Aneta BARTKOWSKA[1], **Aleksandra PERTEK-OWSIANNA**[1], **Damian PRZESTACKI**[2]
[1] Institute of Materials Science and Engineering, Poznan University of Technology
[2] Institute of Mechanical Technology, Poznan University of Technology
pl. M. Skłodowskiej-Curie 5, 60-965 Poznan, Poland
e-mail: aneta.bartkowska@put.poznan.pl

LASER MODIFICATION OF B-Ni GALVANIC-DIFFUSION LAYER

Summary

The paper presents test results for boronickelized C45 steel after laser surface modification. Influence of laser heat treatment on the microstructure, microhardness, cohesion and wear resistance of surface layer was investigated. The process of galvanic-diffusion boronickelized layer consists of nickel plating followed by diffusion boronizing. For nickel plating Watts bath was used, which uses a combination of nickel sulfate and nickel chloride, along with boric acid. Diffusion boronizing treatment was used in the gas-contact method at temperature 950°C for 4 h in boronizing powder, containing: amorphous boron, KBF_4 as activator and carbon black as a filler. The laser heat treatment (LHT) was carried out with technological laser TRUMPF TLF 2600 Turbo CO_2 of nominal power 2.6 kW. Laser modification of the boronickelized layer was carried out with laser power P 1.04 kW and at laser beam scanning rate v: 0.67 $m \cdot min^{-1}$, 1.12 $m \cdot min^{-1}$, 2.88 $m \cdot min^{-1}$ and laser beam d = 2 mm. After boronickelizing the microstructure of surface layer was composed of: compact-continuous subsurface zone of microhardness 1200 HV0,1, and deeper situated zone , at microhardness similar to needle-like iron borides. After laser heat treatment with re-melting, a new layer was obtained, which included: re-melted zone (MZ), heat affected zone (HAZ) and a substrate, with a mild microhardness gradient from the surface to the substrate. The microhardness measured along the axis of track after laser heat treatment of the boronickelized layer was about 1100 HV0,1. As a result of the influence of laser beam, the new layer was characterized by good properties in comparison to boronized and boronickelized layers.

Key words*: laser remelting, diffusion boronizing, nickel plating, microstructure, microhardness*

LASEROWA MODYFIKACJA WARSTWY B-Ni GALWANICZNO-DYFUZYJNEJ

Streszczenie

W pracy przedstawiono wyniki badań boroniklowanej stali C45 po laserowej modyfikacji. Badano wpływ laserowej obróbki cieplnej na mikrostrukturę, mikrotwardość, kohezję i odporność na zużycie przez tarcie wytworzonej warstwy. Proces wytwarzania galwaniczno-dyfuzyjnej warstwy boroniklowanej składał się z: nakładania wstępnej powłoki galwanicznej niklu i następnego borowania dyfuzyjnego. Do niklowania galwanicznego użyto kąpieli Wattsa, która składała się z siarczanu niklawego, chlorku niklawego, kwasu borowego. Borowanie dyfuzyjne prowadzono metodą gazowo-kontaktową w temperaturze 950°C w proszku borującym zawierającym bor amorficzny, aktywator KBF_4 i wypełniacz w postaci sadzy. Laserowa obróbka cieplna (LOC) była wykonana przy użyciu lasera technologicznego CO_2 firmy TRUMPF TLF 2600 Turbo o mocy nominalnej 2,6 kW. Laserową modyfikację warstwy boroniklowanej przeprowadzono przy użyciu mocy lasera P = 1,04 kW i prędkości skanowania wiązką laserową v: 0,67 $m \cdot min^{-1}$, 1,12 $m \cdot min^{-1}$, 2,88 $m \cdot min^{-1}$, średnicy wiązki lasera d = 2 mm. Po boroniklowaniu struktura warstwy wierzchniej składa się z: przypowierzchniowej zwartej ciągłej strefy o mikrotwardości 1200 HV0,1 i głębiej położonej o strukturze iglastej odpowiadającej mikrotwardości borkom żelaza oraz rdzenia. Po laserowej obróbce cieplnej z przetopieniem otrzymano nową warstwę składającej się z: strefy przetopionej (SP), strefy wpływu ciepła (SWC) i rdzenia o łagodnym gradiencie mikrotwardości od powierzchni do rdzenia. Mikrotwardość w osi ścieżki warstwy wierzchniej laserowo obrobionej cieplnie wynosiła 1100 HV0,1. W wyniku oddziaływania wiązki lasera otrzymana warstwa charakteryzowała się dobrymi właściwościami w stosunku do warstw borowanej i boroniklowanej.

