

## Electron-ion-plasma modification of the structure and properties of commercial steels

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**Annotation.** The work is devoted to the structural-phase analysis of steels of the austenitic and martensitic grade, irradiated with a high-intensity pulsed electron beam of the submillisecond duration of exposure in the mode of the surface layer melting. A thermodynamic analysis of phase transformations occurring during heat treatment in alloys of the composition Fe-Cr-C and Fe-Cr-Ni-C, which are the basis of steels 20X13 and 12X18H10T, is carried out. It is shown that formation of solid solutions on the basis of  $\alpha$ -iron (BCC crystalline lattice) and  $\gamma$ -iron (FCC crystalline lattice) as well as the entire range of carbide phases of a complex elemental composition ( $M_{23}C_6$ ,  $M_7C_3$  и  $M_3C$ , where symbol M refers to atoms of metallic elements Fe, Cr, and Ni) is possible in equilibrium conditions in given materials. The irradiation of steels 12X18H10T and 20X13 with a high-intensity pulsed electron beam of the submillisecond duration of exposure is carried out. It is shown that the electron-beam processing of steel in the melting mode and the subsequent rapid crystallization is accompanied by a significant transformation of the surface layer structure, consisting in complete dissolution of original carbide phase particles; in formation of dendritic crystallization cells of submicron sizes; in occurrence of martensitic  $\gamma \rightarrow \alpha$  and  $\gamma \rightarrow \epsilon$  transformation; in re-allocation of nanosized particles of carbide and intermetallic phases.

### 1. Introduction

The development of new volume-doped materials, which are still the main way to improve the reliability and the longevity of details of mechanisms and machines, is becoming increasingly problematic due to the scarcity and the high cost of doping elements. Under the circumstances, it is economically and technically feasible to develop a fundamentally different approach to the development of materials when the mechanical strength of the part is achieved by using cost-effective, easily workable low-alloy steels, and special surface properties by a solid or a local formation of relatively thin doped layers, or by depositing coating with properties that meet performance requirements. Impulse fusion (high-frequency currents, laser emission, electron beams, plasma flows and jets) and saturation of surface layers of the material with doping elements with the subsequent crystallization and formation of strengthening phases (the so-called coatings of the intermediate type) is currently one of the most promising methods for modification of the structure and properties of



metals and alloys [1, 2]. Generated layers have a metallurgical bond to the substrate with adhesion at a level of cohesion, and insignificantly change the dimensions of the item.

The aim of the study is the detection of evolution patterns of the structure and properties of the surface layer of industrial steels subjected to irradiation with a high-intensity pulsed electron beam of the submillisecond duration of exposure in the melting mode with the subsequent rapid crystallization of the modified layer.

## 2. Material and methods of research

Steels 12X18H10T (AISI 321) and 20X13 (AISI 420) in the hardened condition were chosen as the modified material. The samples had the shape of a plate with a thickness of 10 mm and a diameter of 15 mm. Formation of nanostructured, nanophased surface-doped layers in steel was carried out by the irradiation of samples with a high-intensity pulsed electron beam using the installation "SOLO". Exposure parameters: the electron energy – 18 keV, the density of the electron beam energy – (15-40) J/cm<sup>2</sup>, the duration and the number of exposure pulses – (50-200) microseconds and (3-5) pulses, the pulse repetition rate – of 0.3 s<sup>-1</sup>; the irradiation was carried out in argon at a residual pressure of 0.02 Pa. The given mode provides heating of the surface layer with a thickness of up to 30 micron to melting temperature and quenching from the melt at a rate of up to (10<sup>6</sup> – 10<sup>8</sup>) K/s. The study of the phase and elemental composition of the defect substructure of the surface layer was carried out using methods of scanning and electron diffraction microscopy, X-ray diffraction analysis (Bragg-Brentano geometry, Cok<sub>α</sub>-radiation); physical-and-mechanical properties of the surface layer were studied by measuring the microhardness and the wear resistance.

