ISSN 1027-5495. Functional Materials, 28, No.1 (2021), p. 76-83.
doi:https://doi.org/10.15407/fm28.01.76 © 2021 — STC "Institute for Single Crystals"

Establishment of structure and operational properties of borated layers on 40X steel obtained from paste by induction heating

***S.Knyazev*[1], *O.Rebrova*[1], *V.Riumin*[2], *V.Nikichanov*[2], *A.Rebrova*[1]**

[1]National Technical University "Kharkiv Polytechnic Institute",
2 Kirpicheva Str., 61002 Kharkiv, Ukraine
[2]Kharkiv National University of Civil Engineering and Architecture,
40 Sumskaya Str., 61002 Kharkiv, Ukraine

Received September 15, 2020

Structural studies of borated layers on 40X steel obtained from pastes using high-speed heating (~ 500–1000°C/s) by high-frequency currents are presented. The structural features of the layer formed under conditions of high-speed heating are revealed. Some morphological differences between the layers obtained with high-speed heating were revealed. Fe_2B borides obtained by heating to 1300°C at a rate of 500°C/s have a rounded shape and are included in the matrix structure of the eutectic. Fe_2B borides obtained by heating to 1150°C at a rate of 950°C/s, have a regular shape with straight edges. In both cases, the matrix structure of the borated layer has a cellular morphology, which indicates the mechanism of intergranular diffusion. The elemental composition of the diffusion layer has been established. According to the results of testing the samples by erosion-abrasive wear, the most resistant of the considered borated layers is the layer obtained by high-speed heating at 1150°C with the highest ductility resource.

Keywords: borating, borides, intergranular diffusion, microhardness, high frequency currents.

Встановлення структури та експлуатаційних властивостей борованих шарів на сталі 40Х, отриманих з паст при індукційному нагріві. *С.А.Князєв, О.М.Реброва, В.В.Рюмін, В.В.Нікічанов, А.О.Реброва*

Представлено структурні дослідження борованих шарів з паст на сталі 40Х, отриманих з використанням швидкісного нагріву (~ 500–1000°С/с) струмами високої частоти (СВЧ). Виявлено особливості будови борованого шару, утвореного в умовах швидкісного нагріву. Показано морфологічні відмінності борованих шарів, отриманих зі швидкісним нагрівом, а саме при нагріві до 1300°С зі швидкістю 500°С/с борид Fe_2B має заокруглену форму і знаходиться у матричній структурі евтектики . При нагріві до 1150°С зі швидкістю 950°С/с борид Fe_2B має правильну форму з прямими гранями. В обох випадках матрична структура борованого шару має коміркову морфологію, що свідчить про реалізацію міжзереного механізму дифузії. Встановлено елементний склад дифузійного шару. За результатами випробувань зразків ерозійно-абразивним зношуванням показано, що найстійкішим з розглянутих є борований шар, що отриманий з швидкісним нагрівом при 1150°С та має найбільший ресурс пластичності.

Представлены структурные исследования борированных слоев из паст на стали 40Х, полученных с использованием скоростного нагрева (~ 500–1000°С/с) токами высокой частоты. Выявлены особенности строения слоя, образованного в условиях скоростного нагрева. Показаны морфологические различия слоев, полученных со скоростным нагревом, а именно при нагреве до 1300°С со скоростью 500°С/с бориды Fe_2B имеют закругленную форму и находятся в матричной структуре эвтектики. При нагреве до 1150°С со скоростью

950°C/c бориды Fe_2B имеют правильную форму с прямыми гранями. В обоих случаях матричная структура борированного слоя имеет ячеистую морфологию, что свидетельствует о реализации межзеренного механизма диффузии. Установлен элементный состав диффузионного слоя. По результатам испытаний образцов эрозионно-абразивным износом, показано что самым стойким из рассматриваемых борированных слоев является слой, полученный со скоростным нагревом при 1150°C с наибольшим ресурсом пластичности.