Słowa kluczowe*: laserowe przetapianie, borowanie dyfuzyjne, niklowanie galwaniczne, modyfikacja, mikrostruktura, mikrotwardość*

1. Introduction

Surface engineering plays an important ant role in surface layer modifications whose purpose is to improve the properties of materials [1, 2]. Surface engineering includes treatments such as: heat treatment, thermo-chemical treatment, galvanic treatment as well as laser heat treatment (LHT) [1-3]. A major advantage of laser treatment is the possibility to improve properties of a defined material surface. Currently, the leading processes of laser heat treatment include among others: laser hardening [4, 5], laser alloying with elements, phases or alloys [6-8] and laser remelting of surface layer [9-11]. One method of surface layer modification is diffusion boronizing, which improves properties such as microhardness, wear resistance and corrosion resistance. Boronized layers are composed of two phases: FeB in subsurface, which can demonstrate increased brittleness and delamination from substrate; and Fe_2B phase, which has a needle-like structure and closely related to substrate [9, 12]. Diffusion boronizing is carried out on iron alloys such as steel, cast iron or non-ferrous metals such as nickel, chromium, vanadium and their alloys. Subsurface brittleness can be reduced by single-phase boride layer, which is composed of only iron borides Fe_2B [9, 12], or by modifying with elements which are introduced by various methods [13-25] such as laser modification [3, 9, 10, 11]. Laser remelting, which consists of remelting surface layer with material substrate, produces a new layer enriched in modifying elements. The new layer resulting from laser beam radiation is composed remelted zone, heat affected zone and substrate. As a result the new layer has a mild microhardness gradient between layer and substrate. The appearance of a transition zone – martensite heat affected zone – ensures advantageous properties.

2. Research methodology

The material investigated was medium carbon steel C45 and its chemical composition is given in Table 1. The ring-shaped specimens were used for the study, which had the following dimensions: external diameter 20 mm, internal diameter 12 mm and height 12 mm. The complex layers was formed as a result of combined treatments: galvanic, diffusion and laser.

Table 1. Chemical composition of C45 steel
Tab. 1. Skład chemiczny stali C45

Chemical composition [% wt]					
C	**Mn**	**Si**	**P**	**S**	**Cr**
0.42	0.71	0.18	0.008	0.032	0.11

For nickel galvanic plating Watts bath was used, which uses a combination of nickel sulphate $NiSO_4 \cdot 7H_2O$ and nickel chloride $NiCl_2 \cdot 6H_2O$, along with boric acid H_3BO_3 as well as preservatives and initiating additives. The bath temperature was 25°C at current density of 2.5 A/dm^2. Nickel coatings deposited on C45 steel had 10 μm thicknesses and their average microhardness was 450 HV0.1. Next, diffusion boronizing was performed at 950^{o}C for 4h using gas-contact method. The boronizing mixture used in the process contained: amorphous boron, KBF_4 as activator and carbon black as filler. Boronized and boronickelized specimens were hardened in water from 850^{o}C to room temperature and then tempered. Diffusion boronized and galvanic-diffusion boronickelized specimens were tempered at 150^{o}C for 1h, whereas the galvanic-diffusion laser modified layers were tempered at 560^{o}C for 1h before laser heat treatment process (LHT). The two types of tempering were important to get a more advantageous profile of microhardness.

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 = 1.04 kW, laser beam radiation density q = 33.12 kW·cm^{-2}, scanning laser beam velocity v: 0,67 m·min^{-2}, 1,12 m·min^{-2}, 2,88 m·min^{-2}, laser beam diameter d = 2 mm. Laser tracks were arranged as multiple tracks with distance f = 0.5 mm, where f was distance between axes of adjacent tracks. Laser heat treatment was carried out for laser tracks along a straight line and the helical line. On the basis of straight line laser heat treatment best parameters were selected in order to carry out multi-tracks for a helical line. Multitracks are important in terms of applications such as wear resistance.

The scheme of boronickelized layers production using galvanic-diffusion-laser method is presented in Figure 1. The process of new layer production was composed of: galvanic treatment (Step 1), diffusion boronizing (Step 2) and laser modification (Step 3). Heat treatment was always performed after diffusion boronizing. The samples were first polished by using abrasive papers of different granularities, and, finally with Al_2O_3. Specimens were etched in 2% HNO_3 solution.

