Microstructure, chemical composition, wear, and corrosion resistance of FeB–Fe₂B–Fe₃B surface layers produced on Vanadis-6 steel using CO₂ laser

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Abstract The paper presents the study results of laser modification of FeB–Fe₂B surface layers produced on Vanadis-6 steel using pack cementation method. Microstructure, x-ray phase analysis, chemical composition study using wave dispersive spectrometry method, microhardness, corrosion resistance as well as surface condition, roughness, and wear resistance were investigated. The diffusion boronizing processes were performed at 900 °C for 5 h in the EKabor® powder mixture. The boronized layers had a dual-phase microstructure composed of two types of iron borides, FeB and Fe₂B, and their microhardness ranged from 1800 to 1400 HV. The laser surface modification was carried out on specimens after diffusion boronizing process using CO₂ laser with a nominal power of 2600 W. Laser beam power used in this experiment was equal to 1040 W and was constant. While the three values of scanning speed were used: 19, 48, and 75 mm/s. During laser modification, the multiple tracks were made where distance between of axis tracks was equal to 0.5 mm. As a result of this process, microstructure consisted of remelted zone, heat-affected zone, and substrate was obtained. In remelted zone, the boron-martensite eutectic was observed. Boronized layers after laser modification were characterized by the mild

gradient of microhardness from surface to the substrate and their value was dependent on the scanning speed used and was between 1700 and 1100 HV. Corrosion resistance tests revealed reducing the current of corrosion in case of laser modification process. Wear resistance of laser modified specimens was improved in comparison to diffusion boronized layers.

Keywords FeB–Fe₂B–Fe₃B layers · Diffusion boronizing · Laser modification · Vanadis-6 steel

1 Introduction

Methods and techniques of surface engineering are applicable mainly for materials used to produce machine parts and tools where the fulfillment of certain performance criteria is necessary. It is obviously possible to use other kinds of materials characterized by higher strength, but it generates much more costs of production. However, in most cases, the product durability decides the surface layer conditions, hence, the importance of a study focusing on improving the surface layer properties. The surface layers can be improved in order to obtain better corrosion or wear resistance, higher hardness, heat resistance, or simply to improve appearance. One of the most popular kinds of surface modification is a thermo-chemical treatment, which consists of changing the chemical composition and microstructure of material by saturating the surface using selected elements. The diffusion boriding process is one of the thermo-chemical treatment methods, which enriches the surface layer by boron. Boron diffuses from the surface to the substrate of material (usually steel). The depth of boron diffusion is dependent on chemical composition of substrate material. The increase in boron content in the steel substrate results in the formation of expected iron borides. There are two types of these phases: FeB with microhardness ranged from 1800 to

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1600 HV and Fe₂B with microhardness ranged from 1600 to 1400 HV are formed [1–5]. Besides advantages such as high hardness, wear resistance, and resistance to chemical corrosion in many alkaline and acid solutions, the boronized layers show also some disadvantages. The most important of these is brittleness and flaking in the subsurface area where FeB phase is present. This disadvantage disqualifies boronized layers in many industrial applications. One of the modification methods of boronized layers, which may lead to decrease these disadvantages is production of the single-phase layers consisting only of Fe₂B phase [1]. Another modification method used to obtain the favorable properties is production of the complex layers. As a result of combination of several different technological processes, the layers are enriched in various chemical elements, which in final effect, gives the improvement of the operational properties. Increasing of wear and corrosion resistance, as well as reduction the brittleness of boronized layers can be obtained by modification of these layers using chromium [1, 6, 7], nickel [8–10], and copper [6]. To achieve this purpose, the diffusion methods [1, 6, 8]; laser methods (e.g., laser hardening [11–13], laser remelting [4, 7, 14], laser alloying [15–17], laser cladding [18–21]); as well as the electroplating [8–10] or thermal spraying methods [22] can be applied. Laser remelting of boronized layers allows changes in their microstructure and properties. It is assumed that laser processing with well-chosen parameters causes the homogeneous fine-grained microstructure without pores to be obtained. Modifying of boronized layers by laser modification may leads to extending the life cycle of many machine parts and tools. It is therefore important to undertake research in this area.

The laser modification process nowadays is widely used in the surface treatment of various types of machine parts and tools. In the case of two stage processes which consisted of diffusion boronized and next laser modification, authors can find several uses. These can be, e.g., the tools for metal forming processing as for stamping, forging, or extruding. For this type of product, high wear resistance and high resistance for unit pressures during cyclic operation are required. In addition, the laser modification of boronized layer can be used for agricultural tools working in the soil conditions. This type of tools are subjected both to intensive wear and aggressive corrosive environment. Surface layers after diffusion boronized and laser modification seems to be chemically and mechanically resistant. Additionally, this type of surface layers may be prepared on alloy and non-alloy tools steel.

