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THE INFLUENCE OF HYDROGEN ON THE ELECTROCHEMICAL PROPERTIES OF SELECTED TYPES OF STAINLESS STEEL

WPŁYW WODORU NA WŁAŚCIWOŚCI ELEKTROCHEMICZNE WYBRANYCH GATUNKÓW STALI NIERDZEWNYCH

Abstract: The paper presents the results of the influence of electrolytic hydrogenation on the change of electrochemical properties of selected stainless steels and their susceptibility to the formation of galvanic hydrogen. It has been shown that the electrolytic hydrogenation of steel X5CrNi18-10 and X6Cr17 in the state of delivery, not only changes their corrosion resistance, but also contributes to the formation of galvanic hydrogen cells.

Keywords: hydrogenation, corrosion potential, galvanic hydrogen cell, stainless steel

The penetration of hydrogen into metals or alloys depends on different factors including the state of material, the state of stress and strain or the environmental conditions (Fig. 1) [1-7]. Its presence in the structure of metal or alloy causes adverse changes in their properties, and has very negative influence on machine performance. The degradation of mechanical properties of metals and alloys under the influence of hydrogen sorption revealed both, the change and reduction in strength and plastic properties (elongation and contraction). Hydrogen contained in metals or alloys decreases their resistance to corrosion and leads to the strong surface defect. Local differences in the concentration of hydrogen in metals or their alloys, also contribute to the formation of strong galvanic hydrogen cells (GOW) [8].

Taking into consideration the fact that different types of steel (carbon, stainless steel) used for building various kinds of machines, containers, heat exchangers or pipelines are exposed to hydrogen penetration, it is necessary to examine how this penetration affects the changes in mechanical and chemical properties. Until now, most of the research has been carried out on carbon steel [9]. The research, regarding the change of resistance due to hydrogen destruction of different types of steel, will allow to build a mathematical model

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thanks to which, we will be able to assess, in terms of quantity and quality, steel corrosion resistance to hydrogen influence.

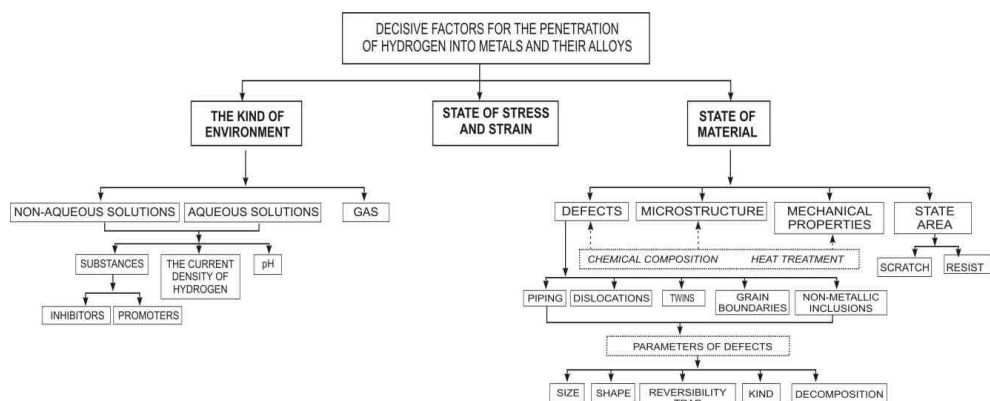


Fig. 1. Factors conditioning the penetration of hydrogen through metals and alloys

Taking the above into consideration, this paper presents the results of the influence of electrolytic hydrogenation on the change of electromechanical properties of stainless steel, but in particular, on the change in values of galvanic cells and electrode potential.

Tested materials

Two types of stainless steel in their initial state without heat processing were used for the test. These two types include: austenitic stainless steel X5CrNi18-10 (1.4301) and ferritic stainless steel X6Cr17 (1.4016). Their chemical composition is shown in Table 1. Mechanical properties of the steel were presented on the base of available standardized data [10].

