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X-RAY PHASE AND MICROSTRUCTURAL ANALYSIS OF HARDENING COATINGS OBTAINED BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS IN COMBINATION WITH HEATING OF A MIXTURE OF $Al + B_2O_3$ BASED ON HIGH-FREQUENCY CURRENT TREATMENT

Ishkov A.A.[1], Malikov V.N.[2], Tikhonsky N.D.[2], Gulyarenko A.A.[3], Remshev E.Yu.[4], Voinash S.A.[5], Sokolova V.A.[6], Orekhovskaya A.A.[7]*

[1] Altay State Agrarian University, Barnaul, Russia
[2] Altai State University, Barnaul, Russia
[3]Seifullin Kazakh Agro Technical University NJSC, Nur-Sultan, Kazakhstan,
[4] Baltic State Technical University “Voenmeh”, Saint Petersburg, Russia
[5] PRO FERRUM Limited Liability Company, St. Petersburg, Russia
[6] Military Academy of Communications named after Marshal of the Soviet Union S.M. Budyonny, Saint Petersburg, Russia
[7] Belgorod State Agricultural University named after, Belgorod Region, Russia, orehovskaja_aa@bsaa.edu.ru

The paper describes the results of studies of hardening boride coatings obtained during the implementation of the process of self-propagating high-temperature synthesis. These coatings were composite materials based on aluminum oxide and boron. The obtained coatings were subjected to X-ray phase and microstructural analysis, which showed the main components of the resulting compositions and made it possible to assess the thickness and structure of the coating-base metal transition area. The different content of silicon and iron makes it possible to assess the occurrence of surface chemical and metallurgical processes during self-propagating high-temperature synthesis when heating of the base mixture samples on high-frequency current treatment. The expediency of using high-frequency current treatment in combination with the process of self-propagating high-temperature synthesis for better-quality spattering of the hardening coating is shown. The appearance of two areas in the coating with different thickness and structure of the coating is established.

Keywords: steel hardening, microstructure analysis, self-propagating high-temperature synthesis, coatings, high-frequency currents.

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Introduction

An increase in the strength of steels and alloys can be obtained by creating ideal structures through targeted process exposure. According to the operating conditions, many products should have high surface hardness and strength, and a ductile core. This combination of properties is achieved by surface plasma or laser hardening of 65G steel. As is known, instead of the widely used 65G steel, manufacturers in the last 3-5 years have been increasingly using boron-containing 30MnB5 steel for the manufacture of working machine bodies (mainly for the working machine bodies), and tungsten-containing 5-6XB2C steel is recommended to replace the said steel in cutting elements (blades). At the same time, oxides which significantly reduce the wear resistance of cutting tools made of high-speed steel, are generated on the working surfaces of these materials in the process of cutting in the high-temperature areas (up to 620–630ºC). To increase the wear resistance of the tool, various methods of hardening are used, including the application of protective coatings [1-3]. To strengthen the cutting edge of the parts under study using modern technologies, methods of applying various hard, wear-resistant, and functional coatings are widely used, e.g. flame, arc, laser and plasma weld surfacing, induction (HFC) weld surfacing, creation of bimetallic elements on the cutting edge using cladding, etc.

Self-propagating high-temperature synthesis (SHS) of solid chemical compounds is a new technological process for obtaining hardening coatings, which is based on carrying out an exothermic chemical reaction of the interaction of initial reagents in the form of combustion [1-2]. As a result of this process, a layer with very good properties, such as high microhardness, good wear resistance, and corrosion resistance, can be obtained [4-7]. Due to the acicular microstructure, the borated layer is characterized by good adhesion to the steel substrate. However, despite these multiple advantages, the borated layers are rather brittle. This disadvantage can manifest itself in the form of chips and peeling from the substrate [4]. At the same time, there are many methods for increasing the strength and stability of such layers [8-11]. One of such methods is heating using HFC during the formation of a diffusion borated layer [7,8]. Therefore, a layer is obtained with a changed microstructure and new properties, such as high hardness, strength, wear resistance, and corrosion resistance [12]. However, most of the currently known methods of borating steel (furnace, gas, or electrolytic) are long-lasting, labor-intensive, non-automated, and poorly integrated into the process schemes of modern production. A significant intensification of borating occurs during high-speed HFC heating of the steel surface under a layer of a special borated charge material [13, 14].

