MICROSTRUCTURE, MICROHARDNESS AND FRACTURE TOUGHNESS OF BOROCHROMIZED LAYERS MODIFIED WITH LASER BEAM

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Abstract

The paper presents the influence of laser beam on properties of borochromized surface layers produced on C45 steel. Microstructure, phase composition, microhardness as well as fracture toughness of newly formed layers were studied. Analyzd layers were produced using by three methods. First was galvanic-diffusion method, second was galvanic-diffusion method with additional laser modification, and third was galvanic method with additional laser alloying using boron paste. During all processes the thickness of galvanic coatings was 5 µm. For samples where diffusion boronizing was carried, temperature of 950 °C and process time of 4 h was applied. As a result of this process dual-zone microstructure was obtained. On surface continuous zone was observed while on subsurface needle-like iron borides was identified. For the samples where no diffusion boronizing was used, amorphous boron paste was applied to the galvanic chromium coating. In these studies the CO_2 laser beam was used for modification processes. Application of laser beam contributed to obtain three microstructural zones: remelted zone, heat affected zone and substrate. In produced layers phases of iron borides and chromium borides were identified. These phases were in accordance with equilibrium diagrams: Fe-B, and Cr-B. An advantageous effect of laser modification on microhardness of borochromized layers was found. Produced layers were compared with diffusion boronized layers. Microhardness profiles showed gradual transition from the remelted zone, through heat affected zone to the substrate. It was found that brittleness of boronized layer decreases after modification with chromium and the laser beam.

Keywords: Boronized layer, borochromized layer, laser modification, microhardness, fracture toughness

1. INTRODUCTION

Currently used technologies of producing surface layers are mainly combinations of various methods. Diffusion [1,2] and galvanic [3] treatments play a leading role; however, laser treatment [4,5] is becoming increasingly important. Surface layer modifications can be carried out with various elements, including Al, Cr, Si, Zr, Cu, Ni, N, C. Their introduction into the substrate by various methods results in new unique properties, which are often incomparable with each other. The essence of substrate modification is the possibility of reducing product manufacturing costs. This is important as it may curb the use of expensive and often difficult-to-machine high-alloy steels. Addition of a modifying element to common surface layers may result in increased or decreased layer hardness. Elements that cause hardness reduction are mainly introduced in order to obtain a milder hardness gradient from layer to substrate. Newly developed layers can also contribute to increasing wear resistance by friction or fracture toughness, but just as well they can lead to increased corrosion resistance. A significant increase in surface layer hardness is associated with a significant drawback, which is reduced crack resistance. The issue of brittleness to a great extent concerns boron, carbide or nitride layers [6-9]. Literature reports indicate that modification of boronized layers with elements such as Ni, Cu, Cr, S results in obtaining beneficial properties. Surface layers obtained by various methods usually have a multi-zone structure, which positively affects properties such as: hardness or layer adhesion to the substrate. There are publications discussing production of complex layers with the use of boron and nickel modification. In these papers, a chemical method of applying coatings was used, and boron was introduced by means of plasma treatment. Diffusion methods are quite commonly used in which two elements are introduced simultaneously. Common processes in this area are borocarburized or carbonitrided. Numerous publications tackle laser heat treatment of layers by their remelting or alloying. Literature analysis points to discrepancies in modification of diffusion layers aimed at reducing their brittleness. The modified boronized layers obtained can be affected by both the modifying element and the method used to introduce it. There are not many publications discussing laser processing of layers produced by galvanic diffusion and galvanic method along with boron paste. Hence, in this paper an attempt was made to modify the borochromized layer produced by various methods and the obtained properties were compared with the boronized layer.

2. METHODOLOGY

The tests were carried out on samples of C45 steel with a content of 0.42% C, 0.71% Mn, 0.18% Si, 0.008% P and 0.032% S. On C45 steel, borochromized layers were produced in three methods. The first was a galvanic diffusion method, the second was a galvanic-diffusion method with additional laser modification, and the third was a galvanic method with additional laser alloying using boron paste. The layers produced were compared with the boronized layer. The chrome plating layer produced was 5 μm thick. The gas-contact diffusion boriding process was carried out at 950ºC for 4h in a powder composed of amorphous boron, KBF_4 as activator, and soot as filler. Boron containing coating of 40 μm thickness was applied in paste form which consisted of amorphous boron, aqueous glass and distilled water. All the samples were additionally hardened and tempered. For laser heat treatment, the TRUMPH CO_2 technological laser with a power density of 33 kW/cm^2 and a scanning speed of 3 m/min was used, with a constant beam diameter of d = 2 mm with a circular cross-section. The distribution of tracks on the machined surface was f = 0.50 mm. Microstructure tests were performed on the Huvitz HRM-300 light microscope and the MIRA-3 TESCAN scanning electron microscope. All the samples were etched with a 2% solution of HNO_3. Phase composition analysis was carried out on the EMPYREAN X-ray diffractometer by PANalytical using Cu Kα radiation. Microhardness tests were carried out on cross-sections of samples using the Future-Tech FM-810 Micro Vickers Hardness Tester. Microhardness tests were carried out under a load of 50 g, with a load time of 15 s for each measurement. The Palmqvist method was used to determine the produced layer fracture toughness. This method consisted in making hardness indentations using the Vickers method on sample surfaces, and then measuring the diagonal of the indentations and the length of cracks branching out of the corners of the indentations. Fracture toughness was tested by the Palmquist method at a load of 196 N, 147 N and 98N on a Vickers hardness tester. As a measure of the susceptibility of layers to sudden cracking, a critical intensity coefficient Kc as expressed by the formula was adopted:

