Influence of irradiation with a high-intensity pulsed electron beam on mechanical properties and structural states of coatings formed by plasma spraying

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Abstract. The purpose of the present studies is to establish the formation patterns of the structure and properties of the surface layer of 060A35 steel modified using a combined method that includes plasma spraying of a powder coating and the subsequent irradiation with an intense pulsed electron beam. Plasma spraying on the surface of a steel powder of the system Ni-Cr-B-Si (PGSR-4 with a fraction of 80-100 μm) was performed on the original installation equipped with two plasma generators. The irradiation of the modified steel layer was carried out with an intense pulsed electron beam on the installation SOLO. The investigation of the phase and elemental composition, the state of the defective substructure were carried out using methods of X-ray phase analysis, optical and scanning electron microscopy. The mechanical properties of the irradiated surface were characterized by microhardness. It is shown that plasma spraying of a powder coating leads to formation of a high-relief surface containing micro- and macropores. The subsequent treatment of the modified surface with an intense pulsed electron beam of a submillisecond duration in the melting mode of the surface layer is accompanied by smoothing of the coating surface, saturation of the crystalline lattice of the surface layer with Ni, Cr, B and Si atoms, formation of dendritic crystallization cells of submicron sizes, release of nanoscale particles of the second phase, formation of a quenching structure. Together, this has allowed to increase the microhardness of the modified layer in 4.6-6.5 times.

1. Introduction

The development of technologies that use concentrated energy flows (plasma flows, high-power ion...
and electron beams, laser beams, etc.) aimed at hardening of surface layers and formation of hardening protective coatings on structural materials is currently one of the promising directions in the development of materials science [1, 2]. It has now been established that the use of plasma technologies allows obtaining highly doped surface layers and coatings with substantially higher performance properties with respect to the hardened part or the item [3-6]. The structure and properties of coatings created using this method depend on many factors. We shall note the main ones that have a significant effect on physicomехanical properties of coatings created using this method: first, the chemical composition and the dispersity of particles deposited on the substrate; second, the chemical composition and the structural-phase state of the substrate; third, technological parameters of the process, which are determined by the preliminary preparation of the workpiece surface, the size and the velocity of particles, and the plasma temperature [3-6]. Combined technologies that include deposition of plasma coatings and layers with a subsequent treatment with concentrated energy fluxes (electron and ion beams, plasma flows, laser beams, etc.) allow in many cases to achieve an additional increase in the physicomехanical and tribological properties of the material [7-12].

The purpose of the present studies is to establish the formation patterns of the structure and properties of the surface layer of 060A35 steel modified using a combined method that includes plasma spraying of a powder coating and the subsequent irradiation with an intense pulsed electron beam.

2. Materials and methods of research
Plasma spraying of a powder of the system Ni-Cr-B-Si of the grade PGSR-4 (0.6-1.0% C, 15-18% chromium, 3.0-4.5% silicon, 3.0-3.8% boron, iron no more than 5%, the rest is nickel) with a fraction of 80-100 μm onto a steel surface (steel 060A35, has a wide application in the industry in manufacture of rolling mills, gears, rollers, rolls, trolley wheels, and other products [13]) was carried out on an original plasma installation with two plasma generators [14]. Nitrogen was used as a plasma-forming gas. The use of two plasma generators has allowed to simultaneously carry out melting of the surface layer of the workpiece and introduction of powder particles into the molten surface layer. The irradiation of the modified steel layer was carried out with an intense pulsed electron beam on the installation SOLO (Institute of High Current Electronics, SB RAS) equipped with a pulsed electron source based on a plasma cathode with a grid stabilization of the plasma boundary [15] with the following electron beam parameters: the energy of accelerated electrons is 18 keV, the energy density of the electron beam is 20 J/cm² and 40 J/cm², the pulse duration of the electron beam is 200 μs, the pulse repetition rate is 0.3 s⁻¹, the number of pulses is 10; the irradiation was carried out in argon at a residual pressure of 0.02 Pa.

Investigations of the elemental and phase composition, the state of the defective substructure of the modified surface layer of the steel before and after the exposure to an electron beam were carried out on the equipment of the Center for Collective Use of the ISPM SB RAS "NANOTECH" using methods of scanning electron microscopy (SEM-7500FA JEOL), X-ray diffractometry (device Shimadzu XRD-7000. The geometry sample survey was performed under the Bragg-Bretano scheme in increments of 0.02° in the angular range of 17-130°. The X-ray diffraction patterns were determined on the basis of the Rietveld method [16]). Mechanical characteristics of the modified layer were detected using the microhardness measurement method with a Berkovich diamond pyramid (device PMT-3).