1. Introduction

High wear-resistance is one the general goals for all surface modification technologies [1]. At the same time, the structure and mechanical properties of the part core must remain unchanged. However, many technologies, for example, vacuum-plasma treatment, are quite expensive and too complicated for practical implementation. Well-known chemical heat treatment methods, including borating, do not currently meet the requirements for saving resources and energy [2, 3]. Therefore, it is necessary to improve existing technologies. One of the directions for improving the modification of the surface of materials is the intensification of diffusion processes by application of high-speed heating by high-frequency currents (HFC). Despite the fact that out-of-furnace treatment with induction heating requires special equipment (generator, inductor), it is still more affordable than vacuum technology, laser and electron beam heating. The use of pastes decreases the consumption of reagents, removes the difficulties that arise when working with a gaseous environment and makes it possible to localize the treatment zone. Increasing the efficiency of machine parts through the introduction of new highly efficient surface hardening technologies is considered an important task for materials scientists.

One of the reasons for the intensification of the borating process by HFC heating is a high number of defects in the high-temperature phase (austenite) that greatly facilitate the diffusion process [4].

Borating with special pastes is much easier comparing to the conventional borating [5]. However, authors [6] describe difficulties associated with the use of high-speed HFC heating: the use of fast (1000°C/s) heating leads to the fast saturation of finely dispersed austenite. In this case, taking into account the developed grain boundaries, the rate of the process significantly increases due to diffusion between grains. The material diffusing during the saturation will be located along the grain boundaries with little penetration into the grain. As a result, the concentration of boron on the steel surface required for the formation of a zone of solid borides cannot be reached. Authors of [4] carried out a high-speed borating of pipes through the HFC heating. A sample of 38HNM steel coated with a mixture of B_4C with polyvinyl alcohol (coating thickness 0.2–0.3 mm) was used. The operating temperature was about 1170–1180°C (temperature was controlled using a photo-optical pyrometer). The hardness of the obtained layers was HV920–980 which is slightly lower than normal. The wear resistance of the samples increased 8 times after the borating. According to the authors, the borating process is provided by the release of boron from B_4C with the participation of atmospheric oxygen and free atoms. Boron interacts with iron in steel at a temperature of 1175°C and forms boride layers.

Despite numerous studies of technological parameters of borating, the resulting structures, such as borated layers with a eutectic type structure, have not been sufficiently studied. Eutectic-typed borated layers are obtained by saturation from pastes with rapid heating to temperatures above the melting point of the ternary (Fe–B–C) or double (Fe–B) eutectic. They can also be obtained through melting single- and two-phase boride layers under the action of a laser beam or by HFC heating in vacuum and in a protective environment or by borating in powder mixtures. When steels are borated, the formation of eutectic begins at the boundary "boride layer — transition zone" then quickly spreads both towards the base metal and to the surface. The structure of the formed layer depends on the borating method, process temperature, operation time, cooling rate and can be either purely eutectic or preor hypereutectic with varying degrees of dispersion [7–10].

Despite some ambiguity in the formation mechanism of eutectic borated layers, researchers mentioned their high operational efficiency [11, 12]. Such layers are less brittle and less prone to chipping [7, 11].

Under the boride zone there is a transition zone of a solid solution of boron in iron which structure differs from the base metal. The thickness of the transition zone significantly exceeds the thickness of the boride layer. Usually, the thickness and

structure of the transition zone depend on the chemical composition of the steel, the method of borating, the cooling rate and the composition of the environment in which the surface layer is saturated with boron. In particular, the thickness, chemical composition and structure of the transition zone determine the nature of the distribution of residual stresses and the strength of the bond of the boride layer with the base metal. In addition, it is necessary to determine its tendency to chips, the conditions for the formation and development of fatigue cracks, the possibility of punching the layer. Therefore, the effect of the structure of the transition zone on these properties should be taken into account when choosing steels and assigning a saturation mode [11, 12].

The authors of [1, 6–10, 12] provide only information on the technology and some properties of borated layers obtained by high-speed heating. The authors of [6] give general information which is inferior to earlier sources. More complete and precise information on the structure is given in [12]. However, [1] should be considered as the most important recent study devoted to borating. Despite its relatively narrow specialization and complexity, this work provides an overview of the classical methods of borating by heating in a furnace. However, [1] contains little information on non-stationary heating conditions under electron beam and laser heating. The recent study of borating by the induction heating [7] does not fully reflect all the states of the layer (for example, does not specify the process rate and processing time), and does not contain reliable and detailed images of the obtained structures. The formation of carboborides at high-speed laser heating, which indicates the key features of structure formation under non-stationary conditions, is shown in [8]. The formation of an essentially natural composite of hard and soft structure on the surface has also been noted, but the use of laser technology to obtain borated layers inevitably leads to significant melting of the surface and complication of the technology. In [8, 9], boron layers were formed under nonstationary conditions of laser heating, but it is surprising that the authors found the formation of only equilibrium structures without the formation of carboborides. One of the recent studies showing the positive role of paste saturation over powder saturation is [10]. The conclusions of the authors in [10] confirm the prospects of using pastes. Unfortunately, only steady-state systems treated in a furnace for 4 h have been studied. The lack of experience in research on metallography of structures obtained using this technology does not allow the development of a purposeful scheme of directed surface modification.