$$\mathbf{Kc = AP/c^{3/2}\ [MPa \cdot m^{1/2}]} \quad (1)$$

where:

P – load [N]

c – radial crack length measured from the centre of the indentations [m]

A – constant; $A = 0.028\ (E/H)^{1/2}$

E – Young's modulus for iron boride Fe_2B [2,6]; $E_{Fe2B} = 2.9 \cdot 10^5$ [MPa]

H – hardness [MPa]

3. RESULTS

Figure 1a shows the microstructure of a diffusion boronized layer which consists of needle-like iron borides. The layer has a thickness of approximately 100 µm. The microhardness of the layer was approximately 1800-1600 HV0.05. On the surface of the sample with the created boronized layer numerous microcracks and porosities in the subsurface zone, i.e. in the area of the appearance of FeB iron borides could be observed. These cracks and high hardness in the subsurface zone may contribute to chipping and exfoliating of such a layer. Therefore, in this study an attempt was made to modify and produce a borochromized layer in a variety of methods. First, a method combining galvanic treatment with diffusion treatment was used. The microstructure after such a process is shown in (**Figure 1b**). The borochromized layer thus produced had a needle-like structure with the subsurface zone that was enriched with chromium. It was found that the formed borochromized layer was thinner than the boronized layer with a thickness of approximately 75 µm. The microhardness of the borochromized layer was in the range of iron borides and ranged from approximately 1700 HV0.05 to 1500 HV0.05. An obvious drawback of this layer, just as in the case of the boronized layer, was subsurface porosity. As this area was enriched in chromium, an attempt was made to further modify the borochromized layer with a laser beam.

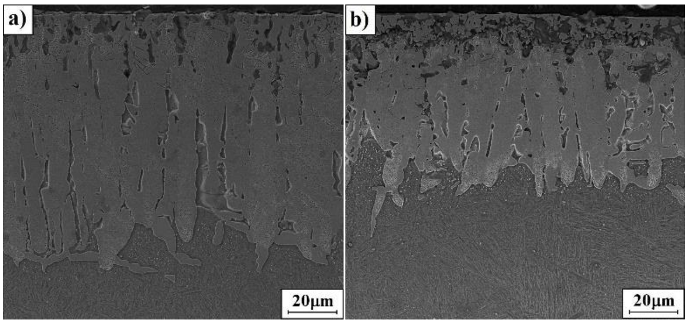


Figure 1 Microstructure of boronized layer (a) and borochromized layer (b)

Based on previous studies [10], laser beam power density of 33 kW/cm² and laser beam scanning speed of 3 m/min were considered to be the most advantageous parameters for the production of modified layers. The microstructure of a borochromized layer produced by the galvanic-diffusion method with additional laser modification is shown in (**Figure 2a-c**). As a result of laser beam interaction, a layer consisting of three zones was obtained: the remelted zone, the heat affected zone and the core. The remelted laser tracks were approximately 280 µm. Microhardness of the borochromized layer remelted with a laser beam is uniform in the area of the entire remelted zone and was in the range of approximately 900 HV0.05-700 HV0.05. Microhardness lower than in the initial borochromized layer was associated with a greater share of iron substrate. **Figure 2a** shows a view of the laser tracks. Figure 2b shows the microstructure of the central area of the remelted zone, while (**Figure 2c**) shows a view of the border between the remelted zone and the heat-affected zone. For comparison, a method was used in which boron applied to the sample was in paste form. **Figures 2d-f** show the layer after boronized laser alloying of the chromium electroplating coating. The depth of the remelted zone for both methods involving the laser beam was quite similar.
Laser-modified tracks had thickness of approximately 90 µm in the area of the remelted zone (**Figure 2a**), while those laser alloyed with boron were approximately 85 µm (**Figure 2d**). It can be assumed that remelt depth is influenced by the nature of laser interaction with the treated substrate. In all the cases the remelted zone was continuous and the heat-affected zones overlapped. Microhardness for borochromized layers obtained as a result of laser alloying with boron of the chromium galvanic coating was very similar regardless of the method used and was approximately 800 HV0.05 – 700 HV0.05. Figure 2e shows the microstructure of the central area of boronized laser alloyed track. It differs slightly in the amount of eutectic forming the skeleton of the structure in which martensite is present. Also, the border of the transition between the remelted zone and the heat-affected zone had a slightly different character. This border was clearly visible while observing