Table 1
Chemical composition and mechanical properties of the tested steel in the state of delivery

Steel identification	Chemical composition of steel [%]								Mechanical properties [10] [MPa]	
	C	Mn	Si	P	S	Cu	Cr	Ni	R _m	R _{p02}
X5CrNi18-10	0.04	1.05	0.42	0.057	0.01	0.3	18.02	8.65	540-750	230-260
X6Cr17	0.05	0.65	0.46	0.033	0.003	0.10	15.67	0.17	450-600	260-280

Research methodology

The assessment of hydrogen influence on electrochemical properties of the examined stainless steel was based both on the measurement of the change in values of electrode potential (corrosion (E)) of the tested samples before and after hydrogenation and on the change in values of electromotive force (SEM) in the created galvanic hydrogen cells. The measurement of changes in time of E and SEM was conducted without the external polarization.

To achieve a high degree of sample hydrogenation the electrolytic hydrogenation process of the tested materials was carried out in the electrolyser (Fig. 2), filled up with 0.1n sulphuric(VI) acid solution with 2 mg/dm³ of arsenic(III) oxide (promoter of hydrogen penetration).

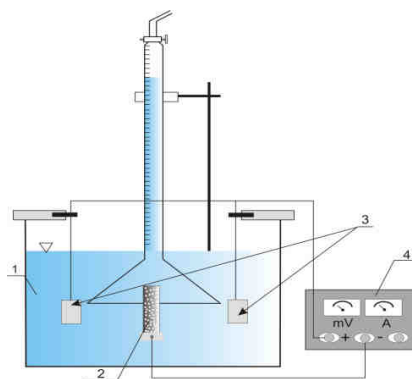


Fig. 2. The system of electrolytic hydrogenation of tested materials: 1 - an aqueous solution of sulphuric(VI) acid with the addition of 2 mg/dm³ As₂O₃, 2 - tested material, 3 - platinum electrodes, 4 - ammeter and voltmeter

During the 180 minutes electrolysis, through the created measurement system flow current with the density of 50 mA/cm². After the hydrogen process, samples were placed in the container located on the station for measuring electrode potential (Fig. 3a). Proper measurement sets, consisted of hydrogenated and non-hydrogenated samples, were created to assess the ability of tested materials to create galvanic hydrogen cells. The sets of such samples, after the process of hydrogenation (180 minutes), were placed on the station for measuring SEM changes of galvanic hydrogen cells (Fig. 3b).

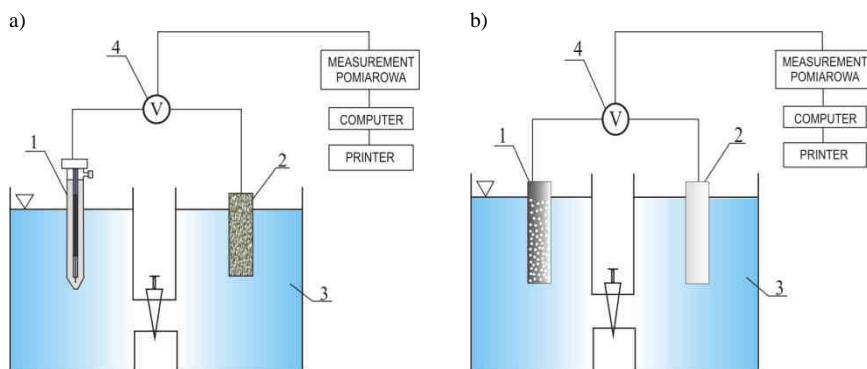


Fig. 3 Diagram of the station for measuring the electrode potential of hydrogenated and non-hydrogenated steel (a): 1 - saturated calomel electrode (NEK), 2 - tested sample (hydrogenated and non-hydrogenated), 3 - 3% aqueous solution NaCl, 4 - voltmeter and diagram of the station for measuring SEM value of created galvanic hydrogen cells in tested materials (b): 1 - hydrogen electrode, 2 - non-hydrogen electrode, 3 - 3% aqueous solution NaCl, 4 - voltmeter

The E and SEM measurement was taken in 21-23°C at 3% aqueous solution NaCl with pH \approx 6.0, used for assessing the influence of sea and mine water. A half-cell calomel was used as a comparative electrode with the saturated solution KCl. The tests of the E and SEM changes of values in tested materials were carried out on the multimeter type UT71E. The results of measurements were registered on a computer with the use of a measuring program.