3. Results and discussion
Using methods of optical and scanning electron microscopy it has been shown that plasma spraying of a powder coating leads to formation of a high-relief surface containing micro- and macropores (figures 1a-b). The subsequent electron-beam treatment of the modified surface in the mode of melting the surface layer with an electron beam is accompanied by smoothing of the coating surface (figure 1c), formation of dendritic crystallization cells of submicron sizes (figure 1d), release of nanosized particles of the second phase, and formation of the quenching structure.
Figure 1. The surface structure of 060A35 steel samples subjected to plasma spraying of a powder coating (a, b) and the subsequent irradiation with an intense pulsed electron beam at a pulse duration of 200 μs, an electron beam energy density of 40 J/cm², and a pulse number of 10. Scanning electron microscopy.

The elemental composition of the coating surface layer was studied using methods of micro-X-ray spectral analysis (figure 2).

Figure 2. The structure (a) and the energy spectra (b) obtained from the surface layer of the coating, identified by a rectangle on (a). The state of the modified layer before the irradiation with an electron beam.

The results of the analysis of the elemental composition of the coating before the irradiation with an electron beam are shown in Table 1. It is clearly seen that the surface layer of the coating is characterized by a significant spread of various regions with respect to the concentration of alloying elements, and it has a large number of impurity elements (O, Na, Al, Cl, Ca). Micro X-ray spectral analysis did not reveal the presence of carbon and boron atoms in the surface layer. The absence of signals from the atoms of these elements on the energy spectra can be conditioned upon the difficulty of separating the signals from light elements and their removal from the flux. The elemental composition of the original powder is given in table 1 (the last column) for comparison. It is necessary to pay attention to a significant decrease in the concentration of chromium atoms in the surface layer of the coating when comparing the analysis results of the elemental composition of the initial powder and the formed coating.
Table 1. Elemental composition of separately located sections 1-5; section 6 are average values (in regards to the area in figure 2a).

| Element, at. % | 1 | 2 | 3 | 4 | 5 | 6 | powder |
|---------------|---|---|---|---|---|---|--------|
| O (Kα)        | 16.15 | 13.04 | 18.32 | 24.53 | 21.49 | 20.62 | 0.0 |
| Na (Kα)       | 1.99 | 0.44 | 0.94 | 3.27 | 3.99 | 1.91 | 0.0 |
| Al (Kα)       | 1.14 | 1.03 | 0.76 | 1.97 | 1.57 | 1.50 | 0.0 |
| Si (Kα)       | 5.48 | 6.27 | 5.85 | 6.43 | 5.71 | 6.08 | 5.5-7.5 |
| Cl (Kα)       | 0.25 | 0.00 | 0.25 | 0.58 | 0.64 | 0.36 | 0.0 |
| Ca (Kα)       | 0.61 | 0.27 | 0.33 | 0.67 | 0.54 | 0.44 | 0.0 |
| Cr (Kα)       | 12.63 | 12.78 | 12.03 | 10.64 | 11.15 | 11.74 | 16.5-19.5 |
| Fe (Kα)       | 1.77 | 1.76 | 2.01 | 2.15 | 1.86 | 1.77 | < 5 |
| Ni (Kα)       | 59.97 | 64.40 | 59.52 | 49.76 | 53.05 | 55.58 | 53.8-63.6 |

The subsequent irradiation of the coating surface layer with an intense pulsed electron beam is accompanied by a significant decrease in the concentration of impurity elements in the irradiated coating. For example, the concentration of oxygen atoms in the coating decreases from 20.5 at.% before the irradiation to 3.9 at.% after the irradiation at an electron beam energy density of 40 J/cm². It has been established that this tendency increases with an increase in the energy density of the electron beam. The irradiation of the coating with an electron beam is accompanied (as the energy density of the electron beam increases) by an increase in the concentration of chromium atoms in the surface layer (11.3 at.% in the coating before the irradiation and 14.4 at.% after the irradiation at an electron beam energy density of 40 J/cm²), as well as an increase in the homogeneity level of the element distribution in the surface layer of the modified material.

Following the elemental composition of the PGSR-4 powder and the modified surface layer revealed using methods micro-X-ray spectral analysis, it is possible to expect formation of a multiphase layer on the steel surface during formation using the combined method (plasma spraying and the subsequent irradiation with an intense pulsed electron beam) of the modified layer. According to the published data, formation of carbide, boride, and silicide phase particles with multicomponent compounds based on binary compounds (Cr₃C, Cr₂C₆, Cr₃C₂, CrB, Fe₂B, and Ni₂Si) and three-component borides (Cr₃NiB₆ and Cr₂Ni₂B₆) and silicides (τ₁, τ₂, σ, π) is possible in addition to a nickel-based solid solution with a FCC crystalline lattice (γ-phase) [17-20]. The conditions for formation of these phases clearly illustrate equilibrium ternary state diagrams of systems C-Cr-Ni, Cr-Ni-Si, Fe-Cr-B, Fe-Ni-Si, Cr-Ni-B (figures 3–5).

