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DC01 STEEL CORROSION RESISTANCE
IN CATHODIC POLARIZATION

ODPORNOŚĆ KOROZYJNA STALI DC01
W WARUNKACH KATODOWEJ POLARYZACJI

Abstract: The aim of the conducted research was to determine the corrosion resistance of the DC01 steel subjected to the cathodic polarization in variable conditions. The electrochemical measurements help to assess the corrosion resistance of the unhydrogenated steel subjected to the cathodic polarization and were taken using methods including the measurement of the open circuit potential as well as recording the $i = f(E)$ relation in polarization research in a tri-electrode measurement system. The measurement system consisted of a sample cell, AMEL PSW01 System 5000 potentiostat and a computer with "CorrWare" software. Hydrogenated steel was conducted in a 0.1 N water solution of the sulfuric acid with the addition of 2 mg/dm^3 of the arsenic trioxide as the penetrator promoter with the current density of 10 mA/cm^2 and 20 mA/cm^2 in the period of 3 to 24 hours. The content of hydrogen in the steel before and after the electrolytic hydrogenation process had been carried out, was marked using the LECO ONH836 analyser. It has been shown that with the hydrogen content decrease in the samples of the DC01 steel taken into consideration in the research (the amount of hydrogen depends on parameters of hydrogenation – the time and cathode current density), the value of the corrosion potential (E_{corr}) decreases. The decrease in the polarization resistance was accompanied only by the simultaneous decrease of the corrosion current density, which results in increased corrosion rate. The higher value of the cathode current density and longer time of hydrogenated, the smaller corrosion resistance of the DC01 steel in a 3% solution of NaCl.

Keywords: hydrogen, hydrogen content, cathode polarization, corrosion resistance

Introduction

The exploitation of products, structures and devices in various corrosion-aggressive environments make them exposed to damages caused by hydrogen. In relation to the time of hydrogen reaction, two types of hydrogen embrittlement: the external hydrogen embrittlement (*HEE*) and internal hydrogen embrittlement (*IHE*). In relation to the temperature, in which the process of hydrogen metal destruction is carried out, two phenomena can distinguished: high temperature hydrogen Aattack (*HTHA*) (tempera-

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tures above 200°C) and low temperature hydrogen attack (*LTHA*). Low temperature hydrogen destruction can be displayed in different ways, as: delayed hydrogen cracking (*HDC*), sulfide stress-corrosion cracking (*SSCC*), hydrogen induced cracking (*HIC*), "fish eyes" type cracking, hydrogen blisters. The intensity of the degradation process of the construction materials (metals, alloys), due to the absorbed hydrogen, is significantly dependent on the hydrogen's ability to dissolute and the diffusion rate. The hydrogen solubility in the hydrogen alloys, beside its gas pressure and temperature, depends on the crystal lattice type. The hydrogen diffusion in steel with regularly body-centred structure (*A*2), in comparison with steel with regularly-centred cubic structure (*A*1) is easier. The hydrogen atoms mobility in the latter is significantly lesser.

In construction materials, the hydrogen distribution is not uniform in the whole volume, while the local hydrogen concentration increase takes place in so-called hydrogen traps. Hydrogen traps can be divided into reversible traps (bond energy equal 60–75 kJ/mole) – decreasing the hydrogen mobility in the metal, at the same time slowing down its transport to locations of nucleation of the structure discontinuity, and irreversible traps (bond energy 25–30 kJ/mole), which accumulate hydrogen, contributing at the same time to cracking nucleation and metal delamination [1]. The difference between the reversible and irreversible traps cannot be stated explicitly. In most cases, the value of about 60 kJ/mole is taken into consideration [2]. In steel, hydrogen traps constitute structure defects, such as: non-metallic inclusions, grain boundaries, non-mantellic inclusions and alloy elements segregation, screw and edge dislocations, discontinuities [3–7]. The traps differ from one another with the hydrogen bond energy. The bond energy of Al_2O_3 with hydrogen is 79–86.2 kJ/mole [8]. Equally intense reaction can be found between the hydrogen atoms of MnS (72 kJ/mole) [9] and Fe_3C (84 kJ/mole) [5]. Significantly lesser energies of bonding with hydrogen have reversible traps (in certain temperature, hydrogen can leave the trap), *ie* grain boundaries, micro-voids as well as dislocations (screw, edge) [5]. The calculated energy of the screw dislocation bond with hydrogen equals 37–42 kJ/mole and 26–29 kJ/mole in case of screw dislocation [1].