The general aim of the current work is to improve the existing technology of borating with pastes at high-speed HFC heating at temperatures below the temperature of formation of an equilibrium boride eutectic; the exposure time should not exceed 9 seconds, otherwise, at a heating rate of about 1000°C/s, the surface may significantly melt and the effect of phase hardening may decrease due to the development of collective recrystallization processes. Also, a detailed study of morphology of the structure of borated layers and establishment of the relationship between structure and erosion resistance of the coatings will be carried out.

To achieve the aim, the following tasks will be solved:

— prepare samples of the borated layer by high-speed HFC heating;

— compare the structure, phase composition, microhardness, distribution of elements in the borated layers after borating in a furnace and high-speed heating of high frequency current;

— confirm the mechanisms of the structure formation for borated layers during high-speed heating on the base of the obtained results;

— test the properties of obtained borated layers under conditions close to operational.

2. Experimental

Samples for research were made of 40X steel; the composition was determined by X-ray fluorescence and diffraction analyses using a SPRUT instrument based on the principles of wave and energy dispersion. The carbon content was determined by calculating the intensity of the diffraction line of cementite in the total spectrum according to the method described in [13]. The composition of steel is given in Table 1.

The distribution of chromium in the near-surface layers was determined by X-ray fluorescence analysis with successive surface grinding. The thickness of the removed surface material was controlled by metallographic analysis on a cross-section with microhardness marks. For the preparation of saturation pastes, the following components were used: substance-supplier of active boron atoms, activator and binder. Commercial boron carbide B_4C with a grain size of

Table 1. Chemical composition of steel, wt. %

Type of steel	C	Cr	Ni	Cu	Mn	Si	S	P
40X	0.410	1.100	0.150	0.110	0.700	0.190	0.025	0.030

60 μm was used as a substance-supplier of active boron atoms. Sodium fluoride (NaF) was used as an activator. Liquid glass (sodium silicate) was used as a binder for the paste.

Before applying the paste, the steel samples were ground on a sheet of sandpaper and degreased. One of the surfaces was covered with the paste and dried with warm air within 3 min.

Furnace borating with low heating rates and relatively high shutter speeds provides the formation of equilibrium structures and was carried out to obtain samples for erosion tests. The experiments were carried out in a laboratory electric furnace with a thermocouple and a microprocessor controller, which made it possible to implement a more complex thermal process in an automatic mode.

High-speed heating was carried out using a high-frequency current generator VCHG 60-3/0.44 (with a frequency of 440 kHz) and a direct-acting inductor. The ferrite core was used to obtain a high power density on the inductor. For the same reason, the gap between the inductor and the sample was 6±0.5 mm and was limited mainly by the thickness of the paste layer and the required heating rate. The sample was processed by continuous sequential movement of the sample relative to the inductor at a speed of 10÷30 mm/s. Two operating modes of the generator were used: (1) the current in the circuit is 3 A, the anode voltage is 5 kV; (2) the current in the circuit is 7.5 A, the anode voltage is 7 kV.

Thermocouples with a diameter of 0.1 mm were used to measure the temperature. They were welded to the sample in a flattened form before applying the saturating paste. This allowed increasing the sensitivity of the sensor. To determine the heating temperature and to set the heating rate of the samples, the thermocouples were used to record the heating curve on a computer via an analog-to-digital converter (ADC). The rate and accuracy were ensured by the ADC by converting thermoelectric force into digital format and subsequent data collection on a computer.

After welding and covering the surface of thermocouples by the paste, the samples were fixed in a special clamp-shaped accessory. The thickness of the paste was controlled by measuring with a caliper. The thickness of the paste was normally 1.5÷2 mm. The use of pastes simplifies the coating required for borating (compared to gas, liquid and electrolytic processes). At the same time, the complexity of preparation for the saturation process increases. The application of pastes under pressure in a thin uniform layer partially eliminates this disadvantage.

