
as-received	324	425	26.4	45.0	-
3 hours	300	383	8.9	19.6	56
12 hours	297	379	6.6	11.6	74
24 hours	281	320	5.2	6.4	86

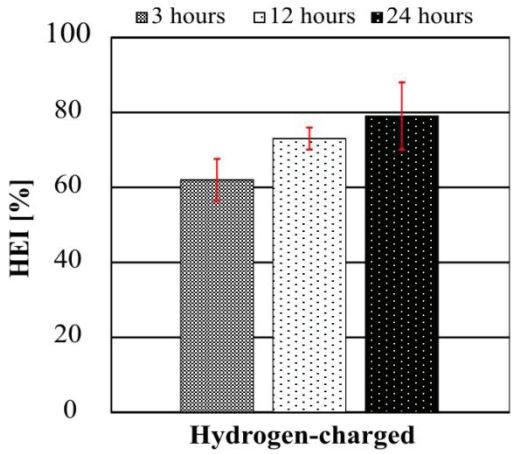


Fig. 4. HEI value S235JR steel.

The fractographic analysis revealed that the surface of the S235JR non-hydrogenated sample was characterized by the morphology typical for the breakthroughs of a plastic nature. Cracking occurred in a plane perpendicular to the direction of maximum tensile stresses (Fig. 5).

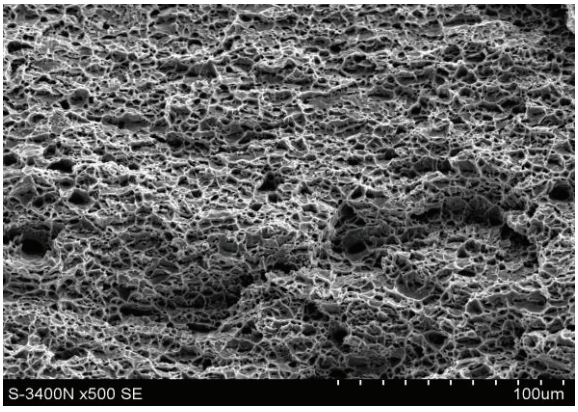


Fig. 5. View of the fracture surfaces of samples of steel unhydrogenated and stretched.

Surface fractographic studies of the surfaces of hydrogenated steel samples and then subjected to tensile tests revealed changes in the morphology of the fractures. The fractographic analysis of the fractal

polarization at cathodic current density showed a ductile and transcristalline mixed fracture (Fig. 6). At the surface of the fractures there were cracks initiated around non-metallic inclusions.

The chemical composition of the non-metallic inclusions was determined on the Hitachi S-3400N scanning microscope using energy dispersive X-ray spectroscopy (EDS). The analysis showed that the extracts consist mainly of sulfur and manganese (Fig. 7).

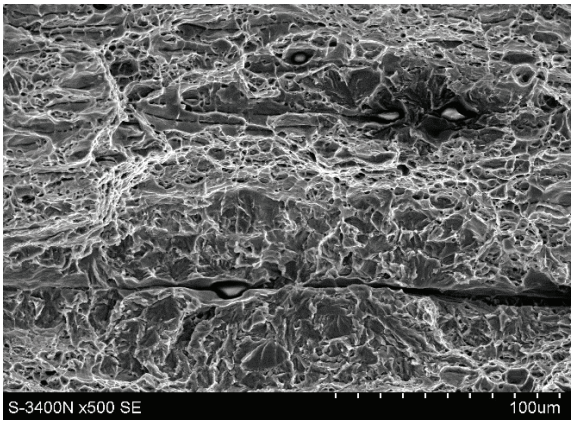


Fig. 6. View of the fracture surfaces of samples of steel hydrogenated for 3 hours and stretched. Cracking with sulfide inclusions.