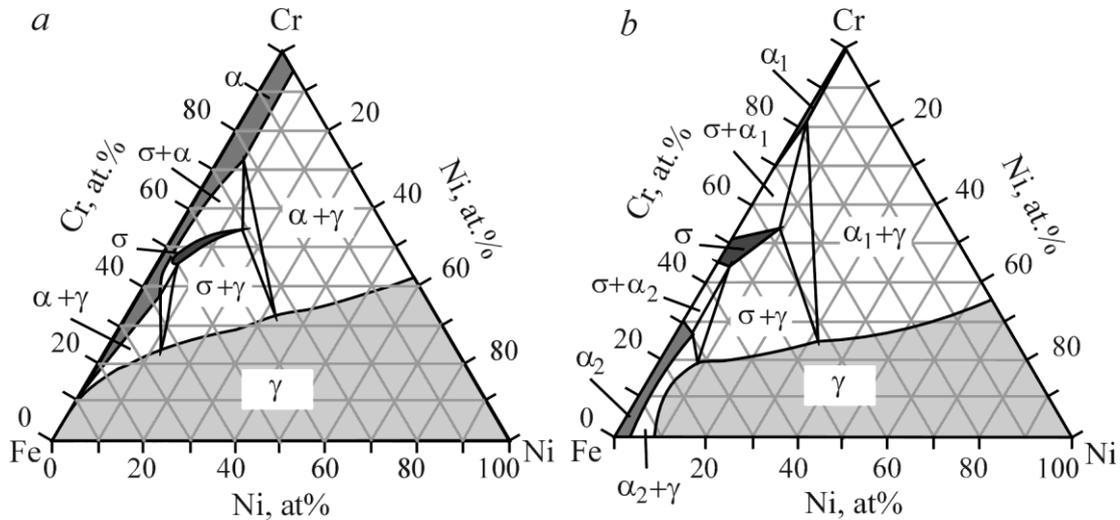
## 3. Results and discussion

We shall briefly consider the features of structural and phase states in binary, ternary, and quaternary systems on the basis of elements Cr, Fe, Ni, and C, which are the main alloy-forming elements in steels of the austenitic class 12X18H10T and the martensitic class 20X13. The feature of structural-phase states of steels under the consideration is the formation of carbide phase particles, the composition, the distribution by sizes and the shape, the location and the morphology of which strongly depend on the mode of the material heat treatment. Carbides forming in steel are divided into two groups, depending on the complexity of the crystalline lattice. The first group is carbides with complex structures: M<sub>3</sub>C, M<sub>23</sub>C<sub>6</sub>, M<sub>7</sub>C<sub>3</sub>, M<sub>6</sub>C. Here, M in the chemical formula represents the sum of metallic elements forming carbide. For example, (Cr,Fe,Ni,Mn)<sub>23</sub>C<sub>6</sub>, (Fe,Ni,Mn)<sub>3</sub>C, etc. The second group is carbides of the MC type (for example, VC) and M<sub>2</sub>C (for example, Mo<sub>2</sub>C), which are the interstitial phases. These carbides have simple crystalline lattices and have high thermal and mechanical stability. Under real conditions, they hardly dissolve in austenite. As a rule, carbides of the second group have higher melting point and greater hardness than carbides of the first group.

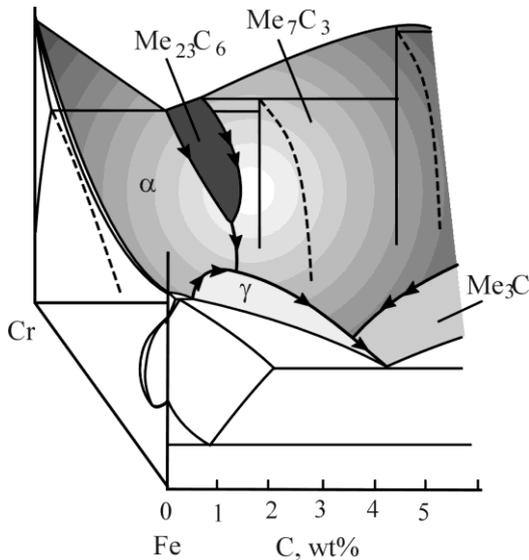
The investigated in this paper steels are complex-alloy materials, the basic elements of which are Fe, C, Cr, Ti, Ni. We shall briefly consider the options of phase transformations occurring during heat treatment of the given steels under equilibrium conditions.