The moving part consisted of the accessory (in which the sample was placed), a rod, a reducer and a drive with an electric motor. The inductor itself remained stationary. The gap between the surface of the sample (taking into account the thickness of the paste) and the inductor was controlled by a set of probes and varied in the range of 1.5÷3.0 mm.

The ZEISS AXIO Vert.A1 inverted microscope was used for metallographic analysis. The measurement of microhardness was performed on the device PMT-3 at a load of 200 g. Images were obtained on a scanning electron microscope (SEM), microanalysis of individual structural components was performed on a Philips XL 30 ESEM instrument.

The test for abrasive wear used the action of sand at a pressure of 5 atmospheres. The samples were weighed with an accuracy of ±0.01 g before and after processing. The nozzle was oriented at angles of 15 deg, 45 deg and 90 deg to the surface.

3. Results and discussion

Borating with HFC heating was carried out for 11 sec at the temperature about 1300°C (heating for 2.6 sec at a rate of 500°C/s). The process took place with a continuous translational motion of the sample relative to the inductor.

The thickness of the borated layer reaches 400 μm; on the edges, the thickness decreases to 300 μm due to the reduction of the thermal exposure time under conditions of continuous translational motion of the sample. Images of the layer show that 93 % is a eutectic of a regular structure (Fig. 1). The morphology is cellular; some parts are separated by larger plates. The results of a detailed study of the microstructure and the distribution of trace elements are presented in Fig. 2 and in Table 2.

Table 2. Results of elemental microanalysis of the structural components of the borated layer at 1300°C and a heating rate of 500°C/s

Control points (on the Fig. 2)	Elemental composition, % mass				
	Fe	Cr	Mn	B	C
1	90.3	0.13	0.09	9.1	–
2	94.1	1.9	0.3	3.9	0.35

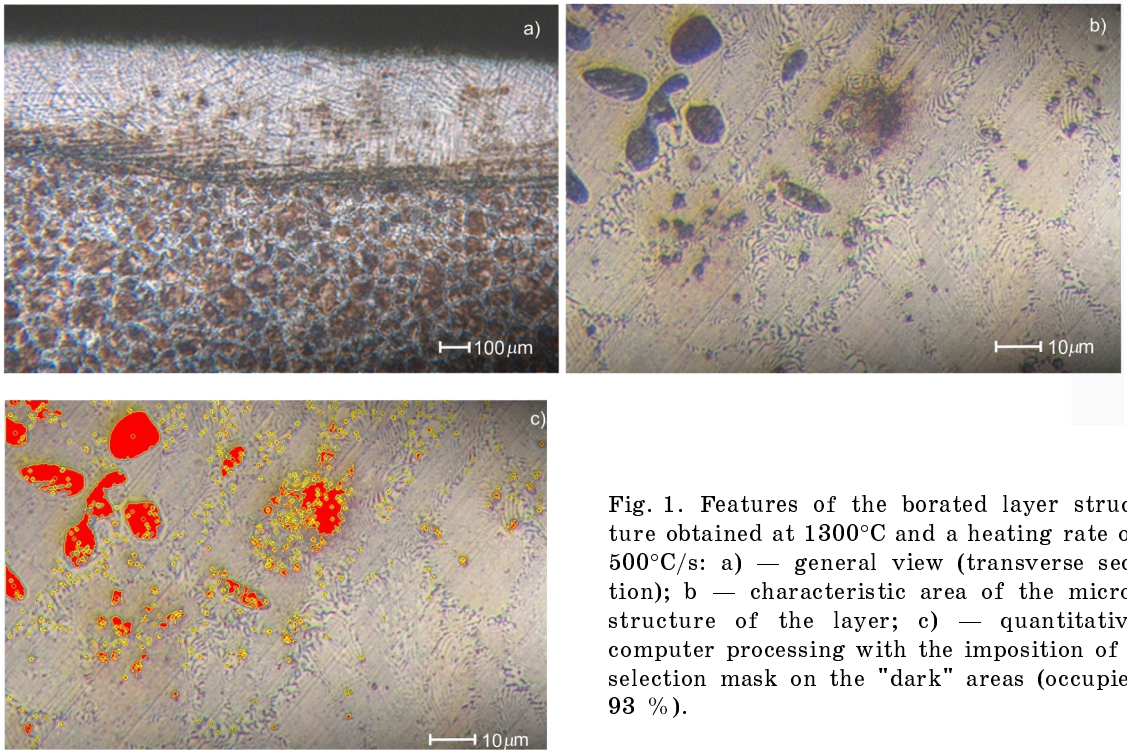

Fig. 1. Features of the borated layer structure obtained at 1300°C and a heating rate of 500°C/s: a) — general view (transverse section); b — characteristic area of the microstructure of the layer; c) — quantitative computer processing with the imposition of a selection mask on the "dark" areas (occupies 93 %).

