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INFLUENCE OF DIFFUSION BORIDING AND LASER BORIDING ON CORROSION RESISTANCE HARDOX 450 STEEL

Summary

The article presented an influence of diffusion boriding and laser boriding on microstructure, microhardness and corrosion resistance of Hardox 450 steel. After the boron modification process of Hardox 450 steel was obtained an increase result of microhardness and resistance to corrosion. After the diffusion boriding obtained needle-like microstructure of microhardness 1800-1500 HV0.1. Whereas after laser boriding microstructure was consisted of a remelted zone (MZ), heat-affected zone (HAZ) and core. In the remelted zone enriched in boron the microhardness was about 1600 HV 0.1. Corrosion resistance tests showed, that the higher corrosion resistance in solutions of pH = 3.5 and pH = 7.0 have a diffusion boriding layers, whereas in the pH = 11.0, the laser boriding layers.
Key words: *diffusion boriding, laser boriding, microstructure, microhardness, corrosion resistance*

WPŁYW BOROWANIA DYFUZYJNEGO I LASEROWEGO NA ODPORNOŚĆ KOROZYJNĄ STALI HARDOX 450

Streszczenie

W artykule przedstawiono wpływ borowania dyfuzyjnego i laserowego na mikrostrukturę, mikrotwardość i odporność korozyjną stali Hardox 450. Po procesie modyfikacji stali Hardox 450 borem uzyskano zwiększenie mikrotwardości i odporności na korozyjnej. W wyniku procesu borowania dyfuzyjnego warstwa miała iglastą strukturę o mikrotwardości ok. 1800–1500 HV0,1. Natomiast w wyniku borowania laserowego uzyskano budowę strefową składającą się ze strefy przetopionej, strefy wpływu ciepła oraz rdzenia. W strefie przetopionej wzbogaconej w bor mikrotwardość wynosiła ok. 1600 HV0,1. Badania odporności korozyjnej wykazały, że lepszą odporność korozyjną w roztworach pH = 3,5 oraz pH = 7,0 posiadają warstwy borowane dyfuzyjnie, natomiast w pH = 11,0 warstwy borowane laserowo.
Słowa kluczowe: *borowanie dyfuzyjne, borowanie laserowe; mikrostruktura, mikrotwardość, odporność na korozję*

1. Introduction

The Hardox steels are characterized by high resistance to wear by friction, impact strength, good ductility, weldability and the possibility of the use of machining. The disadvantage of this type of steel is low corrosion resistance, which limits their application to the details of operating in aggressive environments [4]. There are only a few articles on the corrosion resistance of the Hardox steels [7, 14].

The authors [14] have studied the corrosion resistance of Hardox 400 and 500 steels. The obtained results were compared to data obtained by the producer of steel. According to the manufacturer Hardox 400 steel at 3% NaCl (pH = 7) the corrosion rate is 0.51 mm/year, while at pH = 6.25 to 1.62 increases mm/year. The studies of corrosion, the authors, the corrosion rate of Hardox 400 steel in salt spray chamber was 1.51 mm/year and a special test chamber with 2.77 mm/year but for Hardox 500 steel in salt spray chamber 1.62 mm/year in a special test chamber with 2.20 mm/year. The results correspond with the results provided by the manufacturer. According to the standard PN-78/H-04608 corrosion rate of Hardox 400 and 500 steels in the range 1.51-2.77 mm/year is classified into 8 degree of corrosion resistance, resistance group defined as unstable materials in these environments. In addition, Hardox 400 steel exposed in a chamber with a special test showed marked pitting corrosion, and therefore determined the rate of corrosion is not an appropriate measure of the corrosion resistance of the material.

In reference [7] carried out a comparative study of corrosion resistance in salt spray chamber of Hardox 400 and 500 steels with HTK 700H, 900H HTK and AR 400. Studies have shown greater resistance corrosion of Hardox steel than others. The HTK steels and AR 400 were observed occurrence of pitting corrosion in Hardox 400 and 500 steels dominated uniform corrosion. It was found that the corrosion resistance of low-alloy, high strength martensitic steels in environments used is small and close to unalloyed steels.