It is assumed that conducting a combined process of applying a functional coating on the surface of steel parts with the joint implementation of SHS, HFC heating, and the method of high-speed HFC borating, which we are developing, is capable of providing better characteristics of the obtained boride coatings and achieving a significant increase in the strength of the steel part. Carrying out studies of SHS processes in the basic model system and its modified versions is required to establish the laws of initiation and combustion of a charge material of various compositions, as well as to control this process with the possibility of further obtaining high-quality hardening boride coatings on the surface of a steel part with a thickness of at least 150-200 microns and to develop a prototype of the existing technology.

In addition, it is required to experimentally test the possibility of obtaining such coatings on hardening HFC installations, which make up the main equipment fleet of operating agricultural machine-building enterprises. Theoretically, such a possibility is predicted since the maximum temperature reached on such installations on the surface of the part T_{hard} = 850-950°C (due to the limited power of the generators, the element base usedб and the design specifics of the inductors), which is insufficient for the implementation of the high-speed HFC borating process (T_{bor} = 1150-1250°C), can be increased due to the heat released during the combustion of the exothermic $Al+B_2O_3$ mixture.

To obtain a qualitative result and a sufficient amount of experimental data, it is required to perform work on the study of the main characteristics of SHS processes in a model system suitable for obtaining hardening, mainly boride coatings (study of the conditions for initiation of SHS and the stability of the process, determination of the combustion rate, the maximum temperature of the process, thermal structure combustion waves, structure and phase product composition, etc.).

1. Materials and Methods

A high-temperature redox reaction in the B_2O_3+Al system was chosen as a model system for the implementation and study of SHS processes. The chemical interaction of the components in this system can be described by the following stoichiometric equation:

$$B_2O_3 + 2Al = 2B + Al_2O_3,\ \ \Delta H_p < 0 \tag{1}$$

As a result of the chemical interaction in the B_2O_3+Al system, a component is generated, which, during HFC heating in the presence of the P-0.66 borate flux, can interact with the steel surface of the part, thus forming boride wear-resistant and hardening compounds in the Fe-B system of various compositions.

The B_2O_3+Al model system is sensitive to moisture content, which is caused by the interaction of boric anhydride with water and the generation of metaboric acid, and, after that, orthoboric acid:

$$B_2O_3 + 3H_2O = 2H_3BO_3$$

Therefore, before preparing the initial charge material, it is required to dehydrate thoroughly the available boric anhydride or to have a freshly synthesized product. For dehydration, the available boric anhydride was crushed and placed in a stainless steel tray, which was closed with a perforated lid capable of passing vapors of crystallization and chemically bound water. The tray was installed in a SNOL-type muffle furnace heated to 120-150°C for 1-2 hours. During this time, all crystallization water escaped from boric anhydride. After that, the temperature in the furnace rose to 750-800°C and upon reaching it, boric anhydride was soaked for another 1-2 hours. During this time, almost all chemically bound water escaped from the product. After the end of calcination and cooling, the tray was removed from the muffle, where the resulting glassy mass was recovered from it. The resulting product was crushed in a jaw crusher and then ground in a ball mill. After sieving, a powder of dehydrated boric anhydride of the required fractional composition was

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obtained. To prepare experimental samples for studying the main parameters of SHS processes in the model system, the following method was used: a small amount of the initial charge material was moistened with alcohol or alcohol-acetone mixture to a mushy state and thoroughly mixed. A 10 mL disposable injection syringe with a cut-off bottom was filled with the resulting wet mixture; the syringe was placed with its open part on filter paper and the mass was tapped; the plunger was inserted and loaded for 2-3 sec without removing the syringe from the paper. Then, raising the syringe, the resulting cylindrical sample was carefully pushed out onto paper and dried in the air until the smell of alcohol disappeared. The final drying of the sample took 2-3 hours.