Analysis of particular sections shows that at point 1, boride of the Fe_2B type (12300 MPa) (Table 2) with rounded edges is formed (Fig. 2). This indicates that some micro-volumes have become liquid. In the point 2, a small amount of boron was found; there are two phases: a solid solution of boron in iron and boride Fe_2B. Microhardness of the eutectic is 7000 MPa, it is considered a relatively plastic structure. At the cell boundaries with a slightly coarser eutectic, the microhardness is 9000 MPa.

The heating modes were changed in order to eliminate the effect of melting of individual micro-volumes. Heating was performed at 1150°C at a rate of 950°C/s for 1.2 sec. The duration of borating was about 7 sec. The speed of movement of the sample was increased, the gap between the surface of the sample and the inductor was slightly reduced according to a decrease in the thickness of the applied paste from 3 to

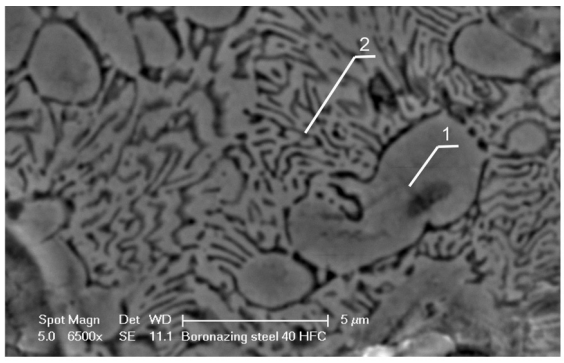

Fig. 2. SEM image of features of the structure of the borated layer obtained at 1300°C and a heating rate of 500°C/s (×6500).

1.5 mm. The morphology of the obtained borated layer w ith a thickness of 250 μm is different from the previous one. Fig. 3 shows a heterogeneous structure: the matrix is a solid solution of boron in iron with

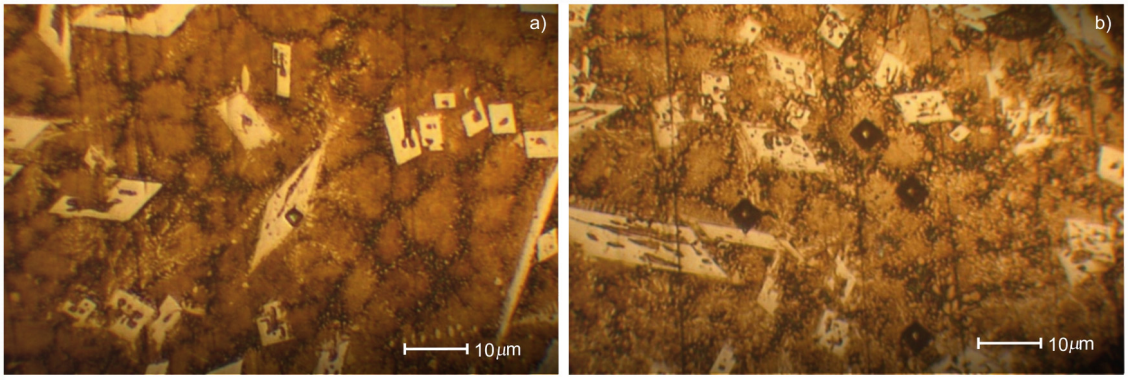

Fig. 3. Features of the structure of a borated layer obtained by high-speed HFC heating at 1150°C and a heating rate of 950°C/s (with imprints of microhardness measurements): a) — area of hardness measurements near the edge of the surface borides; b) — zone at the interface "layer — metal matrix" (measurements of the microhardness of a solid solution of boron in iron (×1000).

an average microhardness of 6000 MPa with inclusions of boride of a regular shape and carboborides of the $Fe_{23}(C,B)_6$ type. The microhardness of $Fe_{23}(C,B)_6$ clusters reaches 8000 MPa. The microhardness of Fe_2B is on average 14000 MPa. Unlike the previous processing mode, borides have sharp regular faces (Figs. 3, 4), which follow the structure of the crystal lattice. The boride composition is completely stoichiometric (Table 3), while the concentration of boron in the matrix structure is lower in comparing to the structure obtained at 1300°C. The change in morphology is associated with a change in non-stationary formation processes. It has been found that after borating using HFC heating, the distribution of chromium in steel is uniform (Fig. 5) and corresponds to the average concentration in the used 40X steel.