### 3.1. System Cr-Fe-Ni [3]

Wide ranges of solid solutions based on the α-phase (disordered phase on the basis of the structure A2) and the γ-phase (disordered phase based on the structure A1) are present in the ternary system Cr-Fe-Ni at high temperatures (T = 1100 °C). A decrease in the temperature in the region of the equiatomic composition on the side Cr-Fe of the isothermal triangle leads to formation of the σ-phase. This leads to formation of two three-phase regions (α + γ + σ), two two-phase regions (α + σ), and one two-phase region (γ+σ) (Fig. 1).



**Figure 1.** Isothermal sections at different temperatures of the ternary system Fe-Cr-Ni; *a* –  $T = 900\text{ }^{\circ}\text{C}$ ; *b* –  $T = 700\text{ }^{\circ}\text{C}$  [3].



**Figure 2.** The metastable Fe-Cr-C phase diagram in the region of carbon concentration less than 5 wt. %. Thick black lines on the diagram separate regions of solid solutions. One arrow on thick lines corresponds to the eutectic type of the reaction. Two arrows on thick lines correspond to the peritectic type of the reaction. Dashed lines correspond to solidus lines [4].

Thus, it is possible to state that doping of alloys Fe-Cr with carbon leads to a significant change in the structure-phase state and has a significant impact on existence regions of carbides  $M_{23}S_6$ ,  $M_7S_3$ , and  $M_3S$  with  $\alpha$ -ferrite and  $\gamma$ -austenite.

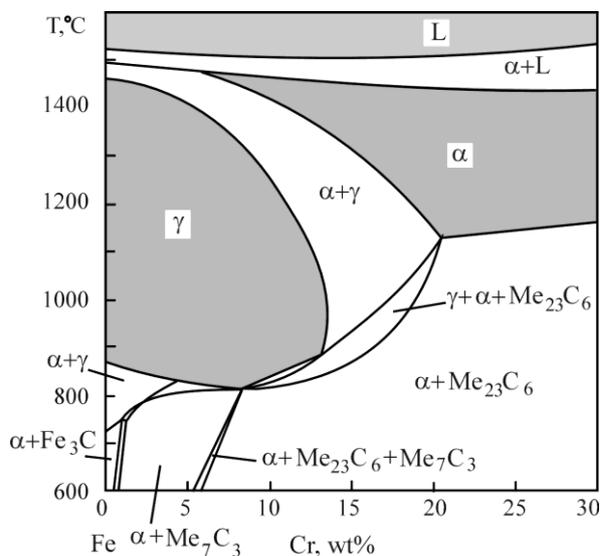
**System Fe-Ni-C** is characterized by formation of a single carbide with the composition  $M_3C$ . The analysis of the equilibrium diagram Fe-Ni-C, shown in Fig. 4, shows that in the Fe-corner on the

### 3.2. System Cr-Fe-C

Fig. 2 schematically presents three-dimensional liquidus surfaces on the diagram Cr-Fe-C bounded by binary systems Fe-C and Cr-C [4].

The diagram in Fig. 2 shows five liquidus surfaces corresponding to formation of five phases in binary systems:  $Fe_3C$ ,  $Cr_7C_3$ ,  $Cr_{23}C_6$ ,  $\alpha$ -ferrite and  $\gamma$ -austenite. Here, ferrite means  $\alpha$ -(Fe,Cr) and  $\delta$ -(Fe,Cr) in the binary system Fe-Cr, as these two elements (Fe and Cr) in the given temperature range form solid solutions on the basis of a BCC lattice;  $\gamma$ -Fe in the binary system Fe-C. Three four-phase regions can be identified in Fig. 2: 1 –  $L + \alpha + M_{23}C_6 + M_7C_3$ ; 2 –  $L + \alpha + \gamma + M_7C_3$ ; 3 –  $L + \alpha + M_7C_3 + M_3C$ . Here, M represents, as mentioned above, the sum of metal elements Cr and Fe that form carbide. L represents the alloy in the liquid state.