The previously obtained dried cylindrical sample was placed on a ceramic support. 4-5 turns of a nichrome coil connected to the laboratory transformer were placed on its upper base and the coil was pressed to the end of the cylinder so that the turns were 1/3 immersed in the charge material, after which the current was passed along the spiral, gradually increasing the voltage on the autotransformer. mAs soon as a stable combustion zone was initiated at the end of the sample, the current from the coil was turned off and the propagation of the SHS front was monitored. If the case of the need for the study of the SHS process during high-speed HFC heating, a dried cylindrical sample was placed on the surface of a steel plate with dimensions of 20*50*5 mm, which was in turn placed in a single-loop inductor connected to an HFC generator. The generator was turned on and the steel was heated until the onset of SHS on the lower base of the sample. As soon as a stable combustion zone is initiated at the end of the sample, the inductor current is switched off and the propagation of the SHS front is monitored. For the study, prepared samples of the basic composition in the form of molded cylinders (No.1, 3) with a diameter of 10 mm and a length of 20-30 mm, as well as in the form of a powder (No. 2), were used.

The SHS process was initiated in all cases by high-frequency heating of samples installed on the surface of steel plates with dimensions of 10-20*30-50 mm and thicknesses of 3-6 mm, made of structural alloyed steels of domestic (65G) and imported (S355) production. The molded cylindrical specimens were freely installed on horizontally fixed plates, after which they were heated using HFC until the occurrence of the SHS process, which was visually registered (bright flash) and further until the plate material reached a temperature of 1,100-1,200°C (white-yellow heat). The powder of the basic composition was moistened with alcohol to a mushy consistency and freely applied to a previously prepared (cleaned) plate with a layer of 2-3 mm thick, and then dried. The SHS process and HFC heating of the powder sample (coating) were initiated similarly to the molded samples.

2. Experimental Results

Combustion products of cylindrical molded and powder samples are black, easily crumbling sinter close to the original sample in dimensions and shape. Combustion products are weakly bound to the steel substrate. In the places where the base composition is applied on steel plates, after its combustion, surface changes associated with the formation of coatings and the melting of the base metal are visible. The combustion products of the basic composition obtained during the SHS process were subjected to X-ray phase analysis (XPA) using a powder method on a Shimadzu XRD 6000 diffractometer (equipment of the GOSNITI Nanocenter, Moscow). According to the results of the XPA of the charge material, the diffraction patterns shown in Fig. 1 were obtained. Fig. 1 shows that the diffraction patterns of all three samples coincide; therefore, the composition was determined only for one of them. The determination was carried out by the computer program of the device by comparing the most intense peaks and their groups with the built-in database. The results of determining the composition of the SHS products in the base mixture during HFC heating are shown in Fig. 2. As follows from the data in Fig. 2, the SHS products of the samples contain aluminum oxide, aluminum nitride, and boron (identified by the operator as zirconium boride) as the main components, which confirms the occurrence of the SHS process in the basic composition according to reaction equation 1. It should also be noted that it is difficult to identify the phase composition of the products by the selected method of physicochemical analysis since the main reflexes of the main phases coincide. Only the Al_2O_3 and AlN phases are reliably identified.