The features of this process should be taken into account when analyzing the possibility of formation of a multicomponent multiphase alloy as a result of plasma spraying of PGSR-4 powder onto the surface of a steel plate (060A35 steel). First, the powder PGSR-4 is attributed to self-fluxing multiphase materials. The removal of low-melting slags, which contain some of fluxing components (Si and B), will have a significant effect on formation of the elemental and phase composition of the melt from the deposited powder. Secondly, the process of substantially nonequilibrium crystallization of the molten powder coating will have a significant effect on formation of the structural-phase state of the modified layer. The nonequilibrium of the crystallization process is conditioned upon the mechanism of depositing powder particles in the form of droplets onto the steel surface of the substrate, which ensures high cooling rates. Thirdly, active processes of mutual diffusion of elements from the steel substrate with the elements of the deposited powder result in the change in the chemical composition of the coating and, as a consequence, the structural-phase state of the
modified layer of the material.

Figure 3. Isothermal sections of ternary state diagrams of the following systems: \(a\) is C-Cr-Ni \((T=800\,^\circ\text{C})\) [17]; \(b\) is Cr-Ni-Si \((T=850\,^\circ\text{C})\) [18].

Figure 4. Isothermal sections of ternary state diagrams of the system Cr-Ni-B \((T=800\,^\circ\text{C})\) \((a)\) [19, 20] and the system Cr-Fe-Ni \((T=900\,^\circ\text{C})\) \((b)\) [21].

The phase composition of the modified layer was studied using methods of X-ray diffraction analysis. Indexing of diffractograms, regardless of the method for production of the modified layer (plasma effect or combined treatment), has allowed revealing formation of a multiphase mixture. It has been established that the main phase is a solid solution based on \(\gamma\)-(Ni, Cr) with a small (about 8%) content of carbide, boride, and silicide particles. The irradiation of the modified surface layer with an intense pulsed electron beam is accompanied by a slight increase in the lattice parameter of the \(\gamma\)-solid solution from 0.35375 to 0.35380 nm, which may be conditioned upon additional doping of the \(\gamma\)-phase with melt elements and
the stress field formed in the surface layer as a result of high cooling rates of the material.

![Isothermal sections of ternary systems](image)

**Figure 5.** Isothermal sections of ternary systems Fe–Cr–B (a) and Fe–Ni–Si (b) at 850°C [22].

The mechanical properties of 060A35 steel samples modified by forming a plasma sprayed layer using PGSR-4 powder (system Ni-Cr-B-Si) and the subsequent irradiation with an intense pulsed electron beam were characterized by microhardness. It has been shown that the combined treatment of the steel surface allows forming a hardened layer with a thickness of up to 1500 μm, the microhardness of which exceeds the microhardness of the substrate (steel 060A35) in 4.6–6.5 times.

4. Conclusion
It has been shown that plasma spraying of a powder coating leads to formation of a high-relief surface containing micro- and macropores, characterized by the presence of a large number of impurity elements and a lower (relative to the initial powder) concentration of chromium. The subsequent treatment of the coating surface with an intense pulsed electron beam of a submillisecond duration in the surface layer melting mode is accompanied by smoothing of the coating surface, formation of dendritic crystallization cells of submicron sizes, a significant decrease in the concentration of impurity elements, and an increase in the concentration of chromium atoms in the surface layer. The analysis of isothermal sections of ternary state diagrams of systems C-Cr-Ni, Cr-Ni-B, Cr-Fe-Ni, Cr-Ni-Si, Fe–Cr–B, Fe–Ni–Si has been carried out. The forecast of binary and ternary compounds that can be formed in the surface layer of 060A35 steel during formation of the melt of PGSR-4 powder particles as a result of plasma spraying and as a result of the combined treatment that includes plasma spraying and the subsequent irradiation of the modified layer with an intense pulsed electron beam of a submillisecond duration has been carried out. The presence of a solid solution based on γ-(Ni, Cr) with a small content (about 8%) of secondary phases (carbides, borides, and silicides) has been established as a result of indexing the diffractograms using methods of X-ray diffraction analysis of the modified layer of steel. It has been found that the irradiation of a steel surface after plasma spraying of the PGSR-4 powder resulted in an increase in chromium content by 2 at.% Cr in the solid solution γ-(Ni, Cr) based on the FCC lattice. It has been shown that the combined treatment of 060A35 steel, which includes plasma spraying of
a coating using PGSR-4 powder and the subsequent irradiation of the modified layer with an intense pulsed electron beam, allows forming a hardened layer with a thickness of up to 1500 \( \mu \text{m} \), whose microhardness exceeds the microhardness of the substrate in 4.6–6.5 times.

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