The impact of the environment and hydrogen absorbed from it can influence the steel characteristics differently. In most cases, the impact is destructive, causing the mechanical properties, corrosion resistance as well as premature destruction to worsen. Mechanical properties degradation of steel exposed to hydrogen is revealed mostly by the decrease in their plastic properties, *ie*, contractions and elongations [10–13]. In case of stainless steel (ferritic, ferritic-austenitic) factors that can cause the decrease in plasticity include among others: complex microstructural changes in the surface layer induced by hydrogen. The changes are manifested by the creation of micro-twins, resulting in an surface relief effect in the form of needles [14]. The change of mechanical properties can be seen on the surface of fractures after the static stretching test. The hydrogen destruction causes the change in fracture characteristics leading to the trans-crystal and intergranular brittle fracture [15].

The conducted research [16–18] has shown, that electrochemical hydrogenation of metallic material causes their change in corrosion resistance. The change is revealed by the offset of electrode potential value towards stronger activity, the increase in corrosive

current density as well as polarization resistance decrease. In case of stainless steel, hydrogen can considerably disturb and hinder the passivation processes. Moreover, intense defects of the surface layer caused by the hydrogen saturation, influences their pitting corrosion resistance that decreases [14]. A galvanic hydrogen cell (Fig. 1) is created together with slots in metals and alloys accompanied by the simultaneous hydrogen reaction and stretching tensions (stress corrosion). It is caused by the diversity in amount of hydrogen absorbed by the tip and walls of the split. The cell together with the stretching cell and galvanic cell are important factors contributing to the slots' length growth, which is a favourable phenomenon as far as the durability of the loaded construction component in concerned.
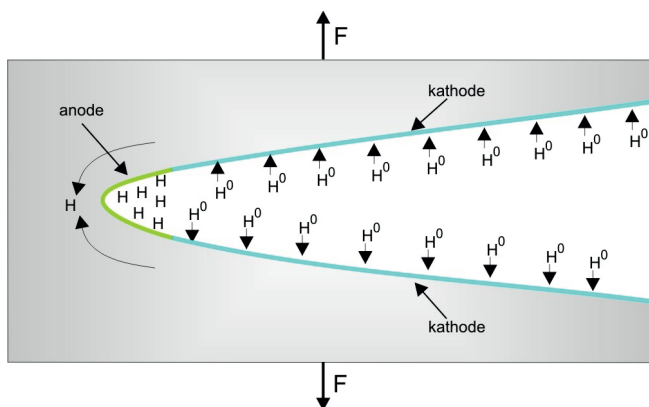

Fig. 1. The diagram of the electrochemical process present in the slot

It is of a great importance then, to conduct a research considering the changes taking place due to hydrogen, especially towards the changes in mechanical and electro-chemical properties of various steel types. The results of the research can constitute not only a valuable tool in designing and creating materials resistant to hydrogen defects, and what is more, can contribute to improve the process of choosing the right materials while designing.

The aim of the research is to assess the influence of hydrogen content on the possible changes in corrosion resistance of the unalloyed DC01 steel and using the process to determine its exploitive suitability in the environment containing hydrogen. These studies complement the assessment of the steel DC01 subjected to cathodic polarization in changing conditions [19].