The generation of a significant amount of aluminum nitride, AlN, is explained by the occurrence at a high SHS temperature of the interaction reaction of a part of the initial aluminum with nitrogen in the air according to the following scheme:

$$2Al + N_2 = 2AlN$$

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Figure 2.a shows a diffractogram of one of the studied samples (Raw Data) with a reflection of the observed reflexes (Peak Data, Figure 2.b) and Miller indices. The diffraction peaks of Al_2O_3 from the ICDD database (Card Data, Fig. 2.d) are also presented. Entry Data (Fig. 2.c) shows a comparison of the observed reflexes of the test sample with the database, Different colors of reflexes on the Entry Data graph show the coincidence of peaks with different substances in the database: Al_2O_3, AlN, ZrB, $Li_4P_4O_{12}$+$2H_2O$.

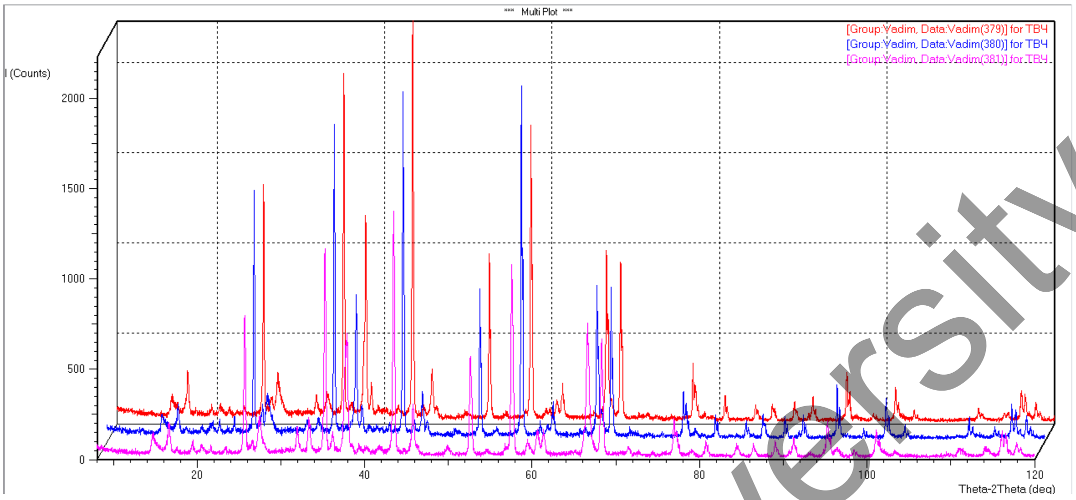
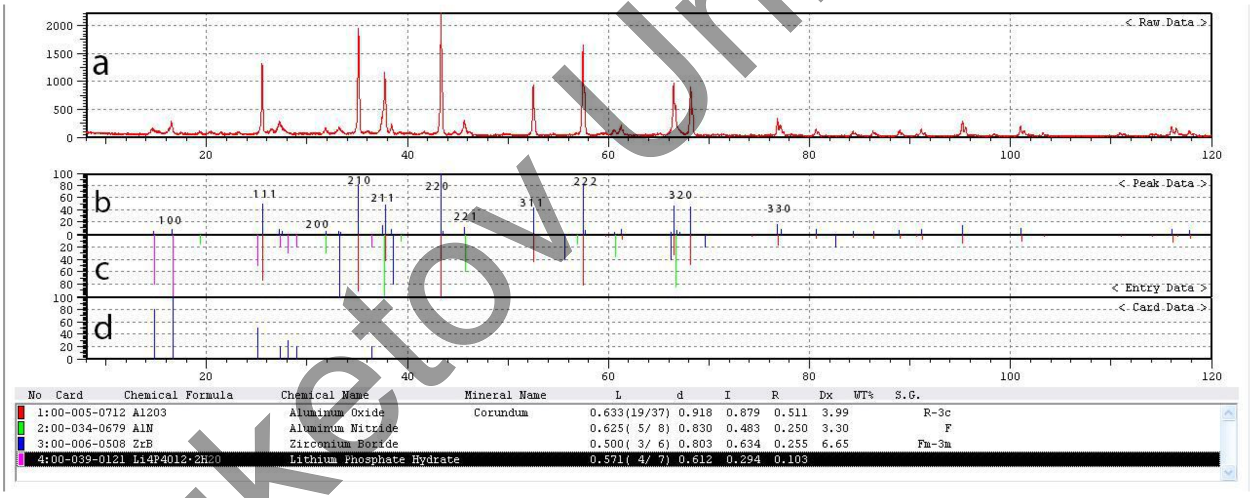


