Hardening of coatings based on chromium steel alloyed with a complex of boride compounds by quenching

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Abstract. This article explores the effect of quenching regimes on the structure and characteristics of a metal deposited by a high-chromium flux-cored wire of a martensitic class with carbide-boride-nitride doping. We established that quenching from a temperature of 1020 °C provides a hardness in the range of 54-58 HRC. It is shown that the hardening is caused by the formation of a martensitic structure, an eutectic composition based on chromium and iron borides, carborubide, carbide and nitride particles for the most part of chromium and titanium with increased microhardness. The hardness of such a metal practically coincides with the hardness of the metal after surfacing.

1. Introduction
Technologies for increasing the operational properties of surface hardening for machine parts operating under difficult operating conditions have found wide application in industry. One of such technologies of hardening is surfacing of working surfaces with wear-resistant flux-cored wires. It is known that high strength and corrosion resistance of coatings provides surfacing by an iron-chrome based flux-cored wires [1–4]. At the same time, when working under abrasive wear, the resistance of coatings on an iron-chromium base is not sufficient, due to the small number of strengthening phases in the structure of the deposited metal.

2. Statement of a problem
One of the ways to increase the wear resistance of the deposited metal is joint solid-hardening and phase hardening by dispersed particles. A promising method of hardening a cast metal is doping it with boron [5–8]. The efficiency of using a complex of boride compounds in flux-cored wires is known [9–11]. Such wires provide increased wear resistance of the deposited metal of martensitic or martensitic-aging classes.

However, the mechanical treatment of a metal in a state after surfacing is difficult due to its high hardness. Therefore, to reduce the hardness of such deposited metal we carry out its tempering. After the mechanical treatment of a tempered metal it is necessary to carry out its quenching in order to restore its properties. At the same time, the quenching regimes and the obtained properties of coatings deposited by chromium flux-cored wires with complex-alloyed boride compounds have not been investigated.

Therefore, the task is to study the hardening of quenched coatings based on martensitic chromium steel with carbide-boride-nitride doping after tempering.

3. Theory
This work examines the effect of quenching regimes on the durometric characteristics, microstructure and phase composition of metal coatings deposited by high-chromium flux-cored wire doped with complex boride compounds with a charge of composition: 15% Cr + 0.5% B₄C + 0.5% BN + 2.5% TiB₂ + 1.0% ZrB₂. In order to reduce the risk of pore formation in the deposited metal, we added
0.5% of sodium silicofluoride to the flux-cored wire. We used a steel band of 08kp size 15 × 0.8 mm with a filling factor of 0.34 as a cover in accordance with GOST 503-81.

Surfacing was carried out on plates of St3 steel with a size of 200×50×10 mm with an experimental flux-cored wire of 2.4 mm diameter in argon in four layers. Surfacing mode: current strength 230 A; voltage 24 V; the rate of surfacing is 20 m/h.

Metallographic studies of the weld metal were carried out on an optical microscope AXIO Observer A1m (Carl Zeiss). The microstructure was detected by chemical etching in a reagent of the following composition: CuSO₄ – 4 g; HCl – 20 ml; H₂O – 20 ml.

Durometric studies were carried out on metal samples after surfacing and thermal treatment with a hardness tester TK-2 by the method of Rockwell and microhardness tester Shimadzu HMV-2 by the Vickers method. The microhardness was measured over the cross section of the deposited coating, starting with the base metal in 0.2 mm increments.

Electron microscopy examination was carried out with a raster-type electron microscope JEOL JSM-6610-LV with add-on device Inca-350 of energy-dispersive analysis (EDA).

The metal was studied in states after tempering and quenching.

4. Results of the experiments and discussion

It was established that as a result of tempering the metal of the test composition, the microhardness over the cross-section of the coating varies within 250 and 450 HV. The hardness of such a metal is in the range of 26-28 HRC. After tempering the investigated metal, we carried out its quenching in three modes recommended for steels of this class: at heating temperatures of 950 °C, 1020 °C, 1100 °C [12]. The results of measuring the microhardness along the cross-section of the metal under investigation after tempering and following quenching in the selected modes are shown in Fig. 1.

As it can be seen, the microhardness of the cross-section of the coating after quenching from a temperature of 950 °C varies within 550-750 HV, after quenching from 1020 °C – within 740-900 HV and after quenching from a temperature of 1100 °C – within 750-940 HV. The highest stability of microhardness values occurs at quenching from a temperature of 1020 °C.

The results of measuring the hardness over the cross-section of the coating metal are given in Tabl. 1.

| Quenching          | Hardness distribution over deposited metal layers, HRC |
|--------------------|--------------------------------------------------------|
| tempering at 800°C |                                                        |
| quenching 950°C    |                                                        |
| quenching 1020°C   |                                                        |
| quenching 1100°C   |                                                        |

Table 1. Hardness distribution over the cross-section of complex-layer coatings after quenching
Analyzing the obtained results, it can be noted that the hardness over the layers of the coating deposited by a flux-cored wire with boride compounds after quenching from a temperature of 950 °C is within 51-54 HRC, after quenching from a temperature of 1020 °C – 52-58 HRC, and after quenching from a temperature of 1100 °C – 53-56 HRC.

As it can be seen, the best results were obtained after quenching from a temperature of 1020 °C. The hardness of the metal after this quenching regime practically coincides with the hardness of the metal after surfacing.

As metallographic studies show, the deposited metal of the coating with borides after such hardening has a complex composite structure (Fig. 2) with an iron-chromium martensitic matrix, boride eutectic and dispersed inclusions of carboborides and high-strength nitrides. The hardness of a metal reaches a maximum value of 58 HRC.