In order to improve the corrosion resistance of steel Hardox is possible to apply protective coatings such as paint, oxide layers, coating the cathode or anode or the use of diffusion methods. To one of them should be diffusion boriding [2, 3, 12, 13, 16] or laser boriding [2, 10, 13,19]. The received layers these methods are characterized, in addition to high corrosion resistance [8, 11, 17, 18], a high microhardness [2, 3, 10, 12, 13, 16, 19], resistance to wear by friction [2, 3, 12, 13, 16], heat-resistant [12, 16] and the resistance in liquid metal alloys [9].

In reference [6] investigated the effect of 10% solutions of HCl, H_2SO_4, HNO_3 and H_3PO_4 on the corrosion resistance of diffusion boronizing of low carbon DC04 steel in 10% Na_2CO_3 and 90% $Na2B_4O_7$ at 900^0C during 1 hour at 200 mA/cm^2. Effect od diffusion boronized was observed on the corrosion resistance test of steel.

The authors [5] studied the effect of diffusion boronizing of H13 steel on the corrosion resistance in a 5% and 30% H_2SO_4 at 950^0C H_3PO_4 during 6h. It was found that the diffusion boronizing positive effect on the corrosion resistance of the tested steel.

In reference [1] investigated the effect of time diffusion boronizing of SAE 1010, SAE 1040, D2 and 304 steels in 10% H2SO4 solution for corrosion resistance. The best corrosion resistance had steels after diffusion boronizing at 900^0C during 8h.

The aim of this study is to investigate the effect of diffusion boronizing and laser boronizing on the corrosion resistance of Hardox 450 steel in solutions of different pH.

2. Research methodology

The material investigated was Hardox 450 steel and its chemical composition is given in Table 1.

Table 1.Chemical composition of Hardox 450 steel
Tab. 1. Skład chemiczny stali Hardox 450

Chemical composition [%wt]							
C	**Mn**	**Si**	**P**	**S**	**Cr**	**Mo**	**B**
0.258	1.239	0.382	0.015	0.001	0.729	0.033	0.002

Source: own study / Źródło: badania własne

Diffusion boronizing was performed at 950^0C for 4h. The boronizing mixture used in the process contained: amorphous boron, KBF_4as activator and carbon black as filler. After diffusion boronizing specimens were hardened in water from 850^0C and then tempered at 560^0C for 1h.

Laser boriding was relied on alloying with boron on Hardox 450 steel as delivered by the manufacturer. Amorphous boron was applied to the steel in the form of paste having a thickness of about 40 microns. Laser heat treatment (LHT) was carried out using TRUMPF TLF 2600 Turbo CO_2 laser of nominal power of 2.6 kW, which is located in the Laboratory of Laser Technology of Department Division of Machining of Poznan University of Technology. The parameters used in the experiment were: laser beam power P = 0.91 kW, laser beam radiation density q = 28.98 kW/cm^2, scanning laser beam velocity v = 3.84 m/min, distance between axes of adjacent tracks f = 0.50 mm and laser beam diameter d = 2 mm.

Microstructure observations were carried out using Metaval Carl Zeiss optical microscope equipped with a camera Moticam.

To determine microhardness profiles a ZWICK 3212B Vickers hardness tester was used. Indention load of 50 G and loading time 15 seconds were used in this study, based on the standard PN-EN ISO 6507-1 [15].

Corrosion resistance tests were performed on a potentiostat - galvanostat 0531 EU & IA Atlas Sollich at 22^0C on the surface is limited to 50 mm^2 in three solutions:

- acid solution: H_2SO_4 (pH 3.5),
- neutral solution: distilled water (pH 7.0),
- alkaline solution: NaOH (pH 11.0).

The auxiliary electrode were platinum electrode and reference electrode was using saturated calomel electrode. The test procedure and recording of the results was performed using computer programs AtlasCorr and AtlasLab. The polarization of the samples was carried out in the direction of the anode in the range of potentials from -1.5 to 1.5 V. The tests were performed at a rate of potential change 1mV/min. Based on the analysis of dynamic curves potentiometer determined corrosion current and corrosion potential.

3. Results and discussion

Hardox 450 steel structure in the initial state is composed of tempered martensite (Fig. 1), while the diffusion boriding and hardening and tempering boronized layer had a needle like structure and was composed of iron borides FeB and Fe_2B which is closely associated with the as a core (Fig. 2). The microhardness of Hardox 450 steel was about 500 HV0.1, while after diffusion boriding was 1800-1500 HV0.1 on the surface (Fig. 3). This layer was about 80 µm thick and was closely related to a sorbite core.