Microstructure observations were carried out on polished and etched cross-sections of specimens by using Metaval Carl Zeiss optical microscope equipped with a camera Moticam. To determine microhardness profiles a ZWICK 3212 B Vickers hardness tester was used. Indentation load of 100 G (HV0,1) and loading time 15 seconds were used in this study, based on the standard PN-EN ISO 6507-1 [26]. Adhesion tests of surface layers were conducted in accordance with the standard VDI 3198 [27], which is a comparison of Rockwell indentations [28] with scale standards appearing in Figure 2. A standard Rockwell tester as a destructive quality test for examined layers was employed in this study and damage to the layers was compared to the adhesion strength quality maps HF1-HF6 (Fig. 2). In general, the adhesion strength quality HF1-HF4 defined sufficient adhesion, whereas HF5 and HF6 represented insufficient adhesion [27]. In the study three Rockwell indentations were made for each layer.

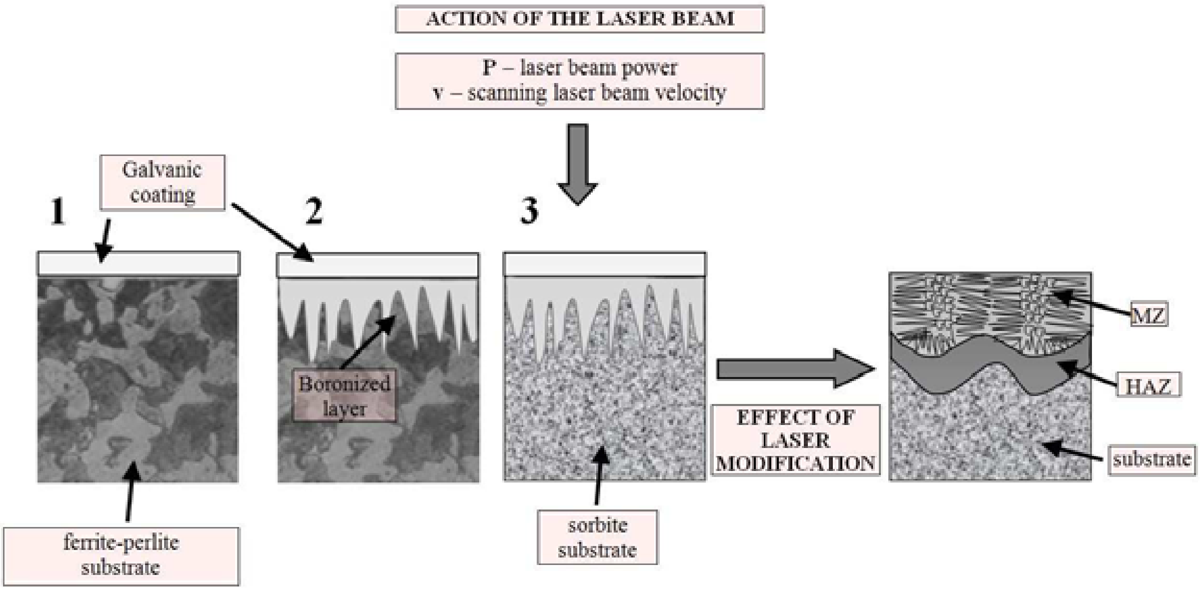

Fig. 1. Scheme of laser modifications of galvanic-diffusion layer
Rys. 1. Schemat przetapiania wiązką laserową warstwy galwaniczno-dyfuzyjnej

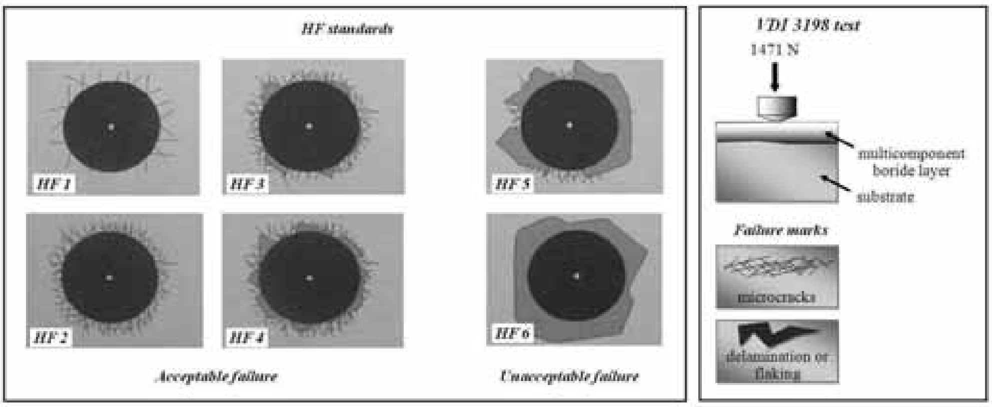

Fig. 2. Scale of models to test cohesion [27]
Rys. 2. Skala wzorców do badania kohezji [27]

Wear resistance tests were carried out with tribometer MBT-01 type Amsler. A ring as specimen and sintered carbide plate S20S as counterspecimen (its hardness was equal to 1430 HV) were used to examine wear resistance (Fig. 3).