In this paper, the influence of laser modification of diffusion boronized layers produced on Vanadis-6 steel was analyzed. Studies were focused on selected properties of produced layers such as microhardness, wear resistance, surface condition, chemical and phase composition, as well as corrosion resistance. In addition, changes in the microstructure were analyzed.

2 Experimental details

2.1 Materials

In this study, the ledeburitic Vanadis-6 steel produced in the powder metallurgy technology was used as a substrate material. Chemical composition of this material was determined using the Solaris CCD PLUS spectrometer and was shown in Table 1. The Vanadis steel group is characterized by very high purity, which is confirmed by low presence or lack of inclusions such as sulfides or oxides. In this study, specimens characterized by the following dimensions were used: diameter 16 mm and height 4 mm (in the case of microstructure, microhardness and corrosion resistance study), and also rings with external diameter 20 mm, internal diameter 12 mm, and height 12 mm (in the case of wear resistance study). Two kind of specimen shapes were applied due to the specifics of conducted study. Wear resistance tests of produced layers were carried out using tribometer of Amsler type; hence, the specimens had to be ring-shaped.

2.2 Diffusion boronizing

The diffusion boronizing were performed using pack cementation method which consists in annealing specimens in container filled by powder. Described process were performed at 900 °C during 5 h in EKabor® powder mixture. Pack cementation method is one of the simplest methods of diffusion saturation. Method used in this study is the improved form of the gas-contact method, because specimens not have direct contact with the powder mixture. Process flow is as follows: (1) preparation of powder mixture, (2) placement of powder mixture on the container bottom, (3) placement of the specimens on mesh, (4) placement of the container in retort, (5) launching of the argon delivery system, (6) insertion of the retort to the furnace, (7) annealing at a specific time and temperature, (8) cooling of the retort. In addition, it should be highlighted that boronizing processes were conducted under lowered pressure using the protecting atmosphere. This prevents air access to the specimen surface. Boron is transported from powder mixture on specimens surface (by means of gas phase), and then by the diffusion phenomenon, creates layer consisting of FeB and Fe₂B phases. After diffusion boronizing processes, specimens were subjected to modification using CO₂ laser.

Table 1 Chemical composition of Vanadis-6 steel used in study [wt.%]

C	Si	Mn	Cr	Mo	V	Fe
2.09	0.98	0.38	6.64	1.48	5.45	Balance

2.3 Laser modification

In order to perform laser surface modification of diffusion boronized layers, Trumpf TLF 2600 Turbo CO₂ laser of nominal power 2600 W was applied. Laser beam power (P) used in this experiment was equal to 1040 W, which corresponds to 40% of the nominal power of laser. Laser beam diameter (d) was equal to 2 mm and it was constant. Such parameters leads to obtain the laser power density (q) equal to 331 W/mm². Energy value, which is supplied to treated material, may be controlled, e.g., by varying of scanning speed (v). In this paper, three values of scanning speed were used: 19, 48, and 75 mm/s. The applied scanning speeds were dependent on the available opportunities of spindle lathe speed which can be adjusted only stepwise. During these studies, the conventional lathe with the stepped speed control was used. Change in scanning speed had a significant influence on the exposure time of laser beam on material (t), and hence, on the laser fluence (F), which describes the energy delivered per unit area. The first parameter was measured according to Eq. (1):

$$t = d/v \text{ [s]} \quad (1)$$

Second parameter was calculated using Eq. (2):

$$F = (P \cdot t) / (\pi \cdot r^2) \text{ [J/mm}^2\text{]} \quad (2)$$

where.

r radius of the laser beam [mm]

Parameters of laser modification of diffusion boronized layers and the calculations results were shown in Table 2. The laser beam, which is possible to obtain using the used type of laser device was characterized by circular shape mode (TEM_{01*}). During laser modification, the multiple tracks were prepared. Between each of the track axis, the constant distance equal to 0.5 mm was applied. Taking into account such parameters as diameter of laser beam and distance between axes of laser tracks, it can be found that overlapping was equal to 75%. However, the power distribution of laser beam in the form of the Gauss curve, significantly causes change in the overlapping of remelting zones and it depends on the scanning speed, because this parameter have influence on the amount of heat delivered to material. The higher the scan speed, the less

of delivered heat and less value of overlapping of remelted zone. During the laser treatment of ring-shaped specimen, the laser head was fixed. The movement was performed by specimen, which was placing in the spindle of lathe (Fig. 1a). In the second case, the flat-shaped specimen was fixed, while the laser beam was moved from point A to B . Then, the laser beam was turned off, and the laser head was moved to point C . In this point, the laser beam was turned on, and was next moved to point D . These cycles were continued on the entire surface of the specimen (Fig. 1b). In Fig. 1c, d schemes of laser modification of surface by remelting of diffusion layer and metallurgical bonding newly created layer to the substrate were shown. Solidification after laser treatment creates new surface layer, which is characterized by the chemical homogeneity. Intensive convection movements in liquid melting pool causes the formation of modified microstructure. In addition, after this process, the microstructure is fine-grained and characterized by the presence of highly supersaturated phases. In Fig. 1c, the direction of laser heat treatment was shown, while in Fig. 1d, scheme of convective movements in the melting pool was shown [23].