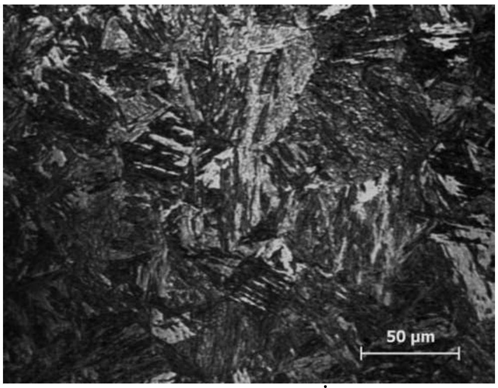

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Fig. 1. Microstructure of Hardox 450 steel
Rys. 1. Mikrostruktura stali Hardox 450

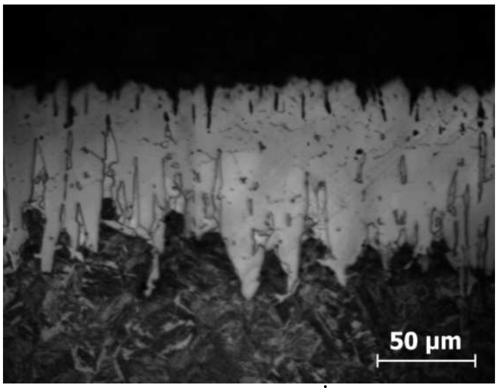

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Fig. 2. Microstructure of diffusion borided layer at 950°C for 4h and quenching and tempering
Rys. 2. Mikrostruktura warstwy borowanej dyfuzyjnie w 950°C przez 4h i ulepszonej cieplnie

Figure 4 shows the microstructure after laser boronizing. The resulting microstructure consists of a remelted zone (MZ), heat-affected zone (HAZ) and core (Fig. 4a). The remelted zone was about 90 µm. In remelted zone there is borides- martensite eutectic, of microhardness lower than iron borides (Figs. 4b and 4c). Figure 5 shows the microhardness of Hardox 450 steel after laser boronizing. In the remelted zone microhardness in alonge the axis of track was 1580÷1600 HV0,1 and decrease to 580-550 HV0.1 in heat-affected zone until the sorbite core of microhardness 400HV0.1.

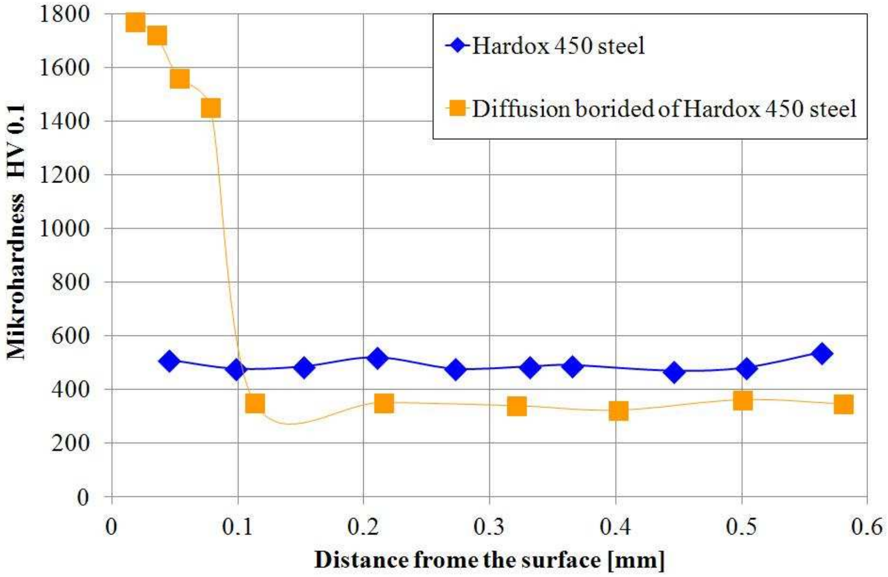

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Fig. 3. Microhardness profiles of Hardox 450 steel of initial state, and diffusion borided at 950°C for 4h and quenching and tempering
Rys. 3. Profile mikrotwardości stali Hardox 450 w stanie wyjściowym oraz po borowaniu i ulepszaniu cieplnym