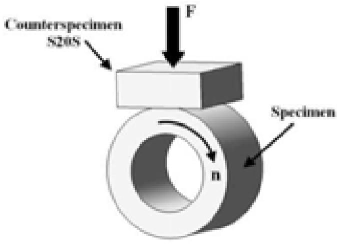

Fig. 3. Scheme of friction pair
Rys. 3. Schemat pary trącej

Wear resistance tests were carried out under the load F = 147 N and at specimen rotation speed of n = 250 rpm, in dry friction conditions (unlubricated sliding contact). Wear resistance was evaluated by specimen mass loss (Δm [mg]) per friction surface (S [cm^2]) in a time unit (t [h]). Wear intensity coefficient (Iw) was determined from the equation: $Iw = \Delta m \cdot (S \cdot t)^{-1}$ [$mg \cdot (cm^2 \cdot h)^{-1}$].

3. Results and discussion

Microstructure of ferrite-pearlite C45 steel with precoat nickel thickness of 10 µm is shown in Figure 4. Microstructure of boronized layer after hardening and tempering of 150°C is shown in Figure 5. Boronized layer had a needle-like structure and was composed of iron borides FeB and Fe_2B. This layer was about 90 µm thick and was closely related to a martensite substrate. As a result of nickel plating and diffusion boronizing a galvanic-diffusion layer was obtained. The galvanic-diffusion layer had a dual-zone structure. The first zone was continuous and was similar to nickel plated coating, the second zone was similar to iron borides (Fig. 6). The first subsurface zone (z_1) was 30 µm thick, and the total thickness of the boronickelized layer (z_2) was about 110 µm. The first zone - continuous, has a microhardness (z_1) reduced to 1200 HV0.1. Than the microhardness increased and in the second zone, was similar to the microhardness of iron borides Fe_2B (Fig. 7).

Next, the increase in the distance from the surface was accompanied by a decrease in the microhardness to about 800 HV0,1 in core of steel after hardening and tempering in 150°C. Microhardness of samples hardened and toughened at 570°C was about 400 HV0,1. Boronickelized layer in the transition area between the continuous zone and needle-like structure zone is porous (Fig. 6), that is why in this area is lowered microhardness can be observed (Fig. 7).

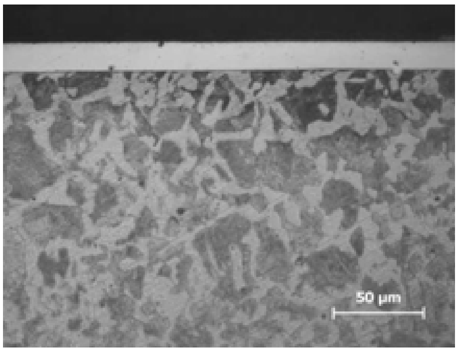

Fig. 4. Nickel coating on C45 steel; Ni thickness: 10 µm
Rys. 4. Powłoka niklowa na stali C45; grubość Ni: 10 µm

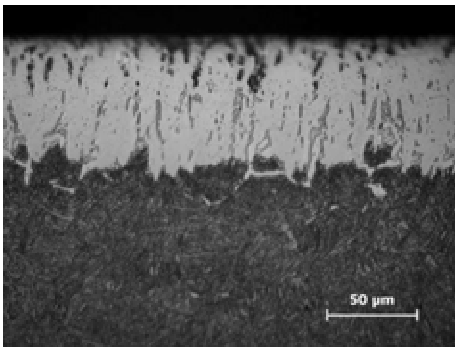

Fig. 5. Microstructure of boronized layer; B: 950°C, t: 4h
Rys. 5. Mikrostruktura warstwy borowanej; B: 950°C, t: 4h