Fig.1. Diffraction patterns of combustion products of samples No.1-3



No	Card	Chemical Formula	Chemical Name	Mineral Name	L	d	I	R	Dx	WT%	S.G.
🟥 1:	00-005-0712	Al203	Aluminum Oxide	Corundum	0.633(19/37)	0.918	0.879	0.511	3.99		R-3c
🟩 2:	00-034-0679	AlN	Aluminum Nitride		0.625(5/ 8)	0.830	0.483	0.250	3.30		F
🟦 3:	00-006-0508	ZrB	Zirconium Boride		0.500(3/ 6)	0.803	0.634	0.255	6.65		Fm-3m
🟪 4:	00-039-0121	Li4P4012·2H20	Lithium Phosphate Hydrate		0.571(4/ 7)	0.612	0.294	0.103			

Fig.2. An example of decoding the diffraction pattern of SHS products of sample No.1

This should be taken into account when calculating the composition of the modified mixture for the future coating technology, increasing the aluminum in content. The low reliability of the determination of boron in the SHS products of the base mixture may be associated with its release under the reaction conditions in the amorphous state, possible partial burnout by the reaction

$$4B^* + 3O_2 = 2B_2O_3,$$

As well as diffusion and interaction with the surface of the steel part with the generation of target products, iron borides, iron carbo borides, and Fe-B, Fe-B-C eutectics.

These processes should also be taken into account when calculating the composition of the modified mixture by introducing various fluxes and additives. Samples for the study were prepared from steel plates with surface changes in the places of application of the base mixture, which had appeared after the SHS process during HFC heating. The structure of the samples in the areas of surface changes (presumably

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formed coatings) and borated layer thickness was studied and determined. Figures 3-6 show the results of the study of the structure of the coating obtained in the SHS process during the high-frequency heating of sample No.1 mounted on a plate made of S355 steel at various magnifications.

As follows from Fig. 3, when the SHS process is carried out during HFC heating of the cylindrical sample No.1, which is molded from the base mixture, at the place of its installation on the surface of a plate made of S355 steel, the formation of a coating with a complex structure of the transition area, which contains several components and porosity, is indeed observed. The thickness of the resulting coating ranges from 150 to 250 microns. The complex structure of the coating-base metal transition area, multi component nature, and porosity of the resulting coating are clearly visible at higher magnification in polarized light (see Fig. 4).

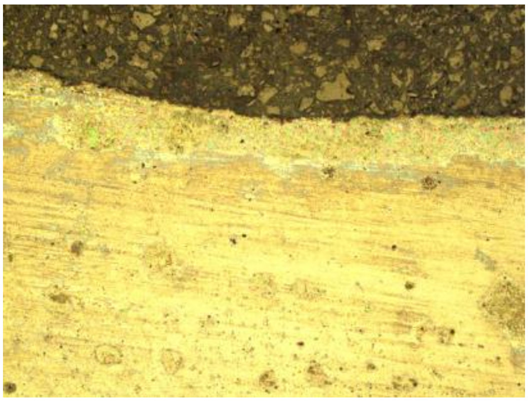

Fig. 3. Microstructure of the coating obtained on S355 steel in the SHS process during HFC heating of sample No.1 (general view, ×100 magnification).