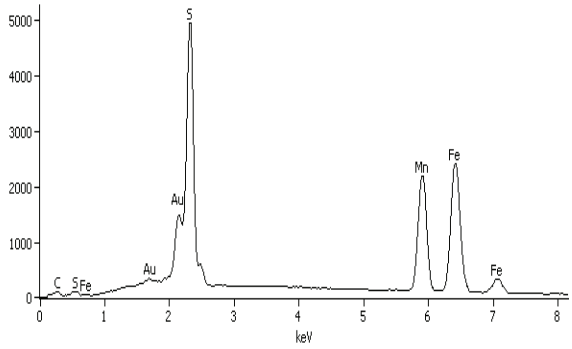


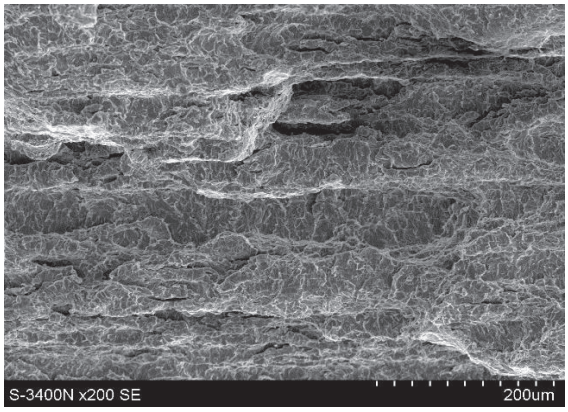
Fig. 7. X-ray spectrum of non-metallic inclusions.

For longer hydrogenation times of steel samples S235JR (i.e. 12 and 24 hours), numerous blisters and cracks were

observed on the side surfaces of the samples. The crack mechanism was transcristalline (Figs. 8-9).

The course of the potentiodynamic curves of the non-hydrogenated and cathodic polarized S235JR steel is shown in Figure 10. The potentiodynamic results are summarized in Table 3. The S235JR value of the corrosion potential (E_{corr}) of hydrogen-free S235JR steel measured in 3% NaCl solution was -507 mV. On the potentiodynamic curve of the samples tested without hydrogen saturation no passive range was observed (Fig. 10). The analysis of the data in Table 3 shows that hydrogen absorbed by the steel causes a change in its value of the corrosion potential (E_{corr}).

Potentiodynamic polarization curves for steel samples subjected to hydrogenation in the period of 3 to 24 hours showed no passive range. The increase in the value of the potential caused a continuous increase in the current density. The potential value measured in 3% NaCl solution, depending on the amount of hydrogen absorbed during the cathodic polarization, ranged from -581 mV to -623 mV. The decrease in polarization resistance was accompanied by an increase in the corrosion current density from 13.90 μA/cm^2 to 19.09 μA/cm^2.



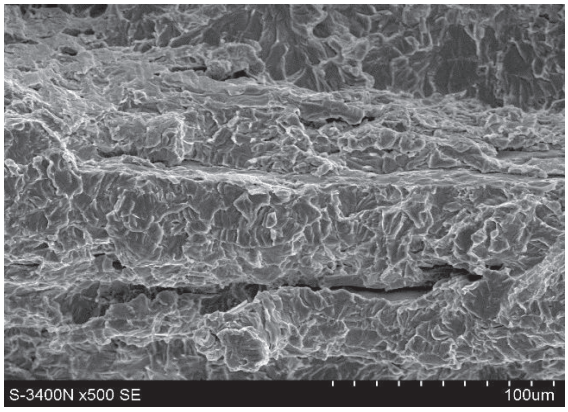
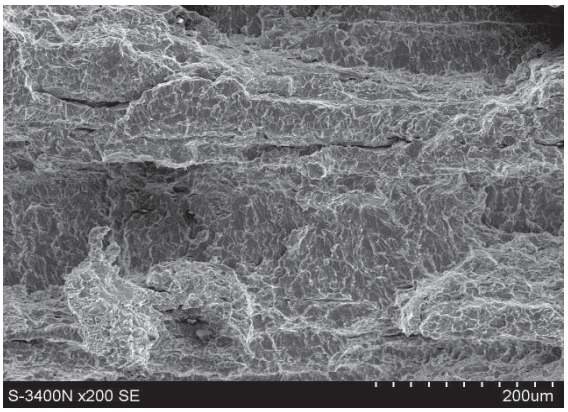


Fig. 8. View of the fracture surfaces of samples of steel hydrogenated for 12 hours and stretched.