samples for which laser boron alloying was used (**Figure 2f**). In the laser remelted borochromized layer the transition to the heat-affected zone was more smooth (**Figure 2c**). The borochromized layers affected by laser beam were characterized by a milder microhardness gradient from the surface towards the core due to the presence of a heat-affected zone.

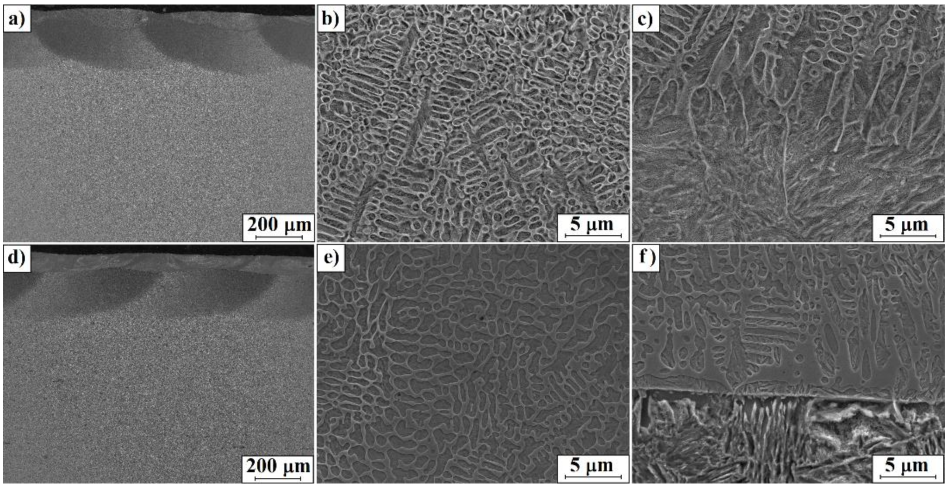


Figure 2 Microstructure of borochromized layer produced by galvanic-diffusion method with additional laser modification (a-c) and galvanic method with additional laser alloying using boron paste (d-f)

Phase composition of the tested borochromized layers was analyzed and the results are summarized in **Table 1**. The produced layers were dominated by various types of chromium borides. As a result of remelting the borochromed layer, additional peaks derived from iron and chromium were detected. It is most likely chromium martensite. A non-equilibrium phase of Fe_3B boride was also detected. Phases derived from iron borides and chromium borides were present in the borochromed layer obtained as a result of boron laser alloying. It should be borne in mind that as a result of the turbulence of the chemical composition in the liquid pool, chromium phases with both high and low percentage by weight of boron content were obtained.

Table 1 Phase composition of borochromized layers

Kind of treatment	**Phase**						
	FeB	**Fe_2B**	**Fe_3B**	**Cr_2B**	**Cr_5B_3**	**CrB**	**Fe-Cr**
Borochromizing	-	-	-	+	+	+	-
Galvanic-diffusion method with additional laser modification	-	-	+	+	+	-	+
Galvanic method with additional laser alloying using boron paste	-	+	+	-	+	+	-

A summary of fracture toughness of steel after borochromizing is presented in (**Figure 3**). It can be observed that the addition of chromium, as well as subsequent modification, reduce the brittleness in the layer in relation to boronized layers. The higher the load, the higher Kc value as the study covers larger and larger volumes of material with a diverse structure, starting from the surface layer all the way to the steel substrate. Kc values reach a maximum of 16 $MPa \cdot m^{1/2}$; to compare: Kc for medium carbon steel is approximately 50 $MPa \cdot m^{1/2}$ [11], and for iron boride Fe_2B – 5.84 $MPa \cdot m^{1/2}$ [2]. From the graphs it can be concluded that modification with elements and laser beam increases Kc, thus increasing fracture toughness. In calculations of fracture toughness using the Palmqvist method, the size of the indentations and cracks emerging from the corners of the indentations were taken into account. As far as cracks on the sides of the indentations were concerned, those closest to the tips of the indentations were taken into account. Cracks in the produced boronized and modified boronized layers were of different nature. The resulting cracks were classified and based on this it could be seen that their number largely depends on the applied load. The lower the load, the smaller the number of cracks. It was also found that chromium modification reduces crack numbers. On the basis of the studies conducted a scale of layer brittleness patterns following various treatment procedures was determined as shown in **Table 2**. A five-class scale was adopted containing patterns of indentations without cracks and with cracks coming out of the corners or sides of the indentations, as well as the halos around them forming a grid of cracks.