2.4 Surface condition, microstructure, and microhardness

The surface condition of produced layers was visually evaluated using stereoscopic microscope and roughness tester Hommelwerke T1000 equipped in measuring head LV 15. The surface roughness studies was performed on the measuring length $l = 4.8$ mm. In order to perform microscopic examination, the specimens were cut crosswise to the surface and obtained cross-sections were grinded using abrasive papers. Afterwards, specimens were polished using suspension of Al₂O₃ and finally, etched by 2% nital. Observations of microstructure were carried out using Huvitz HRM-300 light microscope equipped in digital camera from Bresser. Used microscope in these studies had the possibility to observation in Nomarski interference contrast. More details of microstructure were observed using two kinds of scanning electron microscope FEI INSPECT and TESCAN VEGA 5135. Microhardness studies were conducted on Zwick 3212B Vickers hardness tester using indentation load equal to 100 g and time 15 s.

2.5 Phase analysis and chemical composition

Phase identification of diffusion boronized layer before and after laser modification were carried out using PANalytical EMPYREAN x-ray diffractometer with Cu K α radiation, 45 kV and 40 mA at temperature of 25 °C. Analysis of chemical composition of obtained layers in micro-areas was performed using FEI INSPECT F scanning electron microscope equipped with a field emission gun (FEG). The quantitative and qualitative analysis of boron was performed using wave

Table 2 Parameters of laser modification of diffusion boronized surface layer

Laser beam power [W]	Scanning speed [mm/s]	Exposure time [s]	Fluence [J/mm ²]
1040	19	0.105	34.85
	48	0.042	13.79
	75	0.027	8.83

Fig. 1 Scheme of laser heat treatment process. **a** Stand for investigation. **b** Order of production of laser tracks. **c** Modification mechanism of boronized layer. **d** Influence of laser beam on convection movements in melting pool

dispersive spectrometry (WDS) applying a light energy x-ray spectrometer (LEXS) by EDAX.

2.6 Corrosion resistance

Corrosion resistance studies of produced surface layers were performed in a 5% NaCl solution at 22 °C on the area of 50 mm² of surface. Tests were performed using ATLAS 0531 potentiostat-galvanostat device. Platinum electrode as the auxiliary electrode and calomel electrode as the reference electrode were used in research. Recording of results were made possible through the use of AtlasCorr software. Polarization of specimens was carried out in anode direction in range from − 1.5 to 1.5 V. A rate of potential change was equal to 0.5 mV/s. Based on analysis of potentiodynamic curves, the main parameters of corrosion (current and potential) were determined.

2.7 Wear resistance

Wear resistance tests were carried out on the ring-shaped specimens using tribometer of Amsler type. The counter specimens were made of sintered carbides (S20S) and had shape

of square tiles. This type of sintered carbide had the following weight composition: 58% WC, 31.5% (TiC + TaC + NbC), and 10.5% Co, as well as was characterized by microhardness of 1430 HV. All tests were carried out under load of $P = 147$ N and at rotation speed of specimens equal to 0.26 m/s. Dry friction conditions were applied, which means that between specimens and counter-specimens, there was no oil film. Wear resistance was evaluated by mass loss of specimens at the friction time. Specimens mass was checked by 5 h every 30 min.

3 Results and discussion

3.1 Macrostructure and surface roughness

For all specimens, the influence of laser beam parameters on the geometrical structure of the surface was analyzed. It was found that modification of boronized surface layer using laser beam causes increase in the parameters of surface roughness. The results of surface roughness test for specimens with boronized layers before and after laser modification were shown in Table 3. It was found that increasing the scanning

Table 3 Surface roughness of boronized layers before and after laser modified

Specimens	Diffusion boronized	Modified by laser beam with scanning speed		
		19 mm/s	48 mm/s	75 mm/s
Average surface roughness	0.62	1.72	1.46	0.92

speed causes decrease in the surface roughness parameters. It is associated with shorter exposure time of laser beam on material and therefore, the smaller remelting of surface. Furthermore, it has been observed that the surface of specimens after the laser modification was characterized by lack of defects such as cracks or porosity, which are sometimes created by wrong selected parameters of laser beam.