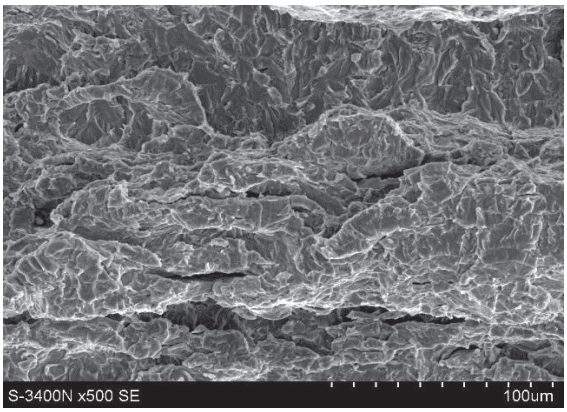


Fig. 9. View of the fracture surfaces of samples of steel hydrogenated for 24 hours and stretched.

Table 3. The results of potentiodynamic measurements S235JR.

Sample	E_{OCP} [mV]	E_{corr} [mV]	I_{corr} [μA/cm^2]	R_p [kΩ/cm^2]
as-received	-606	-507	13.90	1.88
3 hours	-619	-581	15.25	1.70
12 hours	-623	-600	17.37	1.44
24 hours	-662	-623	19.09	1.25

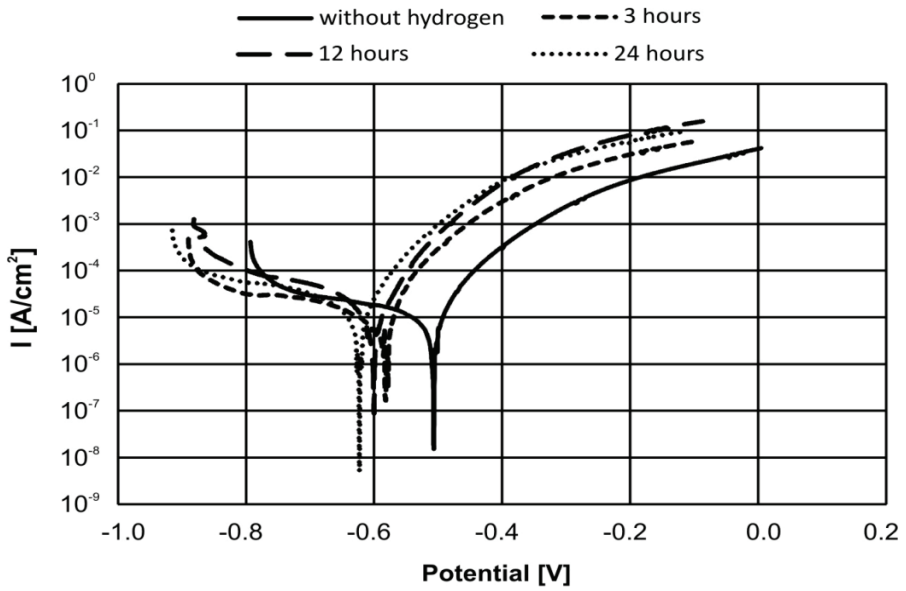


Fig. 10. Polarization curves of S235JR unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution.

4 Summary

The study showed that the duration of cathodic polarization influences the amount of hydrogen absorbed by the tested S235JR steel. With the increase in hydrogenation time, the hydrogen concentration in the steel samples increased. The impact of hydrogen in S235JR steel leads to reduction of its strength and plastic properties, i.e. the elongation and constriction measured in the tensile test. The drop in plastic properties caused by hydrogen has changed the nature of the fracture. Samples stretched in the air had a ductile fracture, and after hydrogen interaction, a mixed and transcrystalline fracture. At the surface of the fractures there were cracks initiated around non-metallic inclusions. The effect of hydrogen in S235JR steel also leads to a deterioration of its corrosion resistance measured in 3% aqueous NaCl solution. It has been found that the hydrogen saturation time contributes to the change in corrosion resistance of the tested steel measured in 3% NaCl solution. It was shown that, as the hydrogen content increased, the value of the corrosion potential (E_{corr}) decreased in the tested samples. The decrease in polarization resistance was accompanied by an increase in the corrosion current density.

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