Results of the research and their further elaboration

The analysis of changes of electrode potential values in tested steels X6Cr17 and X5CrNi18-10 in time (Figs. 4 and 5) shows that the hydrogen absorbed by the steel causes the change of their electrode potential. Due to the influence of absorbed hydrogen, we can observe the change in value of the steel electrode potential X6CrNi17 and X5CrNi18-10 from -0.342 V and -0.3799 V to -0.6 V (steel X6Cr17) and -0.574 V (steel X5CrNi18-10). The increase of steel potentials, respectively by 0.26 V and 0.19 V, in comparison with the recorded values in the first seconds of conducted measurements may indicate not only the defect of their passive layers but also surface and subsurface layers caused by desorbed hydrogen. The quick increase of the potential value for both steels after hydrogenation (Figs. 4 and 5) shows that absorbed hydrogen concentrates largely in their surface and subsurface layers. Above results prove that steel with austenitic structure has got better resistance to hydrogen than the ferritic one. For both tested types of steel, after some time (Figs. 4 and 5), we can observe, at different speed, the decrease of their electrode potentials as well as a different level of hydrogen desorption.

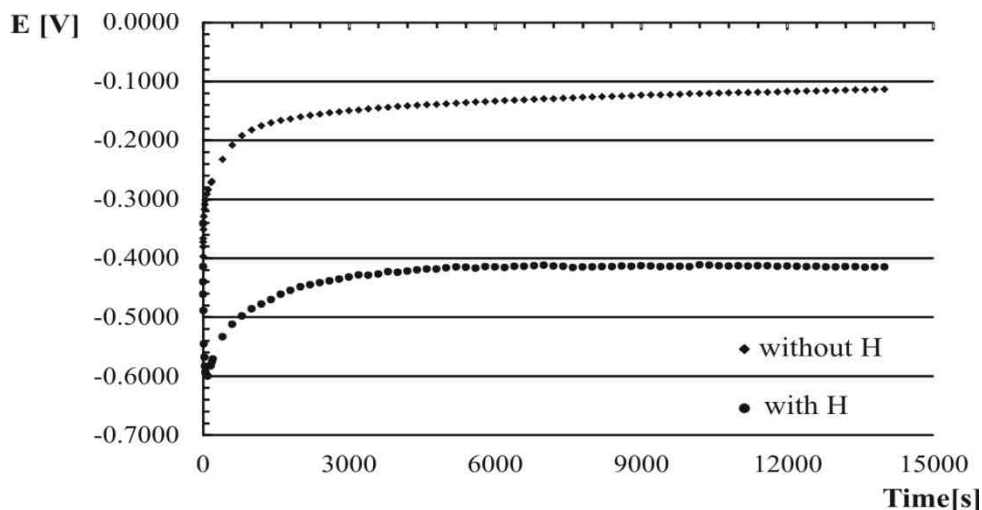


Fig. 4. The course of change in potential values of X6Cr17 non-hydrogenated and hydrogenated steel in 3% NaCl solution

Occurred changes in values of electrode potentials in tested steels with given time, *ie* the process of hydrogen desorption from the subsurface layers (Figs. 3 and 4) proves the existence of reconstruction processes of the damaged passive layers.

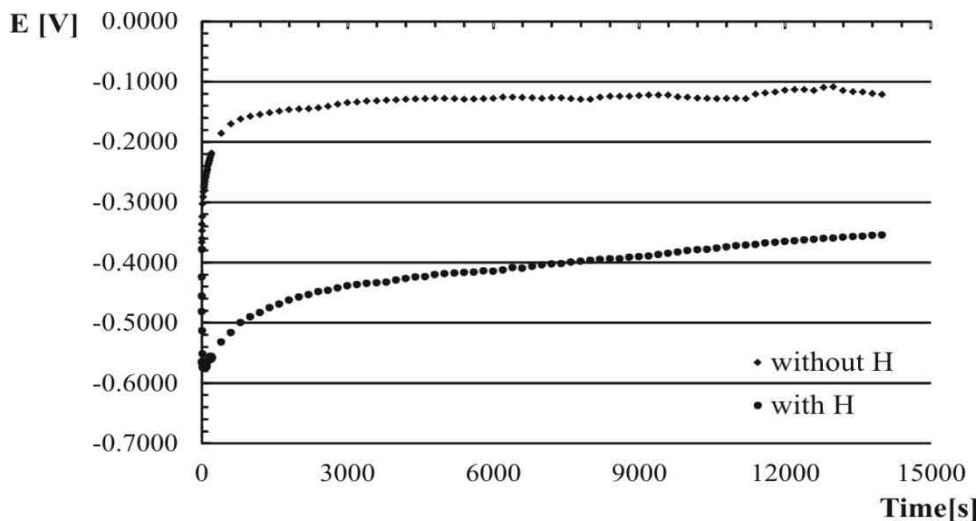


Fig. 5. The course of change in potential values of X5CrNi18-10 non-hydrogenated and hydrogenated steel in 3% NaCl solution

The different levels of damage of surface and subsurface layers in tested types of steel due to the hydrogen influence, are the result of their different chemical compositions, but in particular different contents of chrome and nickel (Table 1) as well as different microstructure.