The state diagram in the system Fe-Cr-C (Fig. 3) along the section at constant carbon concentration  $C=0.1\text{ wt.}\%$  (corresponds to carbon concentration in steel 12X18H10T) has been theoretically obtained in [4]. The data obtained in [4] allow determining regions of existence of two-phase and three-phase alloys. This diagram also shows that carbide  $M_{23}S_6$  is more stable than carbides  $M_7S_3$  and  $M_3S$  and has more extensive regions of existence.

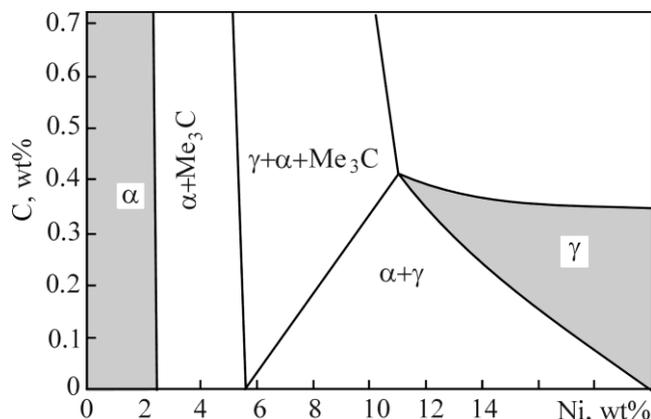


**Figure 3.** The calculated state diagram in the system Fe-Cr-C along the section at a constant value C=0.1 wt. % [4]

conditions in these materials it is possible to form not only solid solutions based on  $\alpha$ -iron (BCC crystalline lattice) and  $\gamma$ -iron (FCC crystalline lattice) but also the entire range of carbide phases of a complex elemental composition ( $M_{23}C_6$ ,  $M_7C_3$  and  $M_3C$  where the symbol M refers to atoms of metallic elements Fe, Cr, and Ni).

### 3.4. Results of experiment

The steels under the investigation in the initial state (before irradiation with an electron beam) are multiphase materials. Particles of carbide  $M_{23}C_6$  act as the second phase. The particles have a globular shape, are distributed randomly in the volume of the grain; the average particle size is 167 nm (the size of actual particles ranges from 30 nm to 450 nm).



**Figure 4.** The isothermal section of the ternary system Fe-Ni-C at 600 C [5]

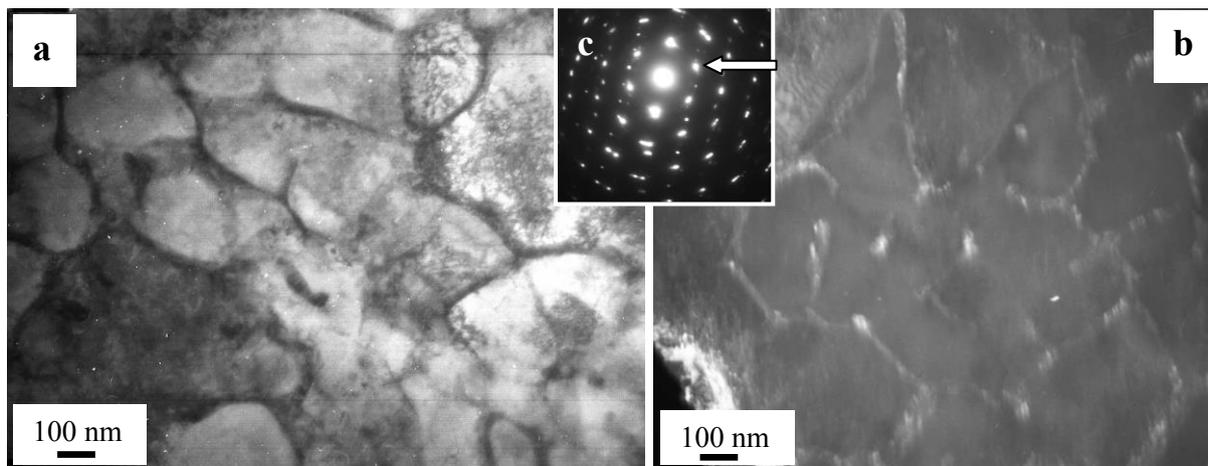
isothermal section there are three two-phase regions ( $\alpha + M_3C$ ,  $\gamma + M_3C$  and  $\alpha + \gamma$ ) and one three-phase region ( $\alpha + \gamma + M_3C$ ) [5]. Here, M denotes the sum of metal elements Ni and Fe that form carbide of the composition  $M_3C$ . It should also be noted that carbides  $M_{23}C_6$  and  $M_7C_3$ , which are metastable, have been synthesized in alloys Fe-Ni-C at high pressures [5].