Studied material and research methodology

The material taken into account in the research is DC01 type of steel in a form of a cold-rolled sheet metal 2.0 mm thick. The chemical composition of the steel, made in the optical spectrometer, as well as element composition for steel according to PN-EN 10152 [20] gathered in Table 1.

Table 1

The chemical composition of the tested DC01 steel

Chemical element	Contents [wt. %]	
	PN-EN 10152	spectra analysis
C	0.12	0.04
Mn	0.60	0.29
Si	—	0.02
P	0.045	0.009
S	0.045	0.004
Cu	—	0.05
Cr	—	0.02
Ni	—	0.03
Fe	—	Bal.*

* Balance.

The process of electrolytic hydrogenation of steel samples has been carried out in 0.1 N water solution of the sulfuric acid with the addition of 2 mg/dm^3 of the arsenic trioxide. The current density of 10 mA/cm^2 and 20 mA/cm^2 in the period of 3 to 24 hours were taken into consideration. Once the hydrogenation process was finished, the samples were taken out from the sample cell intended for electrolytic hydrogenation, rinsed in distilled water, dried with absorbent paper, and then put in the measuring vessel. The measurements were taken in temperature of 21–23°C. All parameters were studied in 3 tests.

The amount of hydrogen in samples of the steel taken into account in the research and after the hydrogenation process was marked using the LECO ONH836 analyser (Fig. 2). Hydrogen marking included the melting method in the atmosphere of inert gas. The measurements of hydrogen content in steel were taken from three samples in the delivery conditions and after the hydrogen saturation. In order to limit the risk of

Fig. 2. LECO analyser of oxygen, nitrogen and hydrogen ONH836

hydrogen absorption from the alloy, until the analysis of its concentration in the sample was conducted, the samples were kept in liquid nitrogen.

The microscope observations of the steel in the delivery conditions, as well as after cathode hydrogen saturation, were conducted using the Scanning Electron Microscopy (*SEM*, *EDS*) method. The research was carried out using a Hitachi S-3400N scanning electron microscope. A 3% solution was used to pickle the steel surface samples.

Electrochemical measurements contribute to the assessment of the corrosion resistance of the unhydrogenated steel and subjected to cathode polarization, were taken using the methods including the measurement of the open circuit potential (E_0) and recording the $i = f(E)$ redundancy during the polarization research in a tri-electrode measuring system. The guidelines for the performance concerning taking the potentio-dynamic polarization measurements, including the procedures and their implementation, are determined by the PN-EN ISO 17475:2010 norm [21]. The research included also a system which included a counter electrode (*CE*) and reference electrode (*RE*), AMEL PSW01 System 5000 potentiostat and a computer with "CorrWare" and "CorrView" software (Fig. 3). The counter electrode is a platinum electrode, while the reference electrode is a saturated calomel electrode (*NEK*). A 3% NaCl water solution with pH ≈ 6.0 was also used in the research, kept in temperature around 23°C. Depending on the research type, the work electrode (*WE*) were a properly unhydrogenated and hydrogenated 50 mm^2 steel samples. The samples were grinded with water abrasive paper with the 1200 grain-size, and then carefully rinsed with distilled water, avoiding greasing the grinded surface. Grinded samples were cleaned with ethylic alcohol, using a ultrasonic washer, rinsed with distilled water and dries with absorbent paper. Samples
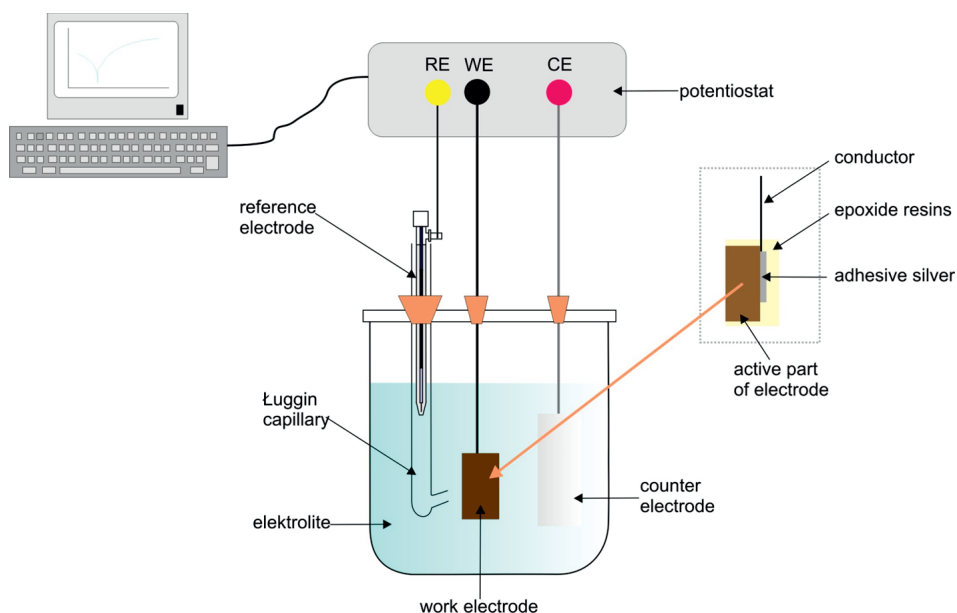