As for the ferritic steel X6Cr17, after 500 seconds, we can observe a significant stabilization of electrode potential value at the level of 0.471 V (Fig. 4). However, the same process cannot be observed with the austenitic steel X5CrNi18-10 (Fig. 5). The difference in values of electrode potentials in hydrogenated steels X5CrNi18-10 and X6Cr17, between the first measurement point and the point in which we can observe the stabilization of the potential, amounts to 25 and 73 mV, respectively.

The potential value of the latter steel, after the stabilization process, is higher than the value recorded during the first seconds of measurement.

The course of change of electromotive forces SEM in galvanic hydrogen cells was presented in Figure 6. Tests show that the difference in the amount of absorbed hydrogen by steel electrodes causes the formation of galvanic hydrogen cells of a significant value.

In both tested types of steel, in the initial period of time (*ie* about 140 seconds), we can observe the increase of SEM value in created galvanic hydrogen cells. In 3% aqueous solution NaCl, cells made of X6Cr17 steel reach the maximum value of 350 mV and those made of X5CrNi18-10 steel reach the level of 417 mV. Lower value of the galvanic cells created from X6Cr17 steel comparing with X5CrNi18-10 one indicates a bigger penetration and trapping of hydrogen in the depth of its structure. After about 140 seconds, for both tested types of steel, the SEM value of galvanic hydrogen cells goes down. The SEM stabilization process of galvanic hydrogen cell created from the samples made of X6Cr17 steel takes place after about 4000 seconds and for the samples made of X5CrNi18-10 steel after a much longer time *ie* 1200 seconds. The stabilization is observed at the level of 260 and 220 mV, respectively. It is mainly caused by a different susceptibility of both steels

to absorb hydrogen. The X6Cr17 steel, which has got a ferritic structure, indicates a higher ability to absorb hydrogen than the austenitic one X5CrNi18-10. This phenomenon is consistent with the already known susceptibility of different steel microstructures for gas diffusion. For the steel with a ferritic structure the network diffusion coefficient estimates at the level of 10^{-7} - 10^{-9} cm²/s, and for the steel with a austenitic structure is lower - 10^{-11} cm²/s.

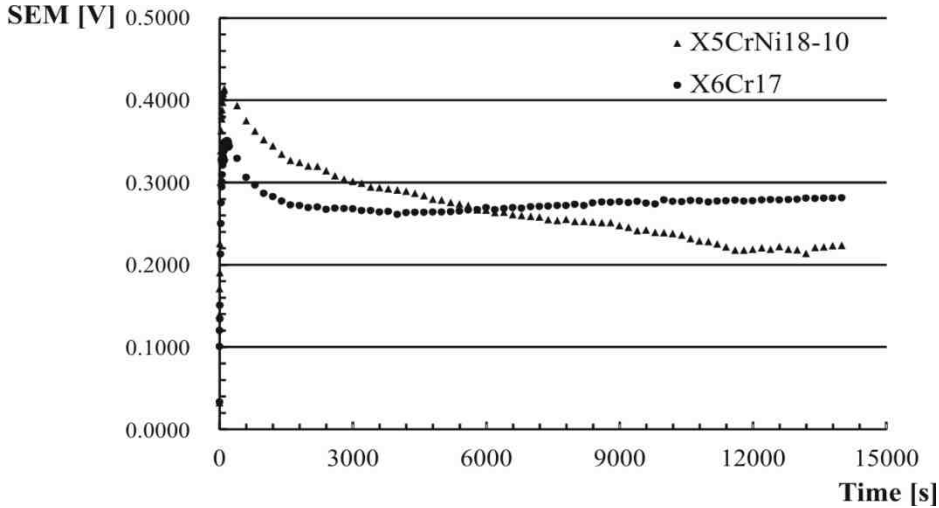


Fig. 6. The course of change of SEM values of galvanic hydrogen cells created from X5CrNi18-10 and X6Cr17 steel in 3% NaCl solution