3.2 Microstructure examination

Microstructure of diffusion boronized layer on Vanadis-6 steel was shown in Fig. 2. This image was taken in Nomarski interference contrast. Typical boronized layer has a needle-like microstructure consisting of two type of iron borides: FeB and Fe₂B. In the metallographic cross section, the FeB phase, which are located closer to the surface, can be identified, and below of it, Fe₂B phase is located. First of them are situated closer to the surface, whereas second are located closer to the substrate. Additionally, microstructure of such diffusion layer can also be observed in the zone enriched in boron which is situated under the needle-like iron borides. Total thickness of the obtained diffusion boronized layers was approximately 50 μ m. The needle-like iron borides and the diffusion zone enriched in boron had good bonding with the steel substrate. In this case, the microstructure of substrate consisted of secondary and primary particles of carbide evenly distributed in

Fig. 2 Microstructure of boronized layer on Vanadis 6 steel (Nomarski contrast)

pearlite. This is typical for microstructure of ledeburitic steel. Literature provides information on phase and chemical composition of Vanadis-6 steel. These are mainly carbides containing chromium (Cr₇C₃) and vanadium (VC) [11]. In paper [3], the authors described research in which Cr–V ledeburitic tool steels for cold work were boronized. Steels with different chromium and vanadium contents were applied. The boronized zones were composed of both the iron boride phases (FeB and Fe₂B). The only exception was steel

Fig. 3 Microstructure of boronized layer on Vanadis 6 steel after laser remelting. View of a laser track: **a** 19 mm/s, **b** 48 mm/s, **c** 75 mm/s. View of a remelted zone: **d** 19 mm/s, **e** 48 mm/s, **f** 75 mm/s

Fig. 4 X-ray diffraction pattern of layers on Vanadis-6 steel diffusion boronized only and diffusion boronized laser modified

characterized by ultra-high vanadium content. The thickness of boronized layers increases with increasing boronizing time. The maximal thickness has been found for steel containing 12% Cr and 0.95% V. With such chromium content, the influence of vanadium on thickness of layer is negative. The increase in vanadium content resulted produced thinner layer. Higher vanadium content but lower chromium content generally led to producing even much thinner layers. In Fig. 3, the laser tracks of boronized layer obtained in this study after laser remelting process were presented. A newly formed layers consisted of remelting zone (MZ), heat-affected zone (HAZ), and substrate. In Fig. 3a, laser track produced using scanning speed equal to 19 mm/s was shown. In Fig. 3d, the

magnification of area which was marked by square in Fig. 3a was shown. As a result of laser remelting of boronized layer, microstructure of the remelted zone was composed of the boron-martensite eutectic with martensite. It can be observed that this kind of eutectic had prismatic shapes (Fig. 3d). The depth of remelted zone in produced laser tracks was approximately 280 μm , and total thickness of laser tracks was equal to 490 μm . In the heat-affected zone, the obtained microstructure consisted of carbides on the martensite background. Whereas in microstructure of substrate, pearlite and carbide phases were presented. In Fig. 3b, the laser track produced using scanning speed equal to 48 mm/s was presented, while in Fig. 3e, magnification of areas marked by square from

Fig. 5 WDS mapping for diffusion boronized layer

Fig. 6 Microstructure of boronized layer and laser modified boronized layers with marked points measurement of chemical composition (WDS). **a** Diffusion boronized layer. **b** Boronized layers modified by laser $v = 75$ mm/s. **c** Boronized layers modified by laser $v = 48$ mm/s. **d** Boronized layers modified by laser $v = 19$ mm/s

Fig. 3b was presented. The microstructure of remelted zone was composed of the boron-martensite eutectic which many various rounded shapes was characterized (Fig. 3e). The thickness of melted zone was approximately 200 μm , and the total thickness of the laser tracks was equal to 350 μm . In Fig. 3c, the microstructure of laser track produced by using scanning speed equal to 75 mm/s was presented. In Fig. 3f, the magnification of area obtained using these parameters was presented. Area marked by square was studied. The microstructure of remelted zone was composed of the boron-martensite eutectic which characterized by dendritic (branched) shape (Fig. 3f). The thickness of melted zone in produced laser tracks was approximately 100 μm , and the total thickness of the laser tracks was equal to 240 μm . It was found that the boundary area between melted and heat-affected zones was characterized by good bonding. The microstructure has changed significantly due to the degree of supercooling of the produced layer. Using low laser scanning speeds, the specimens were heated to higher temperatures and finally were cool down slower. At the higher scanning speeds (75 mm/s), the specimens were cooled rather quickly, which prevented the growth of boron eutectic. In the case of specimens produced using scanning speed of 75 mm/s, only the nucleation sites of the eutectic formation were observed. When the scanning speed

decreases, to the specimens, more heat was added, which resulted in the growth of the boron eutectic. Summarizing in Fig. 3, nucleation of eutectic using 75 mm/s (Fig. 3d), growth of eutectic using 48 mm/s (Fig. 3e), and eutectic microstructure obtained using 19 mm/s (Fig. 3f) were observed, respectively.