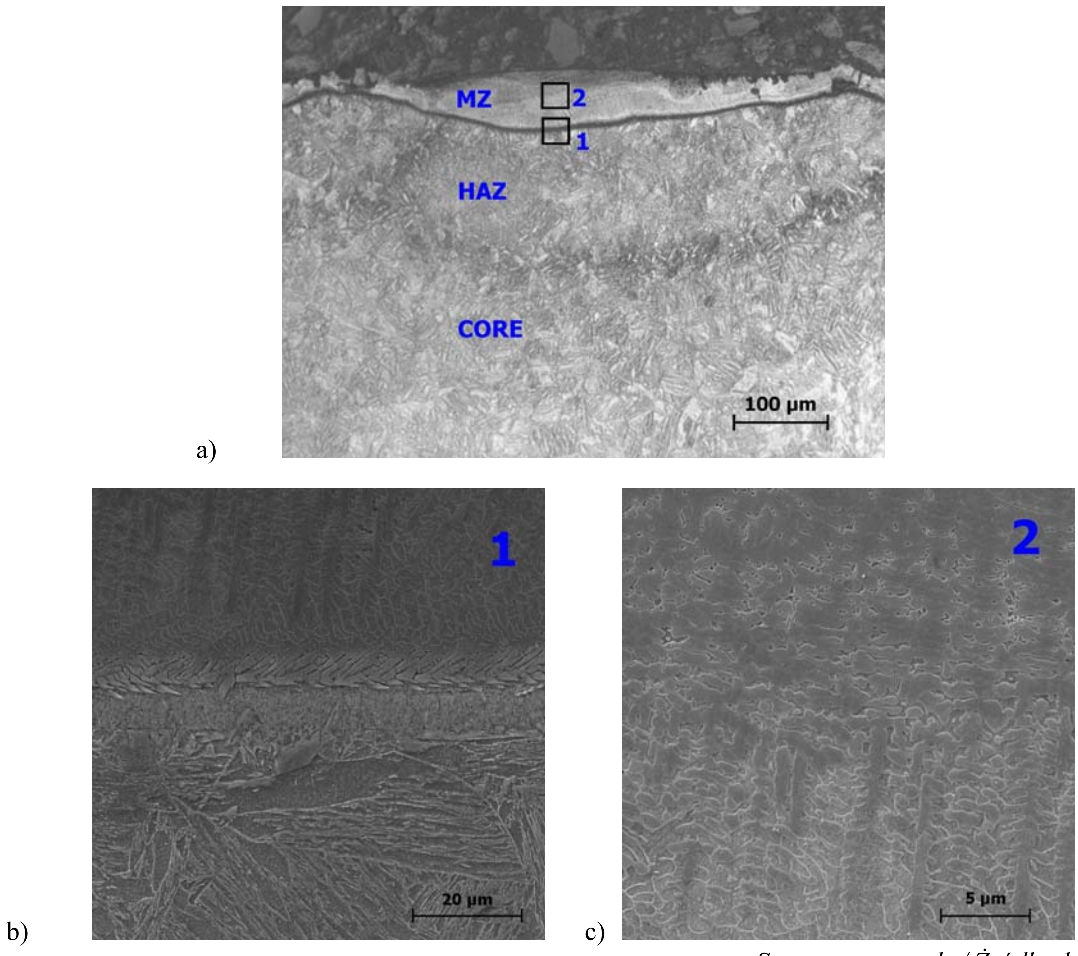

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Fig. 4. Microstructure of laser borided layer; LHT: P = 0,91 kW, v = 3,84 m/min, f = 0,50 mm;
a) laser track, b) boundary between MZ and HAZ, c) MZ
Rys. 4. Mikrostruktura warstwy borowanej laserowo; LOC: P = 0,91 kW, v = 3,84 m/min, f = 0,50 mm;
a) ścieżka laserowa, b) granica między SP a SWC, c) SP