The assessment of changes in electrochemical properties of stainless steels under the influence of absorbed hydrogen was based on the values of electrochemical sensitivity (1)-(3), formed on the basis of the electrode potentials measured in the 1st and 14000th second, and the maximum SEM value present in the initial period of cell formation and after its stabilization, *ie* in 14000th second (Fig. 7):

$$\beta_1 = \frac{E_{(1)}}{E_{H(1)}} \quad (1)$$

$$\beta_2 = \frac{E_{H(1)}}{E_{H(14000)}} \quad (2)$$

$$\beta_{SEM} = \frac{SEM_{(max)}}{SEM_{(14000)}} \quad (3)$$

where: $E_{(1)}$, $E_{H(1)}$ - the electrode potential value of non-hydrogenated and hydrogenated steel occurred in the first second, $E_{H(14000)}$ - the electrode potential value of non-hydrogenated and hydrogenated steel, measured in the 14000th second, $SEM_{(max)}$, $SEM_{(14000)}$ - the SEM value of galvanic hydrogen cells at the maximum and occurred in the 14000th second of the measurement.

The smaller value of the electromechanical sensitivity indicator, the bigger susceptibility and consequently smaller resistance to hydrogen penetration.

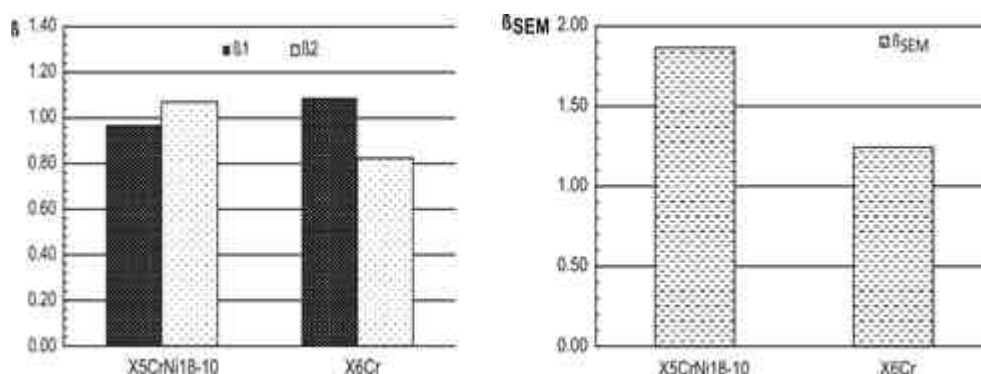


Fig. 7. The value of electrochemical sensitivity indicators to hydrogen influence on the tested stainless steel

The analysis of value changes of electrochemical sensitivity indicators of tested stainless steels shows (Fig. 7) that hydrogen causes substantial changes in their electrochemical properties. It was also proved that X6Cr17 steel is more susceptible to hydrogen operation than X5CrNi18-10 one.

Summary

Conducted research showed that the electrolytic hydrogenation of stainless steel X5CrNi18-10 and X6Cr17 changes the values of electrode potentials comparing to the output levels. The phenomenon of increased electrode potentials of tested steels upon absorption of hydrogen results in a change of their corrosion resistance. It was proved that different levels of hydrogen absorption in tested steels may lead to the formation of galvanic hydrogen cells. On the basis of this study, it can be concluded that constructions or machines made of stainless steel X6Cr17, which operate in environments containing hydrogen, will be more susceptible to hydrogen degradation than constructions and machines made of steel X5CrNi18-10.

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Abstrakt: Przedstawiono wyniki badań wpływu elektrolitycznego wodorowania na zmianę właściwości elektrochemicznych wybranych gatunków stali nierdzewnych oraz podatności ich do tworzenia galwanicznych ogniw wodorowych. Wykazano, że elektrolityczne wodorowanie stali X5CrNi18-10 i X6Cr17 w stanie dostawy powoduje zmianę ich odporności korozyjnej, ale także przyczynia się do powstawania galwanicznych ogniw wodorowych.

Słowa kluczowe: wodorowanie, potencjał korozyjny, galwaniczne ogniwo wodorowe, stal nierdzewna