In paper [14], the authors present the study results of laser surface modification of borided layers produced on C15 steel using CO_2 laser. After laser modification, typical eutectic microstructure were observed. In the C15 steel had not observed effect after the martensitic transformation due to the very low carbon content.

3.3 Phase analysis and chemical composition

In Fig. 4, the x-ray diffraction pattern of diffusion boronized layer before and after laser heat treatment was presented. In diffusion boronized layers, phases of iron borides such as FeB and Fe_2B were detected. After laser remelting of boronized layers, in the remelted zone, the equilibrium phase (Fe_2B) as well as non-equilibrium phase (Fe_3B and $\text{B}_{0.7}\text{C}_{0.3}\text{Fe}_3$) were detected. The peaks intensity generated by the boronized layer after laser modification was dependent on the laser processing parameters. Increase of scanning speed causes increased

Table 4 Chemical composition of boronized layer before and after laser modification in micro-areas marked in Fig. 6

Kind of heat treatment process	Measurement point	Wt. [%]						
		B	Si	Mo	V	Cr	Mn	Fe
Diffusion boronized	1	23.06	–	–	1.67	4.05	–	71.22
	2	13.40	–	–	2.22	6.70	–	77.68
	3	5.02	–	9.38	69.24	9.04	–	7.32
	4	4.41	–	2.27	4.00	11.11	–	78.22
	5	1.59	0.44	2.67	9.88	28.55	–	56.88
	6	0.77	1.41	1.34	7.13	3.94	–	85.41
Diffusion boronized modified by laser $v = 75$ mm/s	1	13.18	0.03	1.98	6.72	6.16	0.40	71.53
	2	10.90	0.04	2.36	7.82	6.87	0.44	71.57
	3	9.25	0.04	2.27	7.62	6.74	0.49	73.58
	4	1.08	0.06	2.51	8.94	7.37	0.46	79.58
	5	0.91	0.06	2.72	9.49	6.64	0.44	79.74
	6	0.84	0.06	3.22	12.64	7.11	0.40	75.73
	7	0.89	0.06	2.96	10.54	7.57	0.43	77.57
	8	0.84	0.06	2.82	9.97	7.68	0.44	78.20
	9	0.76	0.05	3.30	12.70	8.00	0.36	74.83
	10	0.84	0.05	3.30	12.78	7.94	0.52	74.56
	11	0.74	0.06	2.78	9.91	7.82	0.47	78.22
Diffusion boronized modified by laser $v = 48$ mm/s	1	3.82	0.06	2.39	8.29	6.85	0.43	78.17
	2	4.34	0.06	2.32	8.13	6.91	0.53	77.72
	3	4.13	0.05	2.42	8.22	6.91	0.54	77.73
	4	4.10	0.05	2.45	8.17	6.89	0.42	77.90
	5	4.05	0.06	2.31	7.83	6.82	0.43	78.51
	6	1.40	0.06	2.53	5.67	8.06	0.56	81.73
	7	0.73	0.05	3.29	11.84	8.60	0.56	74.92
	8	0.54	0.06	3.53	11.30	7.65	0.82	76.10
	9	0.69	0.05	3.31	11.67	9.15	0.53	74.59
	10	0.62	0.05	3.64	13.36	9.35	0.69	72.30
	11	0.61	0.06	3.04	10.21	7.86	0.49	77.74
Diffusion boronized modified by laser $v = 19$ mm/s	1	3.32	0.05	2.37	7.90	7.02	0.57	78.77
	2	3.84	0.05	2.36	7.87	7.10	0.49	78.29
	3	3.47	0.06	2.27	7.81	6.72	0.50	79.17
	4	3.64	0.06	2.32	7.65	6.77	0.44	79.12
	5	3.84	0.05	2.36	7.57	6.77	0.46	78.94
	6	3.96	0.05	2.36	7.86	6.82	0.47	78.47
	7	3.91	0.06	2.39	7.93	6.82	0.44	78.45
	8	2.41	0.06	2.34	7.65	6.69	0.48	80.36
	9	1.16	0.06	2.33	7.54	6.80	0.51	81.59
	10	0.86	0.06	2.03	7.88	6.66	0.46	82.04
	11	0.80	0.06	2.77	9.75	7.50	0.44	78.69