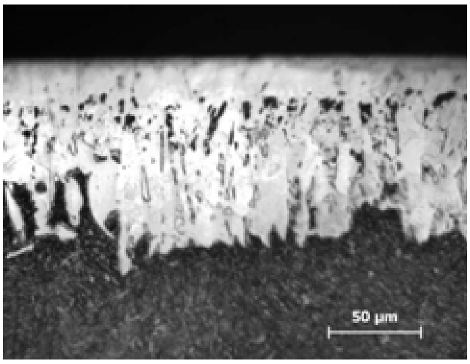

Fig. 6. Microstructure of boronickelized layer before laser modification; Ni thickness: 10µm; B: 950°C, t: 4h
Rys. 6. Mikrostruktura warstwy boroniklowanej przed laserową modyfikacją; grubość Ni: 10 µm; B: 950°C, t: 4h

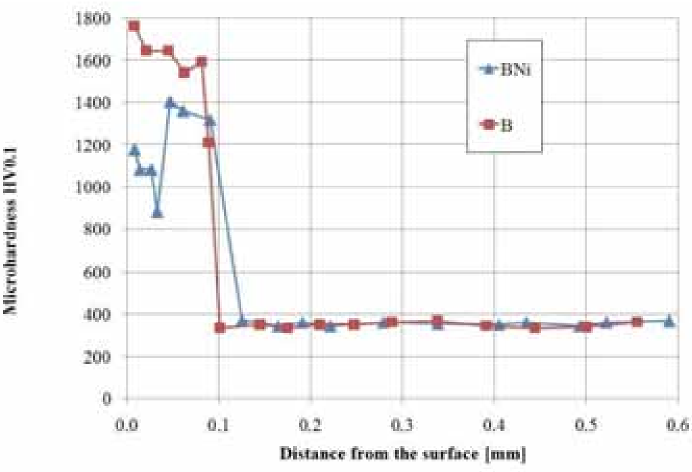

Fig. 7. Microhardness of boronized and boronickelized layers
Rys. 7. Mikrotwardość warstw borowanej i boroniklowanej

The microstructure of laser heat-treated boronickelized layer formed on C45 steel is characterized by: remelted zone (MZ), heat-affected zone (HAZ) and substrate.

Table 2 summarizes the parameters and properties of the boronickelized layers which were laser treated in a straight line, in relation to on the scanning speed of the laser beam at a constant laser power. It can be seen that with the increase in scanning speed the depth of melted zone, decreases as well as the overall dimension of the laser tracks, whereas the microhardness increases in the remelted zone.

Table 2. Microhardness and dimensions of the laser tracks along a straight line
Tab. 2.

P [kW]	v [m/min]	Microhardness in MZ HV0.1	Depth of MZ [mm]	Total depth of tracks (MZ + HAZ) [mm]
1.04	0.67	800-900	0.48	0.65
	1.12	900-950	0.18	0.35
	2.88	950-1000	0.14	0.30

Based on studies of the microstructure and microhardness is selected advantageous parameters of laser heat treatment in a straight line were selected in order to further investigate laser heat treatment for helical multitracks. The selected parameters of laser heat treatment are: laser power beam P = 1.04 kW, scanning speed laser beam v = 2.88 m / min, distance between tracks f = 0.5 mm. Macroscopic view of the sample with a laser modified boronickelized layer is shown in Figure 8.

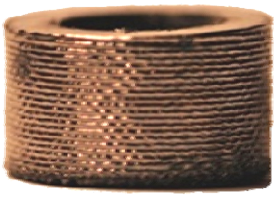

Fig. 8. A sample of the surface layer after laser modification
Rys. 8. Próbka z warstwą powierzchniową po laserowej modyfikacji

Figure 9 shows the microstructure of a laser modified boronickelized layer. The resulting microstructure consists of a remelted zone, where there in the axis was a complete melting of galvanic-diffusion layer with the substrate, while at the border of the laser tracks endings of unremelted borides can be seen.

As shown by the authors of the study [24, 25] in the remelted zone there is boron-martensite eutectic, of microhardness lower than iron borides.

It is probable that the increase compaction of tracks on the workpiece surface or increase in the laser beam power would cause uniform melting of galvanic-diffusion layer at a scanning speed v = 2.88 m / min, but simultaneously it would mean a reduction in microhardness in the remelted zone.

The resulting microhardness in both axis and at the interface between tracks has similar values and in the remelted zone it is approximately 1100 HV0.1 (Fig. 10).

Slight differences exist in the heat-affected zone, which are caused by the presence of tracks tempering reciprocally, which is inevitable in the case of larger tracks overlapping each other.