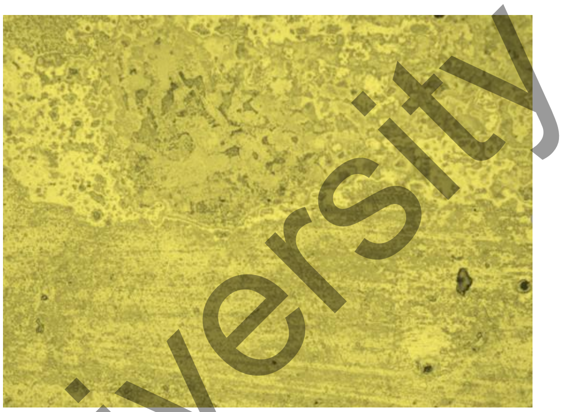

Fig. 4. Microstructure of the coating obtained on S355 steel in the SHS process during HFC heating of sample No.1 (transition area, ×500 magnification).

Structures similar to those observed above were obtained also on S355 steel and in the SHS-process during high-frequency heating of sample No.3, which was placed on the surface of the steel plate, with the only difference that their thickness was 70-100 microns. A decrease in the thickness of the coatings formed in the SHS process during high-frequency heating of sample No.3 is explained by its lower height (volume, mass), as a result of which a smaller amount of surface-active products generated during combustion is observed. The coatings obtained in the SHS process during HFC heating of sample No.2 (sheath) have a completely different structure (Fig. 5, 6).

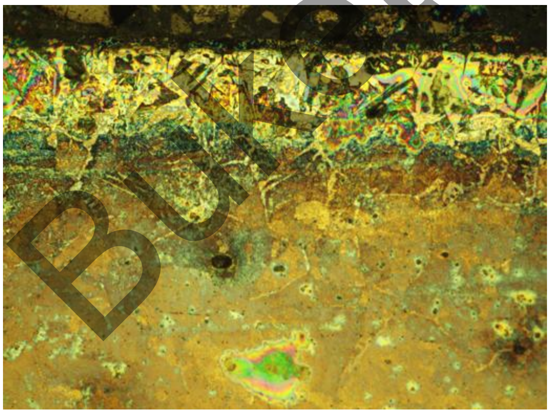

Fig. 5. Microstructure of the coating obtained on S355 steel in the SHS process during HFC heating of sample No.2 (section 1, coverage, ×500 magnification).

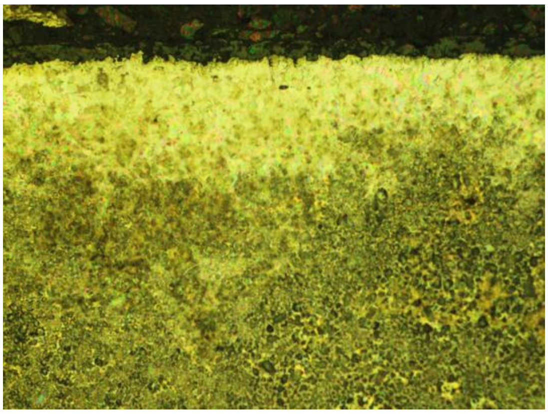

Fig. 6. Microstructure of the coating obtained on S355 steel in the SHS process during HFC heating of sample No.2 (section 2, coverage, ×500 magnification).

Fig. 5-6 clearly show two areas (zones) with different thicknesses and structures of the coating are formed in the coating formed in the SHS process during HFC heating of sample No.2 with a thickness of 2-3 mm, of the base composition applied to the surface of S355 steel. The central coverage area (section 1) is

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formed in the place that was subjected to the strongest HFC heating of a steel plate coated with a sheath from the base composition; the peripheral coating area (section 2) is formed along the edges of the boundaries of sheath application, in the areas subjected to the lowest heating. The obtained images show that the microstructure of the coating of the periphery area is similar to the microstructure of the coating obtained in the SHS process during high-frequency heating of samples Nos.1, 3 (see Fig. 6, section 2). The microstructure and composition of the coating of the central area differ from the previously obtained coatings (see Fig. 5, section 1). The coating of area No.1 has a minor thickness (50-70 microns) and a structure characteristic of boride phases is noticeable, i.e. closed dark carbide regions, light interlayers of iron-boride and iron-carbo-boride eutectic.