Fig. 3. The diagram of the electrochemical measurement station

prepared in such a way, depending on the research type, were placed directly in the electrochemical cell or electrolytic cell in order to saturate the samples with hydrogen.

Before commencing the polarization measurements of unhydrogenated and hydrogenated samples, the open circuit potential (E_0) measurements were taken of the researched steel in order to determine the values of the initial corrosion potential (E_{corr}). After the measured value of the open circuit potential was stabilized, their polarization was commenced; the speed of scanning of the potential was $dE/dt = 1$ mV/s in the area ±300 mV from the value of the open circuit potential (E_0). The value of corrosive current density (I_{corr}), the corrosion potential (E_{corr}) and polarization resistance (R_p) were determined using Stern method.

The results and review

The designated hydrogen content in the researched steel, in the delivery conditions, not subjected to cathode polarization was 1.26 ppm. Together with the increase of current density of the cathode polarization and its duration time, the concentration of the absorbed hydrogen decreased (Fig. 4). After cathode polarization lasting for 3 hours, with the current density of 10 mA/cm^2 and 20 mA/cm^2, the hydrogen concentration reached 13.00 ppm and 18.87 ppm respectively. Prolonging the time of hydrogenation up to 12 hours, with the current density of 10 mA/cm^2 and 20 mA/cm^2 caused the increase of hydrogen amount in relation to unhydrogenated samples for 16.04 ppm and 18.37 ppm respectively. The highest value of the hydrogen content, ie, 22.37 ppm, was noted in samples subjected to cathode polarization lasting 24 hours with the current density of 20 mA/cm^2.
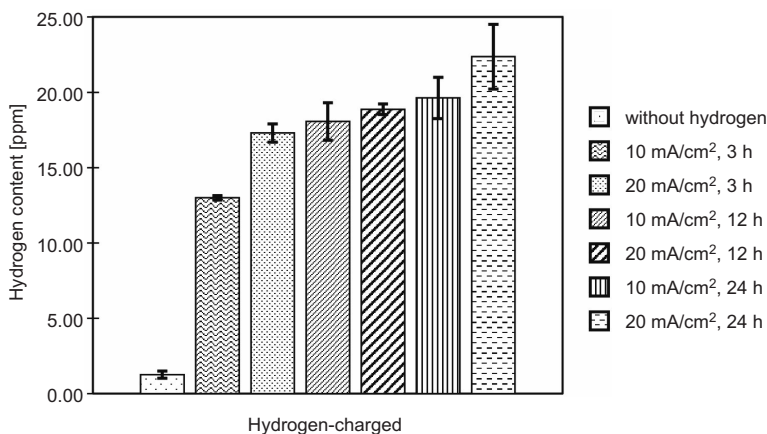