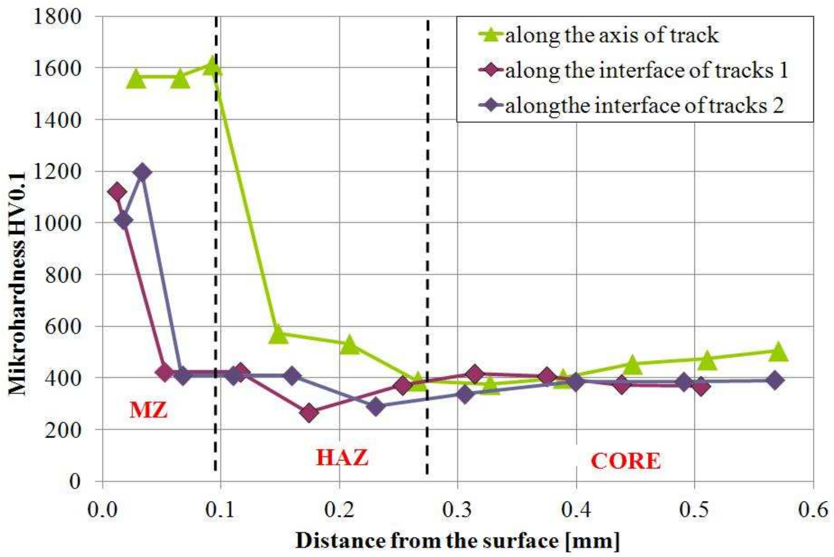

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Fig. 5. Microhardness profiles of Hardox 450 steel of laser borided layer; LHT: P = 0.91 kW, v = 3.84 m/min, f = 0.50 mm
Rys. 5. Profile mikrotwardości stali Hardox 450 po borowaniu laserowym; LOC: P = 0,91 kW, v = 3,84 m/min, f = 0,50 mm

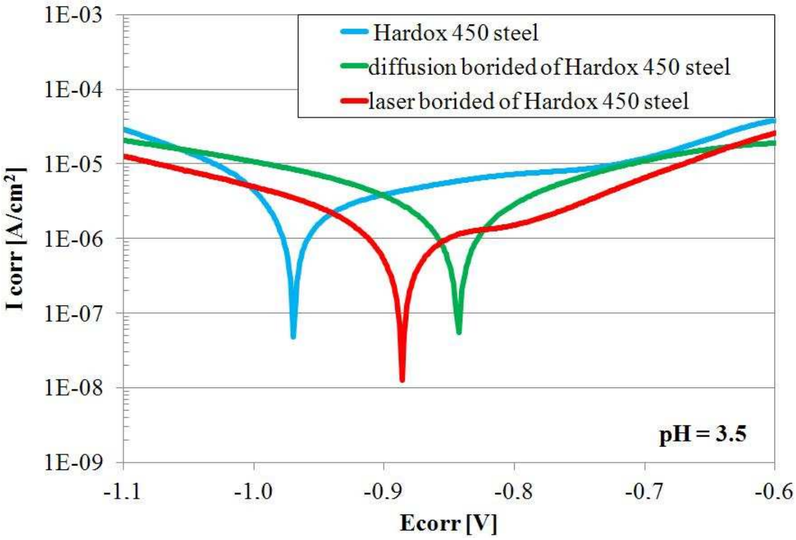

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Fig. 6. Corrosion resistance of Hardox 450 steel in pH = 3.5 solution
Rys. 6. Odporność korozyjna stali Hardox 450 w roztworze o pH =3,5

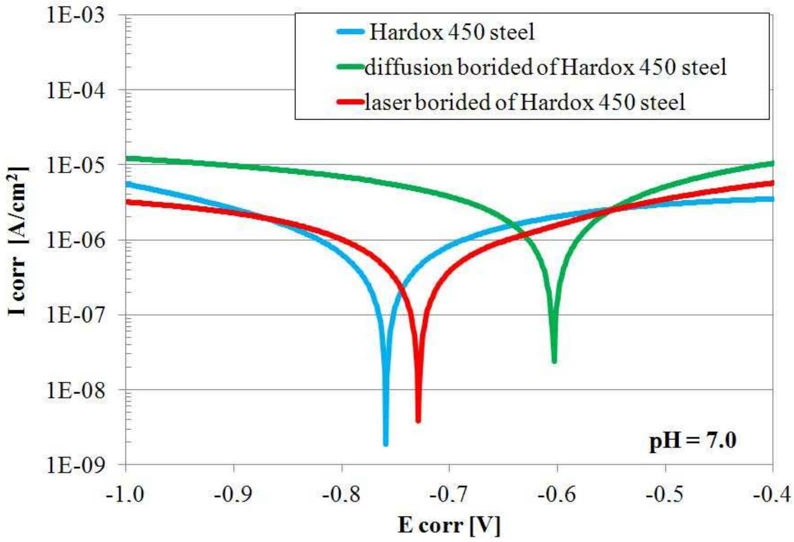

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Fig. 7. Corrosion resistance of Hardox 450 steel in pH = 7.0 solution
Rys. 7. Odporność korozyjna stali Hardox 450 w roztworze o pH = 7,0