To verify the operation properties of the obtained reinforced layers, numerous tests have been performed under abrasive wear conditions. Under the tangential action of abrasive particles, no noticeable wear of a surface was observed on all samples. The samples were tested for several weeks, treated with the same abrasive particles, which hit the surface at an angle of 45 deg; the loss of mass was at the limit of determination. When the angle of contact between the abrasive particles and the boron layer

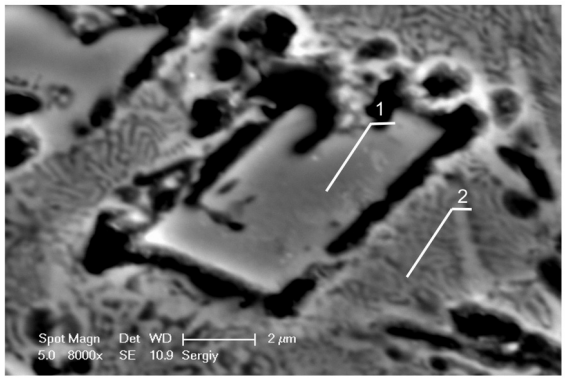

Fig. 4. SEM image of features of the structure of the borated layer formed at 1150°C and a heating rate 950°C/s (×8000).

was 90 deg, after 2 days of testing, their complete penetration through the hardened layer was observed, followed by a catastrophic change in shape. The sample borated by HFC heating at 1300°C was characterized by a gradual weight loss of 0.03 g/h. The sample borated by HFC heating at 1150°C was also characterized by a gradual weight loss of 0.01 g/h. The tests lasted for several days. For comparison, the weight loss of thermally-treated samples was 0.3 g/h after 10 hours of testing; in the annealed state it was 3 g/h in 1 hour.

Table 3. Results of microanalysis of the structural elements in the borated layer at 1150°C and a heating rate 950°C/s

Control points (on the Fig. 4)	Element composition, wt. %				
	Fe	Cr	Mn	B	C
1	91.3	0.10	0.07	8.9	–
2	93.1	3.0	0.6	3.1	0.35

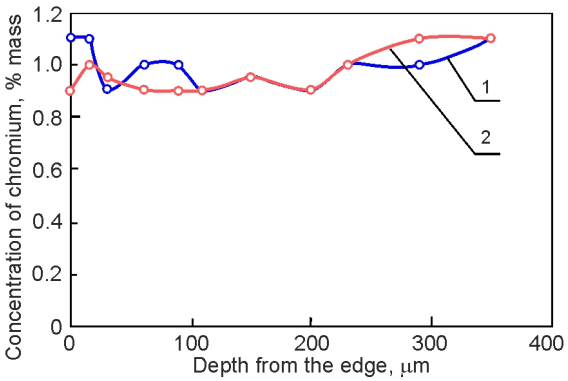

Fig. 5. Layer-by-layer distribution of chromium in the borated layer on steel 40X after borating with HFC heating: *1* — at 1300°C; *2* — at 1150°C.

Microstructure and microhardness of the borated layer obtained by the furnace borating technology indicates the sequential formation of equilibrium borides FeB and Fe_2B, followed by the formation of a transition zone. The slow release of atomic boron from the paste and its transfer to the surface balances the diffusion of boron into steel. Thus, there are no concentration prerequisites for the formation of metastable structures.

