Structure and properties of Ni-Cr-B-Si powder coating formed on A356Gr steel using a combined method

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Abstract. The results of the study of the phase and elemental composition, the state of the defective substructure, the mechanical and tribological properties of the powder coating of the Ni-Cr-B-Si system formed on A356Gr1 steel using a combined method, which includes plasma spraying and the subsequent irradiation with an intense pulsed electron beam in the melting mode of the surface layer, are presented. It is shown that the combined treatment is accompanied by formation of a surface layer with a thickness up to 1500 microns, the microhardness and the wear resistance of which manifold exceed the corresponding characteristics of the reference steel.

1. Introduction

Electron-ion-plasma combined technologies, including formation of extended multi-element multiphase layers [1–4] additionally treated with concentrated energy fluxes [5–10], allow to multiply the performance characteristics of metals and alloys, metal-ceramic, and ceramic materials [11, 12]. Medium-carbon cast steel A356Gr1, which is the object of the study of the present paper, is one of the most affordable materials in production of various parts. It is widely used in various industries in manufacture of mill housing, gears, valves, balances, diaphragms, rollers, cylinders, brackets, and many other parts and products operating under the action of medium static and dynamic loads. One of the drawbacks of A356Gr1 steel is low wear resistance. Therefore, it is used only to manufacture elements that do not work for wear.

The purpose of the studies is to detect and analyze patterns of changes in the structure and properties of industrial steel 35L subjected to combined treatment, which includes plasma spraying of a powder coating of a complex elemental composition and the irradiation in vacuum with an intense pulsed electron beam in the melting mode of the surface layer.
2. Material and method
The material of the study was steel A356Gr1 [13]. Modification of the structure and properties of steel was carried out using a combined method, which includes spraying of a powder coating and the subsequent irradiation with an intense pulsed electron beam. Spraying of a powder coating was carried out using the plasma method. For this purpose, an original installation with two plasma generators was used [14]. Powder of the system Ni-Cr-B-Si of the brand PGSR-4 (0.6–1.0% C, 15–18% of chromium, 3.0–4.5% of silicon, 3.0–3.8% of boron, not more than 5% of iron, and the rest is nickel) with a fraction of 80–100 microns was used. Technically pure nitrogen was used as plasma gas. The use of two plasma generators has allowed to simultaneously melt the surface layer of the workpiece and introduce it into the molten surface layer of the powder particles.

The second stage of the combined treatment of steel consisted in the irradiation of the formed powder coating with an intense pulsed electron beam. For this purpose, the installation “SOLO”, equipped with a pulsed electronic source based on a plasma cathode with a grid stabilization of the plasma boundary was used [15]. The irradiation parameters used in the work were as follows: the accelerated electron energy was 18 keV, the electron beam energy density was 20 J·cm⁻² and 40 J·cm⁻², the pulse duration of the electron beam was 200 μs, the pulse repetition rate was 0.3 s⁻¹, the number of pulses was 10; the irradiation was performed in argon at a residual pressure of 0.02 Pa.

The investigation of the elemental and phase composition, the state of the defective substructure of the modified surface layer of steel before and after exposure to an electron beam were carried out using scanning electron microscopy (LEO EVO 50 (Zeiss, Germany)), X-ray diffractometry (device Shimadzu XRD-7000, the geometry of sampling according to the Bragg-Brittany scheme with a step of 0.02° in the angular range of 17–130°). The diffraction patterns were indexed on the basis of the Rietveld method. The mechanical characteristics of the modified layer were revealed using the method of microhardness with a Berkovich diamond pyramid (device PMT-3). Tribological studies (determination of wear resistance and friction coefficient) were carried out on the tribometer Pin on Disc and Oscillating TRIBOtester (TRIBOtechnic, France) under the following parameters: a ball made of 100Cr6 steel with a diameter of 6 mm, the track radius of 4 mm, the load on the indenter and the track length varied depending on the level of wear resistance of the material under study.

3. Results and discussion
Plasma spraying of a powder coating leads to formation of a high-relief surface, the characteristic electron microscopic image of which is shown in (figure 1). Micropores and microcracks have been detected on the surface, round-shaped powder particles have been revealed, the sizes of which vary in the range up to 10 μm (figure 1b). It is obvious that such a structural state of the formed layer cannot have high tribological properties. Indeed, the modified layer, which has a hardness of 4.6–6.5 times the hardness of the base, is slightly different in terms of wear resistance from the wear resistance (exceeds 1.2 times) of the original steel A356Gr1. It can be assumed that one of the reasons for relatively low tribological properties in regards to the relatively solid surface layer is its increased brittleness, conditioned upon high porosity of the material.

![Figure 1](image-url)
In order to overcome the identified shortcomings, the plasma-formed coating was additionally subjected to high-speed heat treatment by irradiation with a high-intensity pulsed electron beam in the melting mode of the surface layer. As noted above, the irradiation was performed with an electron beam at two electron beam energy densities. The characteristic electron microscopic image of the coating structure, which is formed as a result of irradiation with an electron beam with an energy density of 20 J·cm⁻², is shown in (figure 2). Analyzing the results presented in figure 2, it can be noted that treatment of the steel surface modified using the plasma method with an intense electron beam is accompanied by formation of an island structure (figure 2a). The islands, apparently formed by refractory compounds (figure 2b), are separated by regions with a dendritic crystallization structure (figure 2c). The latter unambiguously indicates melting of the regions of the surface layer of the powder coating and the subsequent rapid crystallization.