Fig. 4. Hydrogen content in the researched DC01 steel

The conducted microscope research showed, that the microstructure of the researched DC01 steel consists of ferrite grains and carbides visible on the ferrite grains boundaries as well as in their insides (Fig. 5).
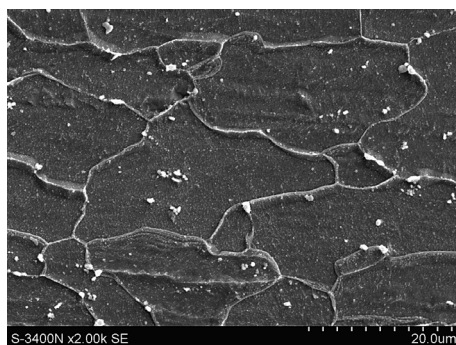
Fig. 5. DC01 steel structure

The observation of the surface of steel samples subjected to cathode polarization showed explicit changes in the microstructure caused by the hydrogen absorption (Fig. 6–8). The carried out observation showed also, that in the surface layer of samples,
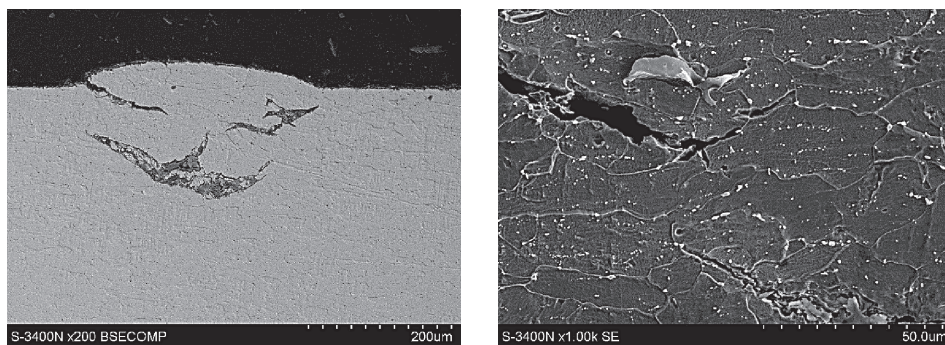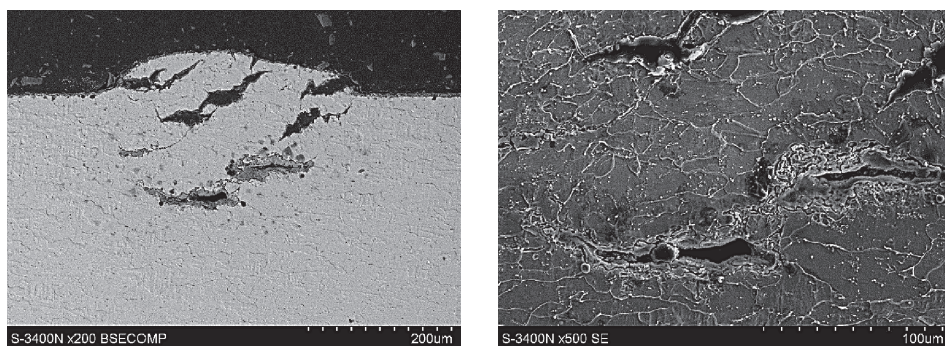

Fig. 6. The view of DC01 steel samples surface subjected to cathode polarization in the environment of 0.1 N H_2SO_4 + 2 mg As_2O_3 with the cathode polarization current density of 10 mA/cm^2, in 12 hours