intensity of iron boride peaks Fe_2B and Fe_3B . The chemical composition of specimens with produced surface layers was analyzed on micro-areas using x-ray microanalysis applying WDS method. In Fig. 5, the WDS mapping for diffusion boronized layer was shown. In this figure, the area with presence of FeB and Fe_2B phases is clearly visible. FeB phase was located in the upper zone of diffusion layer, while Fe_2B phase

was located in the lower zone and was characterized by less participation of boron. The diffusion boronized layer and the substrate of Vanadis steel contain the carbides of chromium and vanadium. These phases were shown in mapping. In the previous paper [4], authors presented the mapping results of this kind of surface layers but after laser modification. This paper presents the quantitative results of chemical

composition in the form of table. The point in cross section of diffusion boronized layer from which taken data for analysis of chemical composition was marked in Fig. 6a. Whereas the case of the laser-modified boronized layer were marked in Fig. 6b–d. In Table 4, results of chemical composition study in the form of weight percent were presented. The boron content of the diffusion boronized layers in analyzed points corresponds to iron boride phases, respectively, for FeB (point 1) and Fe₂B (point 2), which were presented in Fig. 6a. Also, increased content of boron in the area immediately adjacent to the needle-like microstructure of iron borides (points 4 and 5) was found. During the diffusion boronized process carbides were also saturated with boron. It can be assumed that as a result of diffusion process were obtained boron cementite phase Fe₃(B, C) (points 3 and 6).

The content of boron in the analyzed area after laser remelting of boronized layer correspond to phase of iron borides. In conjunction with the melting of boronized layer, the content of boron decreases together with distance from the surface. In the case of laser remelting process which was performed at higher velocity (75 mm/s), the content of boron in the upper area of remelted zone was equal to 13.18 wt.%, and next drops to 1.08 wt.% in a lower area of remelted zone (Fig. 6b, Table 4). Decreasing the velocity to a value of 48 mm/s leads to decrease of boron content in the upper zone to around 3.82 wt.%. In the lower area of the remelted zone, boron content decreased to around 1.40 wt.% (Fig. 6c, Table 4). In the case of remelting process which was performed using lower velocity (19 mm/s), the content of boron was equal to 3.32 wt.% in the upper area of the remelted zone, and decreased to 2.41 wt.% in lower area (Fig. 6d, Table 4). These results clearly indicate that the content of boron was dependent on the laser parameters used and more particularly on the scanning speed of laser beam. Laser beam scanning speed changes the amount of heat delivered to the substrate. The increase of scanning speed resulted in decrease of the exposure time of laser beam on material. Changes in the chemical composition are related to the degree of remelting and thus related to the dimensions of remelted zone. By using a low scanning speed, the contribution of the substrate to the layer is greater and therefore reduce of boron content was observed. It was found that increasing the remelting degree of laser track leads to the decrease of boron content in surface layer. In all specimens, the initial boron content was the same. The formation of a larger remelted zone resulted in the distribution of boron in a larger area. Consequently, lower content of boron in the newly formed layer using low scanning speed was found.

3.4 Microhardness profiles

Boronized layers produced on Vanadis-6 steel had a microhardness from about 1800 HV0.1 to 1500 HV0.1, and these

Fig. 7 Microhardness of boronized layer after laser modification using scanning speed: **a** 19 mm/s, **b** 48 mm/s, **c** 75 mm/s

value rapidly decreased with increasing distance from the surface to the substrate. In paper [3], the authors investigated Cr–V ledeburitic steels after diffusion boronizing process. It was found that in selected cases, microhardness was very high and

Fig. 8 Potentiodynamic curves obtained during corrosion resistance tests of boronizing layer before and after laser modification

exceeded 2000 HV 0.1. On the other hand, they found that steel with ultra-high vanadium content and very low chromium content had the lowest microhardness.

Results of microhardness tests of boronized layer after laser remelting was shown in Fig. 7. Thicknesses of melted and heat-affected zones in the laser tracks (along the axis of track) are marked on the graphs. It may be noted that the laser heat treatment parameters significantly affects the microstructure and consequently on the microhardness of laser tracks. Microhardness was studied along the laser track axes and along the overlap zone of tracks. The microhardness values were associated with the laser heat treatment parameters and with thickness of produced surface layers.