**Figure 2.** Electron microscopic image of the surface of A356Gr1 steel samples after plasma spraying of the powder coating and the subsequent irradiation with an intense pulsed electron beam (20 J·cm⁻², 200 μs, 0.3 s⁻¹, 10 pulses).

An increase in the energy density of the electron beam to 40 J·cm⁻² (while maintaining the remaining irradiation parameters unchanged) leads, firstly, to a substantial (more than twofold) increase in the size of regions with a cellular crystallization structure and, accordingly, an increase in the distance between the islands containing refractory inclusions (figure 3a), secondly, to a decrease in the size of the islands of refractory inclusions (figure 3b), and, thirdly, to the enlargement of the structure of the dendritic crystallization of the surface layer (figure 3c), which, obviously, indicates a decrease in the cooling rate of the material [16].

A negative phenomenon that occurs when a material is irradiated by concentrated energy fluxes, including an intense pulsed electron beam, is the formation of microcracks on the surface of the treated grid [11]. The latter is conditioned upon relaxation of tensile elastic stresses formed in the surface layer of the material as a result of ultrahigh cooling rates from the temperature of the existence of the molten state [17]. In the material under study, microcracks form a spatial grid, whose cells increase with an increase in the energy density of the electron beam (figure 2a, figure 3a).

The phase composition of the plasma sprayed powder coating and the coating additionally treated with an intense pulsed electron beam was studied using methods of X-ray phase analysis. It has been established that the main phase of the sprayed coating is a nickel-based γ-(Ni, Cr) solid solution. The hardening phases are borides (CrB, Fe₂B), carbides (Cr₇C₃), and silicides (FeSi) of iron and chromium.
The subsequent irradiation of the coating with an intense pulsed electron beam practically does not change the phase composition of the material.

Figure 3. Electron microscopic image of the surface of 35L steel samples after plasma spraying of the powder coating and the subsequent irradiation with an intense pulsed electron beam (40 J·cm⁻², 200 μs, 0.3 s⁻¹, 10 pulses).

The elemental composition of the surface layer of the coating was studied using methods of micro X-ray spectral analysis. The main attention was paid to the change in the concentration of boron atoms in the surface layer, assuming that the main hardening phase of the coating are metal borides. It has been established that the concentration of boron atoms in the surface layer of the formed powder coating and the coating additionally irradiated with an electron beam at an electron beam energy density of 20 J·cm⁻² corresponds to the concentration of boron atoms in the reference powder within the measurement error, and is ≈ 3 wt.%. In the coating additionally irradiated with an electron beam with an electron beam energy density of 40 J·cm⁻², the concentration of boron atoms in the surface layer is ≈ 1 wt.% A significant decrease in the concentration of boron atoms in the surface layer of the coating correlates with the facts discussed above, i.e. a decrease in the size and the number of islands of refractory compounds on the coating surface with an increase in the electron beam energy density. In turn, these facts may indicate a decrease in the wear resistance of the modified surface layer of the coating, as a result of the irradiation with an intense pulsed electron beam.

Indeed, tribological tests of A356Gr1 steel in the initial state and after modification have shown that the samples subjected to combined treatment, which includes formation of a plasma-sprayed layer and the subsequent irradiation with an electron beam with an electron energy density of 20 J·cm⁻², have the highest wear resistance. In this case, the wear resistance of the material exceeds the wear resistance of the reference steel by more than 4 times. An increase in the energy density of the electron beam to 40 J·cm⁻² leads to a decrease in the wear resistance of the material. It has been found that the wear resistance of the electron-irradiated powder coating is 2.4 times lower than the wear resistance of the reference steel.

4. Conclusion
It has been shown that a combined modification of the surface layer of A356Gr1 steel, which includes plasma spraying of a powder coating of the Ni-Cr-B-Si system (powder dispersion 80–100 μm) and the subsequent irradiation with an intense pulsed electron beam (18 keV, (20 and 40) J·cm⁻², 200 μs, 0.3 s⁻¹, 10 pulses) leads to melting of the surface layer with formation of an island structure. The
islands containing refractory inclusions are separated by regions with a structure of rapid dendritic crystallization of the submicro-nanoscale range. It has been established that an increase in the electron beam energy density from 20 to 40 J cm\(^{-2}\) is accompanied by a significant (more than twofold) increase in the size of regions with a cellular crystallization structure and, accordingly, an increase in the distance between the islands containing refractory inclusions, a decrease in the size of the refractory inclusion islands, and an increase in the size of the elements of the dendritic crystallization structure of the surface layer. Formation of borides (CrB, Fe\(_2\)B), silicides (FeSi), and carbides (Cr\(_7\)C\(_3\)) of iron and chromium, which are the hardening phases of steel, has been detected in the modified layer. It has been shown that combined treatment, which includes deposition of a powder coating and the subsequent irradiation with an intense pulsed electron beam (18 keV, 20 J cm\(^{-2}\), 200 \(\mu\)s, 10 pulses, 0.3 s\(^{-1}\)), leads to formation of a hardened layer with a thickness of 1500 \(\mu\)m, the microhardness 4.6–6.5 times and the wear resistance more than 4 times higher than the corresponding characteristics of the reference steel. An increase in the energy density of the electron beam to 40 J cm\(^{-2}\) is accompanied by a decrease in the wear resistance of the material by 2.4 times from the relativity of the wear resistance of the original steel.

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