Fig. 7. The view of DC01 steel samples surface subjected to cathode polarization in the environment of 0.1 N H_2SO_4 + 2 mg As_2O_3 with the cathode polarization current density of 10 mA/cm^2, in 24 hours
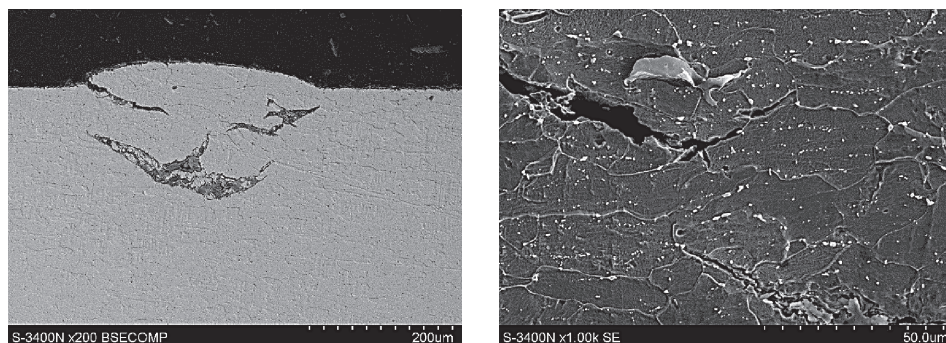
Fig. 8. The view of DC01 steel samples surface subjected to cathode polarization in the environment of 0.1 N H_2SO_4 + 2 mg As_2O_3 with the cathode polarization current density of 20 mA/cm^2, in 24 hours

for which the hydrogen impact is the most intense, in relation to the permanent contact of the surface with hydrogen during the polarization, caused hydrogen blisters and micro-cracks to appear. Defects in form of blisters and micro-cracks are the result of a strong supersaturation of the metallic phase with hydrogen and the recombination of the atomic hydrogen around physical and chemical defects of metals (non-metallic inclusions, pores, micro-cracks).

The corrosion potential value (E_{corr}) of the unhydrogenated DC01 steel, measured in the 3% NaCl solution was –479 mV (Table 2).

Table 2

The results of potentiodynamic measurements

Sample		E_0		E_{corr}		I_{corr}		R_p	
		average	±SD	average	±SD	average	±SD	average	±SD
		[mV]		[mV]		[μA/cm^2]		[kΩ/cm^2]	
Without hydrogen		−571	8	−479	12	14.94	0.31	1.74	0.17
10 [mA/cm^2]	3 h	−599	12	−529	6	15.77	0.19	1.68	0.18
	12 h	−642	7	−546	10	18.39	0.50	1.39	0.22
	24 h	−646	5	−567	12	19.71	0.36	1.32	0.23
20 [mA/cm^2]	3 h	−659	6	−574	9	20.25	0.29	1.29	0.24
	12 h	−678	7	−584	10	22.68	0.90	1.22	0.25
	24 h	−687	6	−646	14	30.34	1.85	0.86	0.35