![Figure 2](image_url)

Figure 2. The microstructure of the coating metal and measurement ranges of the structural constituents microhardness after quenching from a temperature of 1020 °C

The results of investigations of the metal structural constituents microhardness after quenching are given in Tabl. 2.

| Puncture № | 1* | 2 | 3 | 4 | 5 | 6* | 7 | 8 | 9* | 10 | 11 | 12 |
|------------|----|---|---|---|---|----|---|---|----|----|----|----|
| HV         | 1073 | 688 | 971 | 711 | 814 | 1052 | 773 | 723 | 1105 | 697 | 784 | 771 |

From the data given, it can be seen that the microhardness of the matrix is high and lies within the range of 688-784 HV, eutectic – 814-971 HV, particles – 1052-1105 HV. It can be noted that the hardness of the matrix of such a metal is much higher, and the strengthening phases are a bit lower than that of the metal after surfacing.

The results of the chemical analysis (Fig. 3, Tabl. 3) make us suggest that the iron-chromate martensitic matrix includes an eutectic component formed on the boride basis (Fe, Cr)2B having a framework structure, carboborides of chromium and iron (Fe, Cr)7(C, B)3, carbides and nitrides of chromium and titanium, complex titanium carbonitride and zirconium and nitride – ε-(Fe, Cr)23N.
Figure 3. The image of the microstructure of the deposited coating metal with the location of scanning regions using the EDA method

Table 3. Chemical composition of deposited coating metal areas

| Range | B, %  | N, %  | C, %  | Cr, %  | Fe, %  | Ti, %  | Zr, %  |
|-------|-------|-------|-------|--------|--------|--------|--------|
| 1     | 1.95  | 23.37 | 7.59  | 11.40  | 35.13  | 19.47  | 1.09   |
| 2     | 12.96 | 0.75  | 9.16  | 16.48  | 58.45  | 1.16   | 1.04   |
| 3     | 5.65  | 1.37  | 7.77  | 15.08  | 70.03  | 0.06   | 0.04   |
| 4     | 24.89 | 0     | 4.24  | 27.09  | 43.62  | 0.15   | 0.01   |
| 5     | 20.34 | 0.31  | 8.80  | 16.51  | 53.55  | 0.49   | 0.01   |
| 6     | 8.78  | 0.66  | 10.52 | 17.39  | 62.55  | 0.07   | 0.04   |
| 7     | 7.12  | 0.21  | 7.16  | 16.08  | 69.30  | 0.07   | 0.06   |
| 8     | 24.32 | 0     | 5.32  | 24.92  | 45.22  | 0.17   | 0.05   |
| 9     | 7.73  | 0.27  | 6.32  | 15.50  | 70.09  | 0.06   | 0.02   |

The map of the main elements distribution confirms the presence of a significant amount of dispersed inclusions in the metal structure, mostly nitrides and titanium carbides and a small part of zirconium nitrides with a size from 0.2 to 3.4 μm (Fig. 4).
Figure 4. The results of scanning electron microscopy of the investigated metal structure after quenching: a) image of the microstructure with the location of scanning areas; b)-h) a map of elements distribution from the surface of the deposited coating according to EDA data

The results of transmission electron microscopy of the fine structure of a metal alloyed with a complex of boride compounds after quenching are shown in Fig. 5. Such a metal is an α-solid solution supersaturated with doping elements with a developed and closed eutectic. In the structure of the metal, martensite is formed of reticular morphology with a high density of dislocations. The length of the rails averages about 1.5 μm. The martensite contains a large number of twins. On the corresponding electronogram, along with the matrix reflexes of the α phase, there are reflections from twins located at a distance of 1/3 of the main reflections of the α-phase. The structure also contains martensite-like regions, the origin of which is due to the decay of austenite by an intermediate mechanism. Areas of bainitic structure and doped cementite are also revealed.
Figure 5. The microstructure of the metal deposited by the flux-cored wire of the test composition obtained by TEM:  a) fine structure (x 6000); b) electron-diffraction mode; c) microdiffraction; d) decoding circuit

The structure of the metal is characterized by a large number, a special morphology and chemical composition of the eutectic and intermediate phases. Along with the martensitic matrix and the eutectic, there is a significant number of strengthening phases. Transmitting electron microscopy shows the presence of dispersed inclusions of titanium nitride particles TiN and chromium nitrides CrN (Fig. 6).
Figure 6. Strengthening phases in the structure of the metal under investigation, released during the quenching process:
   a) fine structure of the metal (x 8000); b) microdiffraction; c) decoding circuit

Reflexes from both primary Cr7C3 carbides and secondary Cr23C6 carbides are noted. Cr23C6 carbide is a low-temperature form of carbide and is always formed in the early stages of isolation, since it is easily nucleated [13]. Apparently, there is a transition of doped cementite into a special carbide. This carbide releases mainly at the grain boundaries in the form of films, globules and plates [14]. Then - on incoherent boundaries of twins, coherent boundaries of twins and finally on dislocations inside grains [15]. The presence of σ-phase was also observed, which is typical for such steels [16, 17].

Thus, hardening of the deposited metal with carbide-nitride-boride doping is due to the formation of a martensite matrix with an eutectic component based on chromium and iron borides (Fe, Cr)2B, carboboride (Fe, Cr)7(C, B)3 particles, chromium and titanium carbides and nitrides and σ-phase.

5. Conclusion
1. The rational heat treatment of tempered after surfacing coatings based on chromium steel with carbide-boride-nitride doping is quenching from a temperature of 1020 °C, which increases the hardness of the metal to 58 HRC. Such a hardening is due to the formation of a martensitic structure, an eutectic component based on chromium and iron borides, carboboride, carbide and nitride particles, mostly of chromium and titanium, and σ-phase.
2. The proposed quenching regime can be used in the technology of wear-resistant surfacing with flux-cored wires alloyed with boride compounds.

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