The borated layer obtained by induction heating has certain morphological differences, both in phase composition and in structure. These features are strongly influenced by heating modes — temperature and heating rate. Obviously, the structure of the cells is similar to the contours of the matrix material before processing. This structure is determined by heredity and confirms the fact that at the initial stage the boron diffusion proceeded along the grain boundaries, where the primary eutectic was formed. Then the phases increase slightly and turn into more equilibrium borides with less developed boundaries. The morphology of the structure of borated layers obtained with high-speed heating is completely different from the morphology of the layers after furnace borating. After short-term processes, instead of a solid layer of borides, a small number of isolated borides surrounded by a eutectic structure or a solid solution of boron in iron were formed. The microhardness of the matrix structure of the boride layer is lower than the microhardness of borides; therefore, the matrix is more flexible. The difference between the properties of the borides obtained at 1300°C and 1150°C showed that the temperature could be reduced. Increasing the heating rate from 500°C/s to 950°C/s also had a significant impact.

According to the elemental distribution of borated layers, under the conditions of a non-stationary process of heating and saturation, in contrast to borating in a furnace, there is no counter diffusion of chromium to the main boron flow due to the short duration of the process.

Operational tests showed a noticeable change of weight loss for different samples. The borated layer obtained by high-speed heating at 1150°C was the most stable. Samples borated in a furnace are resistant to erosion but can be destroyed by micro-shock. That indicates that the layer borated in a furnace can effectively resist the destruction only in the tangential action of abrasive particles, i.e. can effectively resist cutting. Otherwise, the boride coating gets chipped and the material gets washed out from the sample. Thus, the structure of the borated layer obtained by out-of-furnace borating has a higher plasticity comparing to the borated layer with solid Fe_2B especially under micro-shock conditions. Further development of borating technology is aimed at increasing the heating rates, reducing process duration and the formation of thinner non-equilibrium diffusion layers. This trend is constrained by the complexity of the hardware control of technological processes and the high requirements for the speed of measuring instruments.

5. Conclusions

Under non-equilibrium operation conditions, the morphology of borated layers is completely different and is characterized by a reduced concentration of boron. High-speed processes provide the formation of relatively thick diffusion layers with a thickness of 200–400 μm.

It is known that chromium in steel (at a small concentration of 1 %) in equilibrium processes diffuses towards the main flow of boron. It has been established that this effect is absent under the conditions of short-term non-equilibrium processes.

Peculiarities of the structure of borated layers obtained by HFC heating (cell structure with a coarse eutectic and carboborides at the boundaries) indicate the presence of a grain boundary mechanism of boron diffusion.

Increased ductility of borated layers obtained by HFC heating is provided by the isolation of borides, which are enclosed in a relatively plastic matrix. High plasticity of the borated layer, in comparison to the

layer of solid borides, is confirmed by erosion-abrasive tests.

A disadvantage of this technology is the sensitivity of the process to any fluctuations in heating modes: the gap between the sample and the inductor, electrical parameters, etc. Heating modes must be adjusted for each surface.

References

1. H.O.Postelnyk, O.V.Sobol, L.Kucerova, Osman Dur, *Functional Materials*, **27**, 303 (2020).
2. M.Kulka, Current Trends in Boriding. Techniques, Poznan (2019).
3. H.Masumoto, A.Asada, H.Hasuyama et al., *Welding Intern.*, **11**, 110 (1997).
4. V.Andryushechkin, A.Bashnin, *Materialovedenie i Termicheskaya Obrabotka Metallov*, **4**, 23 (1981).
5. M.Pogribny'j, S.Knyazyev, *Metaloznavstvo ta Obrobka Metaliv*, **1**, 33 (2011) [in Ukraine].
6. A.Matuschka, Boronizing, Hanser, Munchen (1980).
7. V.Ivanayskiy, A.Ishkov, N.Krivochurov et al., *Polzunovskiy Vestnik*, **3**, 201 (2010).
8. D.Mikolajczak, M.Kulka, N.Makuch, P.Dziarski, *Arch. Mech. Tech. Mater.*, **36**, 35 (2016).
9. T.Kusuhara, J.Morimoto, N.Abe, M.Tsukamoto. *J. High Temp. Soc.*, **36**, 295 (2010).
10. S.Yunus, S.Alias, F.Wong et al., *ARPN J. Eng. Appl. Sci.*, **10**, 7821 (2015).
11. V.Labunets, L.Voroshnin, Iznosostoykie Boridnyie Pokryitiya, Tehnika, Kiev (1989).
12. R.Joseph, Surface Hardening of Steels: Understanding the Basics. ASM International, Technology & Engineering (2002).
13. I.Mihaylov, A.Baturin, A.Mihaylov, Rentgenovskie Metodyi Analiza Sostava Materialov: "Pidruchnik NTU HPI" Kharkov (2015).