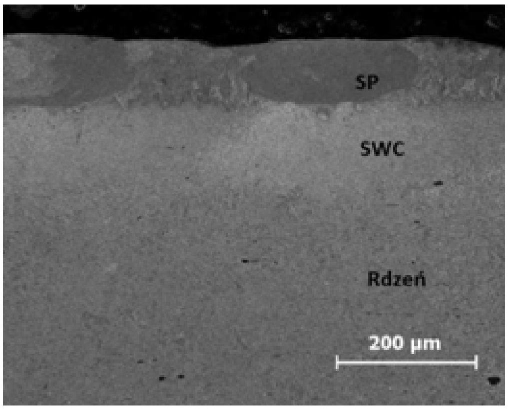

Fig. 9. The microstructure of boronickelized layer after laser remelting; LHT: P 1.04 kW; v = 2.88 m/min
Rys. 9. Mikrostruktura warstwy boroniklowanej po laserowym przetopieniu; LOC: P 1,04 kW; v = 2,88 m/min

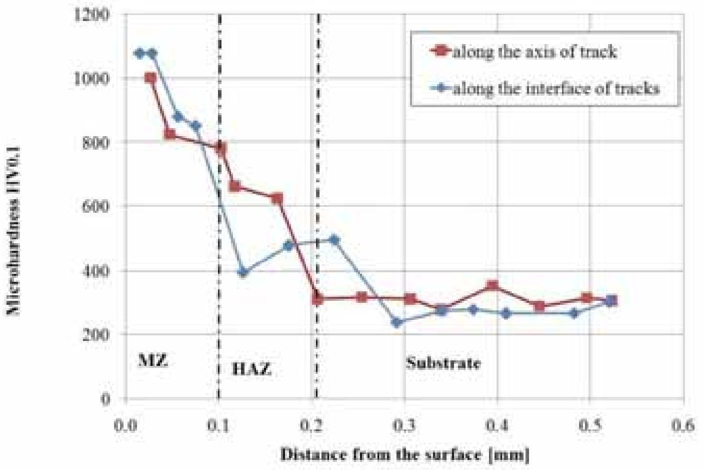

Fig. 10. Microhardness of boronickelized layer before and after laser modification
Rys. 10. Mikrotwardość warstw boroniklowanej przed i po laserowej modyfikacji

Figures 11-13 show the results of the study surface cohesion of the layers. In each case analyzed, surface layers are formed on a scale of acceptable failures based on VDI standard 3198. Figure 11 shows an image of the surface of diffusion boronized layer with Rockwell indentation, from which micro-cracks radiate, and layer adhesion conforms to the standard in terms of HF1 and HF2 (Fig. 2). Figure 12 shows the resulting indentation on steel after the galvanic-diffusion boronickelizing process, which can be classified as standard HF4, the last of acceptable failures. Flaking at the edges can be seen in images. Figure 13 shows an image of Rockwell indentation on the surface laser modified boronickelized steel. It can be seen that an additional treatment – laser heat treatment – affects the layer to substrate cohesion. There are no cracks on the layer and the adge surrounding the indentation is smooth.

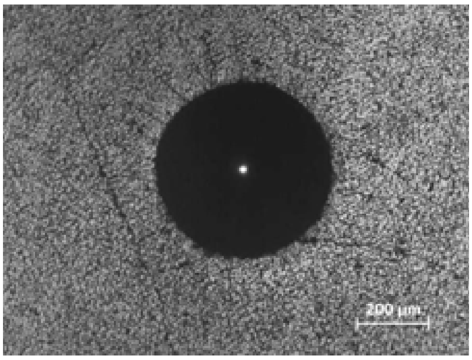

Fig. 11. Rockwell indentation image made on C45 steel after boronizing

Rys. 11. Odcisk Rockwella na stali C45 po borowaniu

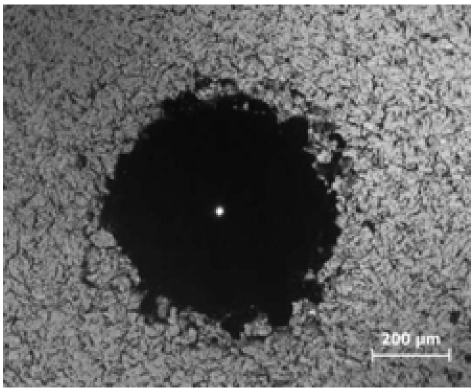

Fig. 12. Rockwell indentation image made on C45 steel after boronickelizing

Rys. 12. Odcisk Rockwella na stali C45 po boroniklowaniu

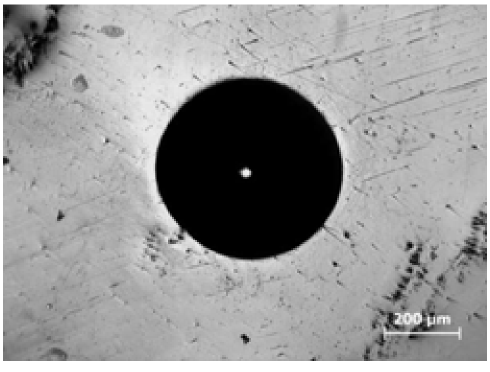

Fig. 13. Rockwell indentation image made on C45 steel after boronickelizing and laser modification