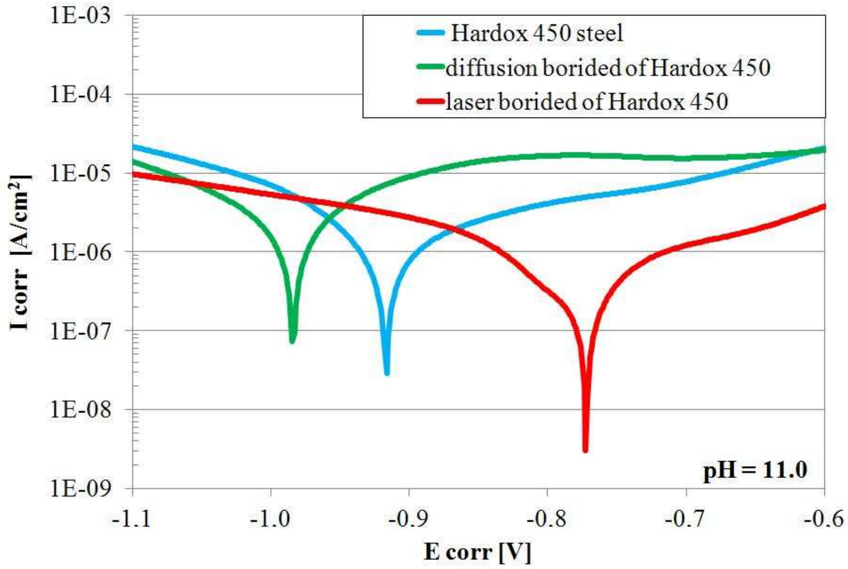

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Fig. 8. Corrosion resistance of Hardox 450 steel in pH = 11.0 solution
Rys. 8. Odporność korozyjna stali Hardox 450 w roztworze o pH = 11,0

Table 2. Corrosion current and corrosion potential of research samples of Hardox 450 steel
Tabela 2. Prąd korozyjny i potencjał badanych próbek ze stali Hardox 450

Sample	Type of medium	Current I_{corr} [A·cm^2]	Potential E_{corr} [V]
Annealing of Hardox 450	pH = 3.5	4.71E-07	-9.70E-01
	pH = 7.0	7.80E-08	-7.59E-01
	pH = 11.0	1.83E-07	-9.16E-01
Diffusion borided of Hardox 450 steel	pH = 3.5	2.72E-07	-8.42E-01
	pH = 7.0	2.17E-07	-6.03E-01
	pH = 11.0	5.21E-07	-9.85E-01
Laser borided of Hardox 450 steel	pH = 3.5	1.26E-07	-8.86E-01
	pH = 7.0	5.54E-08	-7.29E-01
	pH = 11.0	4.96E-08	-7.72E-01

Source: own study / Źródło: badania własne

Results of corrosion tests are shown in Figures 6-8. They show the current density curves as a function of predetermined potential, where as the values of electrochemical parameters determined based on the analysis of the curves shown in Table 2.

In solution at pH = 3.5 the lowest corrosion resistance was characterized in the annealed sample. The better corrosion resistance of the sample had after diffusion boronizing, as obtained for the lowest values of corrosion current and corrosion potential was shifted towards positive values. Inferior corrosion resistance had layer after laser bonizing. Perhaps worse the lowest corrosion resistance results was from the aggressive corroding medium, which is an acid-based solution. The same result was obtained for the solution at pH = 7.0, however, potentiodynamic curves were shifted in direction of more positive corrosion potential. However, for the research for the solution at pH = 11.0 the best corrosion resistance was characterized by the laser treatment sample, because it had the lower corrosion current value of the corrosion potential was shifted toward positive values. A solution of pH = 11.0 is alkaline reagent that is way it had a better corrosion resistance due to the fact that the iron reacts harder more strongly than acids. At the same time the addition of boron in remelted zone positive influence to increase corrosion resistance.

4. Conclusions

- Analysis of literature and studies have shown that it is advantageous use of diffusion boriding and laser boriding in order to improve the corrosion resistance of Hardox 450 steel.
- In the medium of pH = 3.5 and pH = 7.0 diffusion boriding samples characterized by resistance to corrosion then the laser boriding samples.
- In the medium of pH = 11.0 laser boriding samples characterized by resistance to corrosion then the diffusion boriding samples becouse of due to less influence of the iron in alkaline solution.