Laser remelted of boronized layer using laser parameters: $P = 1040$ W and $v = 19$ mm/s allowed to obtain the microhardness in remelted zone approximately 1100 HV0.1 (Fig. 7a). This value decreased both in heat-affected zone and substrate. Microhardness in this zones was similar and was approximately 600 HV0.1. The rate of heat dissipation was low; therefore, the alignment of microhardness values was possible. During the laser modification using low scanning speed, the heat removal was slower, which contributes to the slower solidification of the material. The increase in scanning speed was conducive to faster heat removal. Rapid heating and cooling contributed to obtaining a fine microstructure. This had the effect on higher microhardness obtained during the study. Lower microhardness in zone near surface of laser tracks resulted from slower heat dissipation. Low scanning speed led to obtain good mixing between borided layer and the substrate. By providing a larger amount of heat, slow solidification and reduced microhardness has been found. Slow solidification allows to obtain the equilibrium microstructure. In contrast, quick solidification allows to obtain non-equilibrium microstructures. In this work, fast cooling led to the formation of fine martensite microstructure

with boron eutectic. On the other hand, slower solidification may result in coarse-grained martensite with boron eutectic. The bottom area of the remelted zone solidified as a first. As a result, microhardness near the boundary between MZ and HAZ was approximately 1100 HV0.1. Boron, which was present in remelted zone, promotes the increase of microhardness, while slow heat dissipation resulted to the value of microhardness in HAZ was close to value of microhardness in substrate. Application of laser parameters as: $P = 1040$ W and $v = 48$ mm/s to the surface modification process led to obtain microhardness in remelted zone in the range from 1500 to 1300 HV0.1 (Fig. 7b). It was found that microhardness gradually decreased in heat-affected zone. The highest value of microhardness in remelted zone was obtained for the laser modification of boronized layer using following parameters: $P = 1040$ W and $v = 75$ mm/s. In this case, microhardness along the axis of track in remelted zone had reached the values in the range from 1700 to 1400 HV0.1. It seems to be that the most repeatable microhardness in the remelted zone of laser borided layers is obtained using parameters: $P = 1040$ W and $v = 75$ mm/s (Fig. 7c). However, microhardness, both in the heat-affected zone as well as in the substrate, were similar. The most favorable parameters used to laser modification of diffusion borided layer were the following: $P = 1040$ W and $v = 48$ mm/s. The obtained microhardness was slightly lower but it was characterized by a mild decrease through the remelted zone, heat-affected zone towards the substrate. Such kind of microhardness profile was beneficial because ensured good stress distribution in the produced layer. Appropriate stress distribution in surface layers, plays an important role in further industrial applications.

It was found that the phenomena accompanying the laser heat treatment causes an increase in the concentration of the alloying elements from substrate (B and Cr, V) in the liquid phase during crystallization. During laser modification of

Table 5 Current and potential of corrosion obtained during corrosion tests of boronizing layer produced on Vanadis-6 steel before and after laser modification

Specimen	Corrosion current I [A/cm ²]	Corrosion potential E [V]
Diffusion boronized	8.35E-07	− 4.42E-01
Modified by laser beam Scanning speed 19 mm/s	5.49E-07	− 9.48E-01
Modified by laser beam Scanning speed 48 mm/s	4.22E-07	− 9.21E-01
Modified by laser beam Scanning speed 75 mm/s	7.42E-07	− 7.48E-01

diffusion boronized layer, a part of the substrate (containing chromium and vanadium carbide) were also melted. It caused the phenomenon of enriching the melted area not only into boron and iron but also into chrome and vanadium from carbides. Laser modification parameters affected on the microstructure in remelted zone. Some changes can be observed, e.g., in amount of eutectic iron borides or carbides. Therefore, the different laser modification parameters of boronized layers on Vanadis-6 steel were subjected to study. Also, the thickness of newly boronized layer obtained by laser modification had partial influence on their microhardness. The depth of obtained laser tracks was associated with the thickness of previously produced boronized layer. Therefore, deeper remelting may contribute to reducing of the boron amount. In this case, during the laser modification process, the microstructure containing less eutectic and characterized by lower microhardness may be formed. Layer after boriding and laser modification had a lower microhardness than the only diffusion borided layer. Reducing microhardness gradient between surface layer and the substrate was observed. The

authors of paper [14] observed a similar relationship for steels with lower carbon content.

3.5 Corrosion resistance

The results of corrosion resistance tests of diffusion boronized layers before and after laser modification were presented in Fig. 8. In this graph, the study results of corrosion potential in the range from − 1.2 V to − 0.1 V was shown. Both the potential and current of corrosion were analyzed. It should be taken into account the dependence that when the value of corrosion current was smaller, the corrosion resistance was greater. Based on this studies, it can be generally concluded that in NaCl solution, the diffusion boronized layer had the lowest corrosion resistance than boronized layer after laser modification.