The results of the conducted data analysis contained in Table 2 show, that the hydrogen absorb hydrogenation by the steel causes the change in its corrosion potential value. The steel potential value, depending on the amount of hydrogen absorbed during
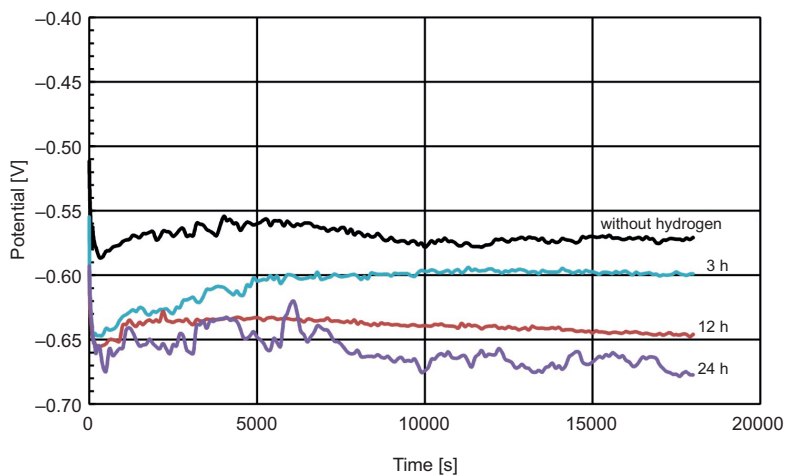
Fig. 9. The course of change in potential values of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 10 mA/cm^2
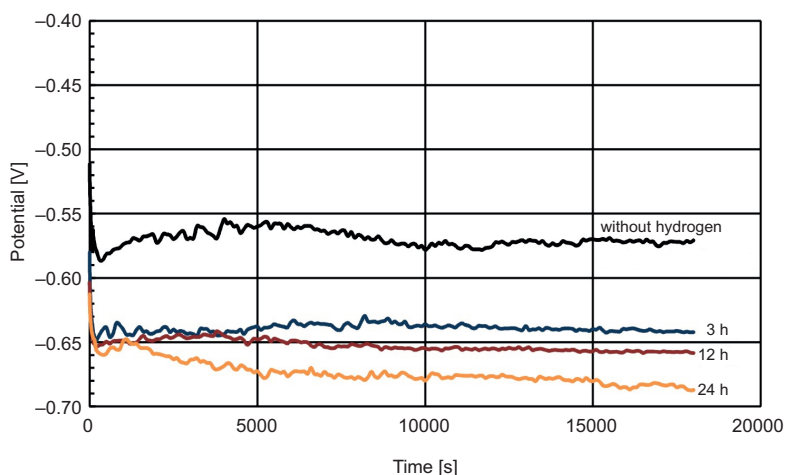

Fig. 10. The course of change in potential values of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 20 mA/cm^2

the cathode polarization was –529 mV up to –646 mV. The decrease of polarization resistance appeared only with the decrease of the corrosion current density from 14.99 μA/cm^2 to 30.34 μA/cm^2, which results in increase of the corrosion speed. On potentiodynamic curves of the researched DC01 steel samples both subjected and non-subjected to the cathode polarization, no passive range has been observed. The increase of potential value caused a constant increase of the current density (Fig. 11–12).
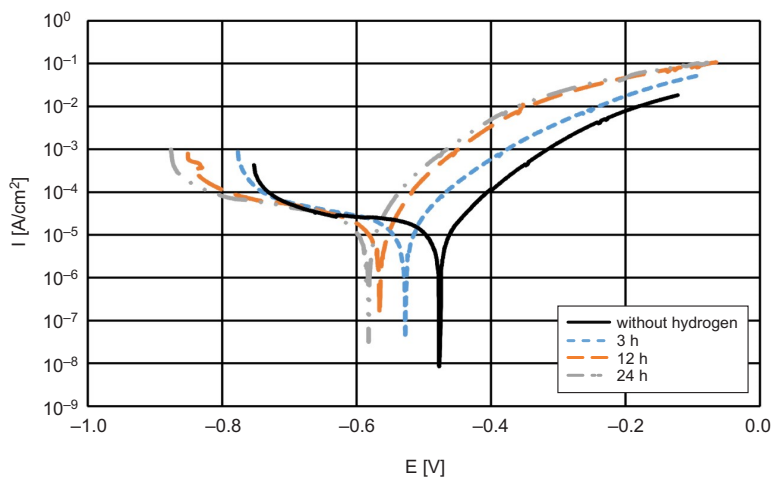
Fig. 11. Polarization curves of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 10 mA/cm^2
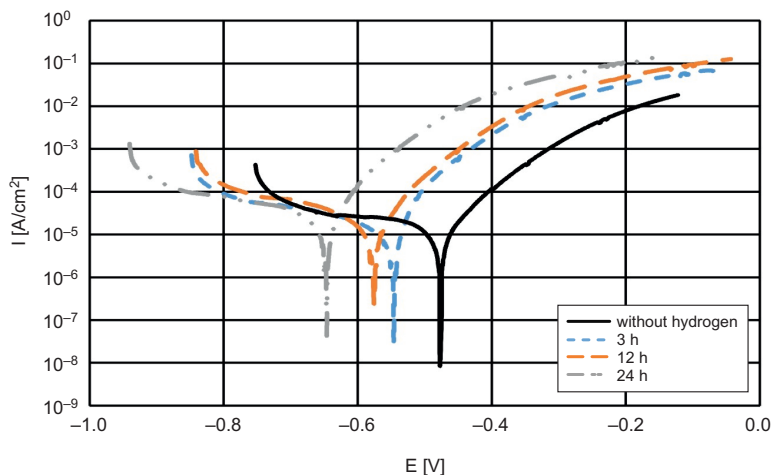