5. References

[1] Atık E., Yunker U., Merıç C.: The effects of conventional heat treatment and boronizing on abrasive wear and corrosion of SAE 1010, SAE 1040, D2 and 304 steels. Tribology International, 2003, 36, 155-161.
[2] Bartkowska A., Pertek-Owsianna A., Bartkowski D.: Odporność korozyjna stali C45 po borowaniu dyfuzyjnym i laserowym. Inżynieria Materiałowa, [in reviewing].
[3] Grachev S. V., Mal'tseva L. A., Mal'tseva T. V., Kolpakov A. S. and Dmitriev M. Yu.: Boronizing and borochromizing in a vibrofluidized bed. Metal Science and Heat Treatment, 1999, 41, 465-468.
[4] http://www.ssab.com/pl/Products--Services/Products--Solutions/Products/ - strona domowa z dnia 5.01.2013.

[5] Kariofillis G. K., Kiourtsidis G. E., Tsipas D.N.: Corrosion behavior of borided AISI H13 hot work steel. Surface & Coatings Technology, 2006, 201, 19-24.
[6] Kartal G., Kahvecioglu O., Timur S.: Investigating the morphology and corrosion behavior of electrochemically borided steel. Surface & Coatings Technology, 2006, 200, 3590-3593.
[7] Konat Ł., Głuszko M., Kłak M., Pękalski G., Świeboda J.: Procesy korozyjne niskostopowych, wysokowytrzymałych stali martenzytycznych (Hardox, HTK, AR 400). Konferencja Naukowo-Techniczna Maszyny i Pojazdy dla Budownictwa i Górnictwa Skalnego, Wrocław, 25-26.09.2008, 272-280.
[8] Krastev D.: Improvement of Corrosion Resistance of Steels by Surface Modification. Corrosion resistance – Chapter 13. InTech, 2012, 295-316.
[9] Lou D.C., Akselsen O.M., Onsøien M.I., Solberg J.K., Berget J.: Surface modification of steel and cast iron to improve corrosion resistance in molten aluminium. Surface & Coatings Technology, 2006, 200, 5282-5288.
[10] Paczkowska M., Ratuszek W., Waligóra W.: Microstructure of laser boronized nodular iron. Surface & Coatings Technology 205, 2010, 2542-2545.
[11] Pertek A.: Corrosion resistance of borided layer produced on constructional steel. Physico-Chemical Mechanics of Materials Problems of Corrosion and Corrosion Protection of Materials, 2002, 3, 520-523.
[12] Pertek A.: Kształtowanie struktury i właściwości warstw borków żelaza otrzymanych w procesie borowania gazowego. Wyd. Politechniki Poznańskiej, Poznań 2001.
[13] Pertek A., Kapcińska-Popowska D., Bartkowska A., Wiśniewski K. Wpływ borowania dyfuzyjnego i laserowego na mikrostrukturę i wybrane właściwości stali Hardox 450. Inżynieria Materiałowa, 2013, 5, 530-533.
[14] Pękalski G., Konat Ł., Haimann K., Kłak M., Łętkowska B.: Makroskopowa, mikroskopowa i grawimetryczna ocena przebiegu korozji stali Hardox. Konferencja Naukowo - Techniczna Maszyny i Pojazdy dla Budownictwa i Górnictwa Skalnego. Wrocław, 25-26.09.2008, 168-178.
[15] PN-EN ISO 6507-1, Metale, Pomiar twardości sposobem Vickersa. Część 1: Metoda badań. Warszawa, czerwiec 2007.
[16] Przybyłowicz K.: Teoria i praktyka borowania stali. Politechnika Świętokrzyska, Kielce 2000.
[17] Tavakoli H., Mousavi Khoie S.M.: An electrochemical study of the corrosion resistance of boride coating obtained by thermo-reactive diffusion. Materials Chemistry and Physics, 2010, 124, 1134-1138.
[18] Wang H., Zhao Y., Yuan X., Chen K., Xu R.: Effects of Boronizing Treatment on Corrosion Resistance of 65Mn Steel in two Acid Mediums. Physics Procedia, 2013, 50, 124-130.
[19] Wiśniewski K., Pertek A.: Struktura i właściwości stali konstrukcyjne borowanej laserowo. Inżynieria Powierzchni 2'2009, ISSN 1426-1723, 123-125.