In the case of modification by laser beam, the newly formed surface layers (laser track) was thicker than that obtained by diffusion boronizing. It was found that process of mixing of FeB and Fe₂B phases with iron from the substrate caused the deterioration of corrosion resistance. It was found that better corrosion resistance had layers which were produced using higher scanning speed (75 mm/s). Greater content of boride eutectic in obtained microstructure (hypereutectic) was the reason of this properties. Lower scanning speed ($v = 48$ mm/s) causes slower solidification of material and formation hypoeutectic microstructure. In addition, higher scanning speed caused less remelting of steel substrate. As a result, the lower amount of iron (which is more susceptible to corrosion) was presented in modified surface layer. This is the additional reason of better corrosion resistance of layers produced using higher scanning speed. Using the higher value of scanning speed of laser beam left more boron content in remelted zone and the presence of only the nucleation of

Fig. 9 Wear resistance of boronized layers before and after laser modification

Fig. 10 Surface condition after wear resistance tests; boronized layer (a, b). Boronized layer after laser modification: $v = 19$ mm/s (c, d). $v = 48$ mm/s (e, f). $v = 75$ mm/s (g, h)

eutectics. At the same time in this zone, the less iron was present. As it is known, the increased amount of iron affects the deterioration of the corrosion resistance. Reducing the scanning speed from 75 by 48 to 19 mm/s had resulted in deeper remelted zone and consequently reduced boron content. Additionally, the content of eutectics was increased. The precoat of diffusion boron was the same for each specimen but the final amount of boron was mixed in different volumes of material, which was dependent on scanning speed. The increase of scanning speed of laser beam contributes to the formation of boron eutectic microstructure. For more dense boron eutectic (as with the applied parameters $v = 75$ mm/s), higher corrosion resistance was found. In this case, the laser modification is designed to reduce both cracks and stress in surface of materials after diffusion boronized process. At the same time, it should be remembered that this process contributes to the mixing of boronized layer with the steel substrate. Corrosion resistance is dependent on the suitably selected laser modification parameters. The values of corrosion current and its potential were shown in Table 5. The corrosive currents were determined using Tafel extrapolation using Atlas Lab software.

3.6 Wear resistance

In Fig. 9, wear resistance results of diffusion boronized layers were shown and compared with results of diffusion boronized layers after laser modification. After laser modification of boronized layer, the wear resistance was beneficial. The obtained microstructure composed of three zones as well as characterized by a mild microhardness gradient which influenced on wear resistance. Higher wear resistance of a laser boronized layer ($P = 1040$ W and $v = 75$ mm/s) was associated with higher boron participation and obtained microhardness. These parameters had influence on friction phenomena and consequently on reducing wear of the produced layer. It was found that the higher scanning speed caused increased of wear resistance. In Fig. 10a–h, the surface condition after wear resistance tests were shown. Diffusion boronized layers without laser modification had been significantly worn. On their surfaces, signs of cracks and micro-cutting were visible. These may be associated with the use of carbide S20S as counterspecimen. On the basis of macroscopic observations, it can be stated that the prevailing friction mechanism is abrasion. First of all, the abrasion of unevenness was observed. Micro-cutting was observed as well as in some cases; it is also possible to observe a tendency of squeezing of softer zones of the produced layer. It was observed these particularly the case in specimens prepared at a lower scanning speed. In other cases (after laser modification), the better surface condition

were observed. On the surface of layer, where the scanning speed used was equal to 19 mm/s, the grid of cracks was observed. This is due to multiple heating and cooling of the material. For the smallest value of scanning speed, the laser tracks were the largest, and in consequence, the material could not quickly reduce temperature. Such multiple heating may contribute to the thermal fatigue. In other specimens, such cracks do not occur. On the basis of this study, we may conclude that the laser modification had a significant influence on the improvement of mechanical properties of the produced boronized layers.

4 Conclusions

The concluding remarks of these studies are the following:

1. It is possible to modify powder steel by methods and techniques of surface engineering, including high-energy methods such as laser alloying. However, the selection of appropriate laser modification parameters should be considered. Well-chosen parameters have a positive influence on the resulting microhardness of the treated surface with a simultaneous increase in corrosion resistance.
2. Based on the research, it can be concluded that the laser modification of the boron layer results in obtaining layers composed of three zones: remelted zone (MZ), heat-affected zone (HAZ), and substrate. It was found that the properties of the layers and their chemical composition could be changed by the selection of scanning speed parameters.
3. By applying laser modifications, a gentle microhardness gradient from the surface to the substrate can be obtained. This is not possible in the case of diffusion boring process.
4. When manufacturing laser-borne layers, special attention should be paid to their microstructure. Obtaining the boron eutectic with martensite microstructure seems to be the most advantageous for the machine parts. However, it should be kept in mind that every machine part sets different properties requirements.
5. Boronized layers on Vanadis 6 steel after laser modification were characterized by lower corrosion resistance than diffusion boronized layer. It is connected to high iron content in the newly formed layer.
6. Laser modification improves wear resistance of boronized layers.

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