### 3.3. System Fe-Cr-Ni-C [6]

Carbides  $M_{23}C_6$  and  $M_7C_3$  with a complex structure, since the symbol M represents the sum of three metal elements Ni, Cr, and Fe that form the carbide, have been found in the system Fe-Cr-Ni-C [6].

Thus, the performed brief thermodynamic analysis of phase transformations that occur during heat treatment in alloys of the composition Fe-Cr-C and Fe-Cr-Ni-C, which are the basis of steels 20X13 and 12X18H10T, shows that under equilibrium

High-intensity electron beam treatment in the melting mode of the surface layer of the pre-hardened steel (regardless of the elemental composition of the material) leads to formation of a gradient multiphase structure. The surface layer, whose thickness ranges from units to tens of micrometers depending on parameters of the electron beam, is characterized by complete dissolution of submicron particles of carbide  $M_{23}C_6$ , which are present in steel of the initial state. The subsequent rapid crystallization is accompanied by formation of a multiphase structure of the cellular type with a cell size of (100-400) nm (Fig. 5).



**Figure 5.** The structure of the cellular crystallization forming in the surface layer of steel 20X13 subjected to electron-beam treatment with an energy density of electron beams of  $30 \text{ J/cm}^2$ ; a – light field; b – dark field, obtained in neighboring reflexes  $[110]\alpha\text{-Fe}$  and  $[331]\sigma\text{-FeCr}$ ; c – micro-electron-diffraction pattern, reflexes in which the dark field is obtained are indicated by the arrow.

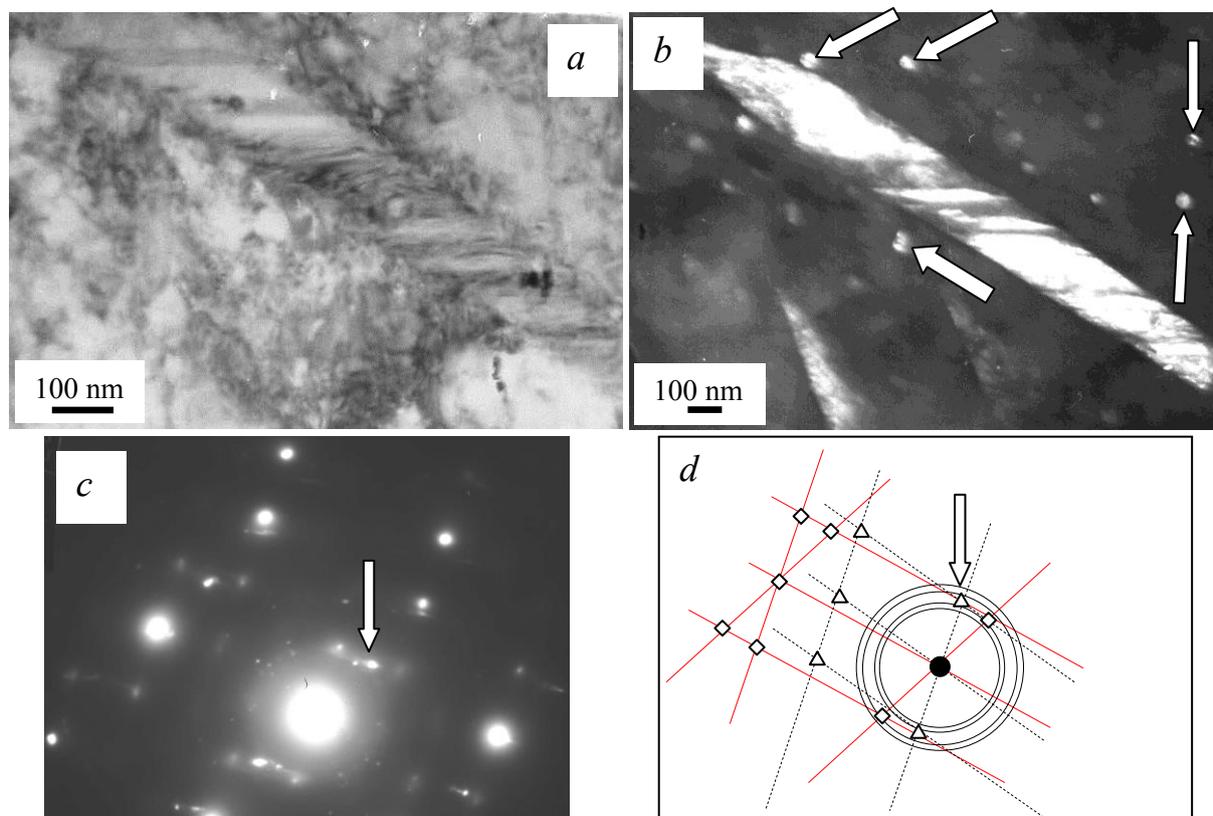
Particles of the second phase are located along cell boundaries and in their volume. The study of the phase composition of the surface layer of steel, carried out using methods of electron-microscopy microdiffraction analysis with the use of the dark-field technique, has revealed the formation of particles of the intermetallic phase ( $\sigma\text{-FeCr}$  and  $\text{Fe}_9\text{Cr}_{15}$ ) (Fig. 5) and the carbide phase of the composition M3C (cementite doped with chromium atoms), chromium carbides of the composition  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_3\text{C}_2$ , and carbide of the type  $\text{M}_{23}\text{C}_6$ . An example of formation of carbide particles  $\text{Cr}_3\text{C}_2$  in steel is shown in Fig. 6, b.