Rys. 13. Odcisk Rockwella na stali C45 po boroniklowaniu i laserowej modyfikacji

Figure 14 shows the results of wear resistance studies of laser treated and nickel boronized layer. Wear resistance studies of galvanic-diffusaion boronickelized layer were not carried out becouse at the zone interface there were areas at reduced microhardness and increased porosity which might probably bring about increased wear coefficient.

Boridies microhardness in the boronickelized layer differed in the entire zone, increasing with its depth, which is not adventageous. The application of laser remelting to boronickelized layers ensured uniform mixing of modified material with substrate, which improves wear resistance. Laser modified boronickelized layers are characterized by lower wear intensity coefficient than boronized layers (Figure 14).

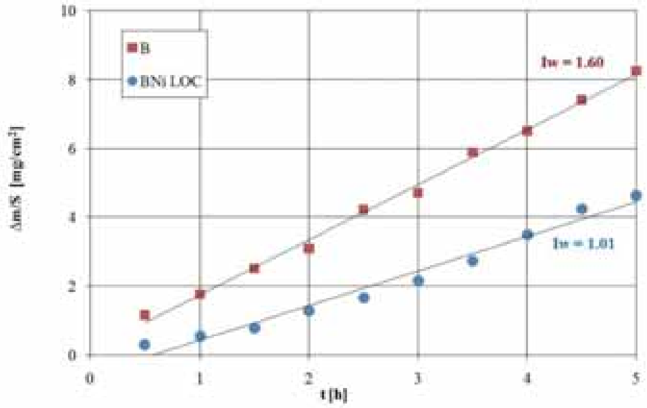

Fig. 14. Wear resistance of boronized, boronickelized and laser modified boronickelized layers

Rys. 14. Odporność na zużycie przez tarcie warstwy borowanej, boroniklowanej i boroniklowanej laserowo modyfikowanej

4. Conclusions

1. Boronized layers have a needles-like structure, well bound to the substrate, with microhardness of up to 1800 HV0.1, but with disadvantageous microhardness gradient between the layer and the substrate.
2. Nickel modified boronized layers have a dual zone structure: at the surface there is a continuous zone of microhardness of 1200 HV0.1, and deeper lies a needle-like zone with microhardness of 1600-1800 HV0.1.
3. Boronized layers modified with nickel and laser beam are characterized by lower microhardness and milder microhardness gradient from surface to substrate compared to boronized layer. The new layer has microstructure consisting of: remelted zone (MZ), heat affected zone (HAZ) and substrate.
4. Wear resistance and cohesion of laser modified boronickelized layers is higher than in layers that were only boronized and boronickelized.
5. The obtained new layers are characterized by constant thickness and microhardness on the axis and on the interface of laser tracks.

5. References

[1] Burakowski T., Wierzchoń T: Inżynieria powierzchni metali. Warszawa 1995.

[2] Kula P.: Inżynieria warstwy wierzchniej. Monografie. Łódź 2000.

[3] Kusiński J.: Lasery w inżynierii materiałowej. Wydawnictwo „Akapit”, Kraków 2000.

[4] Napadłek W., Przetakiewicz W.: Struktura stali 40H hartowanej laserowo. Konferencja Naukowo-Techniczna „Nowe materiały – nowe technologie materiałowe w przemyśle okrętowym i maszynowym”, 1998, 169-176.

[5] Steen W.M.: Laser material processing-an overview. J. Opt. A: Pure Appl. Opt. 5, 2003, S3-S7.

[6] Morimoto J., Ozaki T., Kubohori T., Morimoto S., Abe N., Tsukamoto M.: Some properties of boronized layers on steels with direct diode laser. Vacuum, 83, 2009, 185-189.

[7] Paczkowska M., Ratuszek W., Waligóra W.: Microstructure of laser boronized nodular iron. Surface & Coatings Technology 205, 2010, 2542-2545.