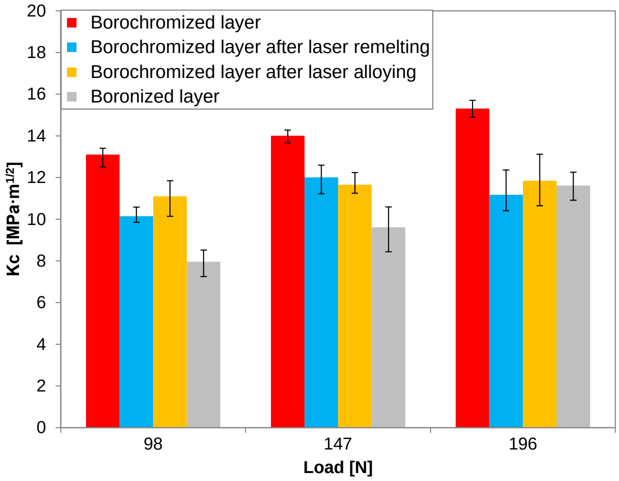
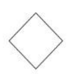
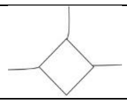
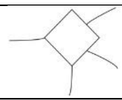
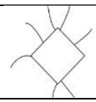
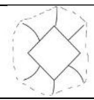


Figure 3 Fracture toughness of steel after borochromizing as well as borochromized and laser heat treaed compared to steel after boronizing

Table 2 Standard scale for assessing the fracture toughness of layers modified by various methods

Class of cracks	1	2	3	4	5
Type of cracks	no cracks	single cracks in the corners of the indentations	single cracks in the corners and walls of the indentations	numerous cracks in the corners and walls of the indentations	cracks in the corners and walls of the indentations, a network of cracks around the indentations
Example					

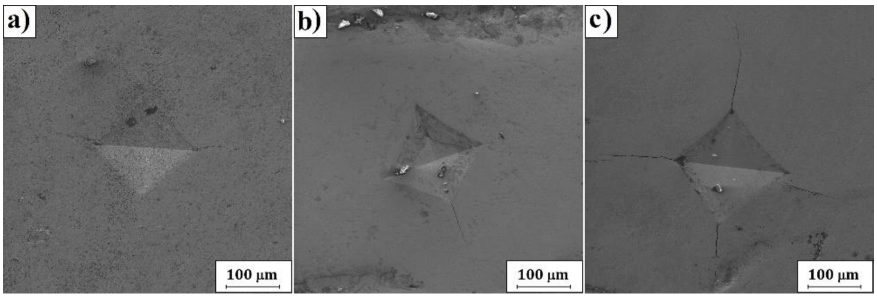


Figure 4 Example of microstructure photos after fracture toughness study: a) borochromized layer, b) borochromized layer after laser remelting, c) borochromized layer after laser alloying

Figure 4 summarizes examples of Vickers indentations with cracks after various processes used for selected individual classes of fracture toughness. Surface porosities visible in the photos of the structures somewhat inhibit the spread of cracks. Additional laser heat treatment results in homogenization of the structure and reduction of porosity; however, significant thermal stresses may occur. The studies show that the lowest number of cracks (Class 1 – 3) is obtained for laser remelted galvanic diffusion layers, as well as for layers produced by boron laser alloying of galvanic coatings.

4. CONCLUSION

1. Microstructure, microhardness and resistance to brittle cracking of layers are affected by the applied parameters of treatment procedures.
2. Borochromized layers, similarly to boronized layers, have a needle-like structure with a microhardness of 1700 HV0.05 – 1500 HV0.05.
3. Laser beam-modified borochromized layers have a milder microhardness gradient from the surface towards the core due to the presence of a heat-affected zone.
4. Phase composition analysis showed the presence of iron and chromium boride phases in accordance with Fe – B, Cr – B diagrams.
5. Modification of boronized layers with elements and a laser beam contributes to the elimination of occurrence of the FeB phase in the surface layer.
6. Layers produced by galvanic diffusion method are characterized by good fracture toughness.
7. High-energy beam-modified borochromized layers (laser remelting, laser alloying) have similar microhardness values. Laser alloying allows to obtain borochromized layers with lower energy consumption in the manufacturing process.

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