The study of macrophotographs (50) of the grinding of reinforcing coatings allows the morphology of their most typical areas to identify the main structures (characteristic phases) that make up the coating and determine their characteristics. In all coatings modified with boron, its spherical inclusions are found, the hardness of which reaches values of 1620-1970 HV. Also, in all coatings, regions (phases) are detected, represented by fine eutectic of the Fe-C-B system, the hardness of which exceeds the value of the unmodified boron phases by 1.2-1.5 times, reaches 1080-1110 HV.

The common features of modified coatings are the melting of their boundary with the base metal, and in non-modified ones - the presence of dendritic regions (phases) with a hardness reduced to 500-700 HV. The main material on all samples has a microhardness of 400-450 HV. Table 1. provides summary information on the characteristic phases of reinforcing coatings obtained on 65G steel, HDPE surfacing by various methods and from various charge materials.

Table 1. Description of characteristic phases of coatings and their properties

Method, charge	Coating phases	Structure type, morphology	Microhardness, HV
Sample 1	1	Fine-dispersed boride eutectic, weakly delimited gray areas with inclusions of octahedral fused and crushed carbides	1080-1100
	2	Melted ledeburite-like eutectic, dark and gray with a fine structure	640-660
	3	Structureless spherical inclusions with a clear boundary	1900-2000
	4	Dendritic structures, columnar, even and branched light formations on the border with the base metal	500-700
	5	Boride eutectic, light areas on the border with the base metal	900-1000
	6	Weakly delimited light areas with needle inclusions	800-900
Sample 2	1	Weakly delimited gray areas with needle inclusions	900-950
	2	Fused boride eutectic, light areas on the border with the base metal	850-900
	3	Structureless spherical inclusions with a clear boundary, cracks	1600-1700
	4	Boride eutectic, light areas on the border with pores and inclusions of boron carbide	1000-1100
Sample 3	1	Boride eutectic, the main type of structure in the deposited layer	700-750
	2	Dendritic structures, columnar, even and branched light formations on the border with the base metal	500-550
	3	Weakly delimited gray areas with octahedral and needle inclusions	900-1000
	4	Needle-like structures in a gray field between dendrites	700-750

The chemical composition of the coatings obtained on various samples was studied using a portable X-ray fluorescence spectrometer NITON (equipment of the GOSNITI Nanocenter, Moscow). The chemical element boron belongs to the "lungs" and is not determined by the X-ray fluorescence method. The results of the study of the chemical composition of the coatings are presented in Table 2.

Conclusion

Therefore, it can be concluded that a significant content of aluminum in the form of oxide is observed in all coatings. The different contents of silicon and iron indicate the passage of surface chemical and metallurgical processes in the implementation of SHS processes during high-frequency heating of samples of the base mixture on the surface of S355 steel, as well as segregation and redistribution of steel components on the surface.

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Table 2. Chemical composition of charge coatings.

Element	Content of the element, %		
	Sample 1	Sample 2	Sample 3
Al	65.52±3.27	69.40±3.20	35.65±2.50
Si	13.68±1.75	19.23±2.66	25.17±2.60
Fe	16.13±2.66	6.39±1.09	7.60±1.26
Cu	1.41±0.32	3.45±0.73	2.09±0.41
Pb	2.88±0.68	1.47±0.35	4.55±0.97

The resulting coatings are composite materials based on aluminum oxide, SHS products in the base mixture, generated through SHS with boron, but due to the high content of aluminum oxide and the occurrence of side reactions, they have a porous inhomogeneous structure, insufficient thickness, and low hardness. The use of HFC heating significantly improves the microstructure of the obtained coatings and provides a better-quality spattering of the coating on the steel part. Obtaining more homogeneous, extended, and harder coatings is possible only when modifying the base mixture, i.e. increasing the aluminum content therein, introducing fluxes, and adjusting the fractional and chemical composition of the powder material.

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