Rapid crystallization of steel is accompanied by martensitic transformation of the  $\gamma$ -phase. Formation of  $\alpha$ -martensite, peculiar to steel 20X13 hardened with low cooling rates, after the irradiation with an electron beam is accompanied with formation of  $\varepsilon$ -martensite, i.e. the occurrence of martensitic transformation under the scheme  $\gamma \rightarrow \varepsilon$ . The typical image of  $\varepsilon$ -martensite crystals is shown in Fig. 6 a, b.

#### 4. Conclusion

A brief thermodynamic analysis of phase transformations occurring during heat treatment in alloys of the composition Fe-Cr-C and Fe-Cr-Ni-C, which are the basis of steels 20X13 and 12X18H10T, has been carried out. It has been shown that formation of both solid solutions on the basis of  $\alpha$ -iron (BCC crystalline lattice) and  $\gamma$ -iron (FCC crystalline lattice) and the whole range of carbide phases of the complex elemental composition ( $\text{M}_{23}\text{C}_6$ ,  $\text{M}_7\text{C}_3$  and  $\text{M}_3\text{C}$ , where the symbol M refers to atoms of metallic elements Fe, Cr, and Ni) is possible in the given materials under equilibrium conditions. The irradiation of steels 12X18H10T and 20X13 with a high-intensity pulsed electron beam of the submillisecond duration of exposure has been carried out. It has been shown that electron-beam treatment of steel in the melting mode and the subsequent rapid crystallization is accompanied by a significant transformation of the surface layer structure, consisting in:

- complete dissolution of particles of the initial carbide phase;
- formation of dendritic crystallization cells of submicron sizes;
- occurrence of martensitic  $\gamma \rightarrow \alpha$  and  $\gamma \rightarrow \varepsilon$  transformation;
- re-allocation of nanosized particles of carbide and intermetallic phases.



**Fig. 6.** The structure of the layer located at a depth of  $\approx 5$  micron in steel 20X13 treated with a high-intensity electron beam; a – light-field image, b – dark field obtained in closely spaced reflexes  $[101]_{\epsilon}\text{-Fe}+[320]_{\text{Cr}_3\text{C}_2}$ ; c – micro-electron-diffraction pattern (the arrow indicates the reflex in which the dark field is obtained), d – indexing scheme of the micro-electron-diffraction pattern (rings indicate reflexes that belong to carbide  $\text{Cr}_3\text{C}_2$ ). In (b) the arrows indicate particles of carbide  $\text{Cr}_3\text{C}_2$ .

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