Fig. 12. Polarization curves of DC01 unhydrogenated and hydrogenated steel, studied in the 3% NaCl solution. The hydrogenation environment 0.1 N H_2SO_4 + 2 mg As_2O_3, the current density of 20 mA/cm^2

Summary and conclusions

The conducted research showed, that the content of the hydrogen absorbed by the DC01 steel influence the conditions of the cathode polarization being carried out. The hydrogen concentration in steel increases together with prolonging the duration of the cathode polarization, as well as the increase in the cathode current density. The

hydrogen reaction in the DC01 steel leads to worse corrosion resistance measured in the 3% NaCl water solution. It has been stated, that current density of the cathode polarization and its duration cause the change in the researched corrosion resistance of the DC01 steel measured in the 3% NaCl water solution. It has been also shown, that together with the increase of the hydrogen content in the DC01 steel samples, the value of the corrosion potential (E_{corr}) decreased. The decrease of polarization resistance appeared together with simultaneous increase of the corrosion current density, which led to the increase of the corrosion rate. The higher value of the cathode current density and longer duration of hydrogenation, the lesser the DC01 steel corrosion resistance measured in the 3% NaCl water solution.

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ODPORNOŚĆ KOROZYJNA STALI DC01 W WARUNKACH KATODOWEJ POLARYZACJI

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Abstrakt: Celem prowadzonych badań było określenie odporności korozyjnej stali DC01 poddanej katodowej polaryzacji w zmiennych warunkach. Elektrochemiczne pomiary służące do oceny odporności korozyjnej stali nienawodorowanej poddanej katodowej polaryzacji przeprowadzono metodami obejmującymi pomiar potencjału obwodu otwartego i zarejestrowania zależności $i = f(E)$ podczas badań polaryzacyjnych w trójelektrodowym układzie pomiarowym. Do pomiarów wykorzystano układ składający się z naczynka pomiarowego, potencjostatu AMEL PSW01 System 5000 oraz komputera z oprogramowaniem „CorrWare". Wodorowanie stali zrealizowano w wodnym roztworze 0,1 N kwasu siarkowego(VI) z dodatkiem 2 mg/dm^3 tlenku arsenu(III) jako promotora wnikania wodoru, przy gęstości prądu 10 mA/cm^2 i 20 mA/cm^2 w czasie od 3 do 24 godzin. Zawartość wodoru w stali przed oraz po procesie elektrolitycznego nawodorowania oznaczono przy użyciu analizatora LECO ONH836. Wykazano, że wraz ze zwiększaniem się stężenia wodoru w próbkach badanej stali DC01 (ilość wodoru zależy od parametrów wodorowania – czas i gęstość prądu katodowego) wartość potencjału korozyjnego (E_{kor}) ulegała zmniejszeniu. Spadkowi oporu polaryzacji towarzyszyło jednocześnie zwiększenie gęstości prądu korozyjnego, co skutkowało zwiększeniem szybkości korozji. Im większa wartość gęstości prądu katodowego i dłuższy czas wodorownia, tym odporność stali DC01 na korozję w 3% roztworze NaCl jest mniejsza.

Słowa kluczowe: wodór, zawartość wodoru, polaryzacja katodowa, odporność korozyjna