[8] Safonov A. N.: Special features of boronizing iron and steel using a continuous-wave CO_2 laser. Metal Science and Heat Treatment, 1998, 40, 1-2, 6-10.

[9] Pertek A.: Kształtowanie struktury i właściwości warstw borków żelaza otrzymanych w procesie borowania gazowego. Wyd. Politechniki Poznańskiej, Poznań 2001.

[10] Kulka M.: The gradient Boride Layers Formed by Borocarborizing and Laser Surface Modification. Rozprawy nr 428. Wydawnictwo Politechniki Poznańskiej, Poznań 2009.

[11] Bartkowska A., Pertek A., Jankowiak M., Jóźwiak K.: Borided layers modyfied by chromium and laser treatment on C45 steel. Archives of Metallurgy and Materials, 2012, vol. 57, nr 1, 211-214.

[12] Przybyłowicz K.: Teoria i praktyka borowania stali. Wyd. Politechniki Świętokrzyskiej, Kielce 2000.

[13] Balandin Yu. A.: Termochemical treatment in fluidized bed. Surface hardening of die steel by diffusion boronizing, borocopperizing and borochromizing in fluidized bed. Metal Science and Heat Treatment, 2005, vol. 47, 3-4, 103-106.

[14] Bartkowska A., Pertek A.: Wpływ powłoki niklu na efekty borowania dyfuzyjnego stali konstrukcyjnej C 45. Inżynieria Powierzchni, 2009, 2, 89-92.

[15] Grachev S.V., Mal’tseva L.A., Mal’tseva T.V., Kolpakovf A.S., Dmitriev M.Yu: Boronizing and borochromizing in a vibrofluidized bed. Materials Science and Heat Treatment, 1999, vol. 41, 11-12, 465-468.

[16] Kolesnikov, Yu.V., Anan'evskii, V.A., Govorov, I.V.: Formation of coatings resistant to contact impact loading by various borochromizing methods. Soviet Materials Science, 1989, vol. 25, 1, 91-94.

[17] Maragoudakis N.E., Stergioudis G., Omar H., Pavlidou E., Tsipas D.N.: Boro-nitriding of steel US 37-1, Materials Letters 2002, 57, 949-952.

[18] Młynarczak A., Piasecki A.: Budowa i właściwości dyfuzyjnych warstw chromoborowanych wytwarzanych na stalach narzędziowych. Archiwum technologii Maszyn i Automatyzacji, 2004, vol. 24, 2, 173-184.

[19] Özbek I., Akbulut H., Zeytin S., Bindal C., Ucisik A. H.: The characterization of borided 99.5% purity nickel. Surface and Coatings Technology, 2000, 126, 166-170.

[20] Pertek A., Jóźwiak K.: Efect of silicon on the structure and properties of iron boride layers. VI Miedzynarodowa Konferencja, nt. Węgliki, azotki, borki. Kołobrzeg, 1993, 53-57.

[21] Przybyłowicz K., Konieczny M., Depczyński W.: Borowanie w pastach z dodatkiem modyfikatorów: siarki, miedzi lub niklu Inżynieria Materiałowa, 1999, 3, 264-266.

[22] Sen S., Sen U.: The effect of boronizing and boro-chromizing on tribological performance of AISI 52100 bearing steels. Industrial Labrication and Tribology, 2009, vol. 61, 3, 146-153.

[23] Wierzchoń T., Bieliński P., Sikorski K.: Formation and propierties of multicomponent and composite borided layers on steel. Surface and Coatings Technology, 1995, vol. 73, 121-124.

[24] Bartkowska A., Pertek A., Jankowiak M., Jóźwiak K., Klimek L.: Mikrostruktura, skład fazowy i mikrotwardość warstw boroniklowanych modyfikowanych wiązką laserową. Inżynieria Materiałowa, 2012, vol. 185, 1, 32-36.

[25] Bartkowska A., Pertek A., Popławski M.: Wpływ modyfikacji laserowej na strukturę i mikrotwardość warstw boroniklowanych i borochromowanych. Inżynieria Materiałowa, 2012, vol. 189, 5, 452-455.

[26] PN-EN ISO 6507–1, Metale, Pomiar twardości sposobem Vickersa. Część 1: Metoda badań. Warszawa, czerwiec 2007.

[27] Verein Deutscher Ingenieure Normen, VDI 3198, 1991.

[28] PN-EN ISO 6508–1, Metale, Pomiar twardości sposobem Rockwella. Część 1: Metoda badań (skale A, B, C, D, E, F, G, H, K, N, T). Warszawa, sierpień 2007.