Modification of wear-resistant coatings of the Fe-Cr-C system with spherical tungsten carbide WC-W₂C

A V Shchegolev¹,², A V Ishkov¹ and V V Ivanayskiy¹

¹ Altai State Agricultural University, Krasnoarmeiskiy pr., 98 656049, Barnaul, Russia
² E-mail: qqq681@mail.ru

Abstract. The article describes the production procedure, studies the structure, and determines the properties of new wear-resistant coatings of the Fe-Cr-C system intended for hardening the working bodies of agricultural machines. To increase the wear resistance and give new consumer qualities to such coatings, they were modified with spherical tungsten carbide WC-W₂C – spherorelite.

It is shown that the introduction of the complex (WC-W₂C+B₄C) into the basic charge allows increasing the hardness of the deposited to 1000 ... 1200 HV100, and wear resistance by 3.1 times in relation to the base material, and by 1.3 ... 1.8 times in relation to the base (not hardened) material.

1. Introduction

To extend the service life and preserve the parameters of the details of the working bodies of agricultural machines, their surface is strengthened with coatings of high-chromium cast irons – alloys and composite materials of the Fe-Cr-C, Fe-Cr-C-B systems and others [1]. Reinforcing coatings can be applied to the part by various methods.

However, the wear resistance of these materials, in some cases (crusher hammers, chopper knives, plowshares, mixer blades, etc.), may be insufficient [3].

Existing methods to increase the wear resistance of these materials are based on: the development of new surfacing materials based on various d-metals or alloys [4]; the introduction of additional components into existing materials (nanoparticles, superhard carbides, ceramics, etc.) [5–6]; a change in the nature of contact interaction with the implementation of the Charpy effect; the formation in the coating or at its borders of new wear-resistant phases [8-11], etc.

However, the most promising, from a technical point of view, is the introduction of small amounts (up to 5 wt.%) of active additives into the finished surfacing materials, for example, the well-known dry friction modifier MoS₂ [12], which allows the known high-performance coating to be used without significant changes induction surfacing technology [1].

For the formation of hardening coatings of high chromium cast iron on the surfaces of the working bodies of agricultural machines by induction surfacing in industry, materials of grades ПГ-С27 and ПГ-УС25 are widely used. Previously, we have already studied similar coatings made of cast iron grade ПГ-УС25, reinforced with an additive of up to 5 wt. % B₄C [13], as well as coatings reinforced with additives up to 25 ... 30 wt. % cermet Cr₃C₁₋₉/ПГ-УС25 obtained by the SHS method [14]. The coatings were deposited with a layer of 0.2 ... 0.3 mm on the blade of the harvester knife part, while their wear resistance increased by 2.5 ... 3.1 times.
Spherical powder of tungsten carbide eutectic WC-W2C – spherorelite is a new, promising material for hardening various parts, as well as giving new properties to known coatings based on Ni, Fe, Cr [15]. This unique product based on one of the hardest, strongest (HV = 2200 MPa, = 700 GPa) and thermally stable materials in the industry – WC, is obtained by the original technology of centrifugal spraying of its ingots. At the same time, the granules have a regular, strictly spherical shape, and due to the atomization of ingots from a WC-W2C carbide eutectic mixture additionally alloyed with d-metals, they also have a stable chemical composition and a fine-grained structure, which ensures high technological effectiveness of the powder and a guaranteed additional increase in material hardness.

However, at present, for the modification of hardening, wear-resistant coatings of the Fe-Cr-C system with tungsten carbide and, in particular, spherorelite, the industry uses more high-energy, but also much less productive than high-frequency welding deposition methods of their application: plasma, electric arc and gas-flame technology [5, 7, 8]. Therefore, the creation of wear-resistant coatings of high-chromium cast iron, hardened with spherorelite, using the method of induction surfacing is relevant.

The purpose of this work is to obtain by method of induction surfacing wear-resistant coatings of hard alloy ПГ-УС25 on steel 65Г, additionally hardened by their modification to 5 ... 10 wt.% spherorelitis КВС-5, as well as their material science research.

2. Experimental procedure
As the initial reagents used: powder of high-chromium hard alloy (cast iron), grade ПГ-УС25); grinding powder of boron carbide B4C, grain size 10 (GOST 5744-85); spherical eutectic tungsten carbide WC-W2C – spherorelite, grade КВС-5 (experimental batch); nickel powder, thermosetting, ИТ-19-01; as well as borate flux for induction surfacing П-0,66 [7]. All powder metal and flux materials were dried, crushed, and sieved through sieves with a mesh, Ø 0.350 and 0.125 mm, respectively, before preparing the charge.

Coatings were obtained by induction surfacing of a basic industrial charge, composition, wt. %: ПГ-УС25 – 85; flux П-0,66 – the rest [3]. The components were dosed by weight and mixed in a biconical mixer for 0.5 ... 1 hour. The modifier, the WC-W2C+B4C complex, was introduced into the charge by reducing metal (up to 75 wt.%), or non-metal (up to 10 wt. %) parts.

The coatings were surfaced on an ELSIT-100/75 HDTV unit with a water-cooled one-turn slotted inductor made of a profiled copper tube, Ø 15 mm, applying the finished mixture with a layer of 2–3 mm thickness on experimental samples made of 65Г steel, 50 × 20 × 5 mm in size, with high-frequency heating (ν = 65 ... 75 kHz) to a temperature of 1150 ... 1250 °C, for a time of 45 ... 60 sec. The obtained samples were used to optimize the compositions and refine the surfacing technology, evaluating the state of their surface and the hardness of HRC (TK-2 press).

Metallographic studies were carried out on a CARL ZEISS AXIO OBSERVER-Z1 M microscope and MN-6 microhardness meter according to standard ASTM methods: E 3, E 407, E 1558, E 883, E 384. X-ray phase analysis of the products was carried out on a DRON-6 diffractometer (Cu, K-radiation, λ = 1.5418 Å), phase identification – in the PDWin software package, using card files: PDF-2, ICDD.

X-ray fluorescence microanalysis was performed on a Philips SEM515 with an EDAX ECON IV microanalyzer.

Wear resistance was determined according to the original method, which combines friction tests on loosely fixed abrasive particles GOST 23.208-79 (ASTM G174-04 (2017), and according to the finger-ASTM G99 (2010), on a special laboratory tribometer, load 40 ... 45 ± 0.25 N, internal standard – steel 65Г, hardened to 55 ... 57 HRCs.

Relative wear was determined by weighing the samples on a ВЛК-500 balance, with an accuracy of ± 0.01 g.

3. Results and discussion
The experimental batch of spherorelite КВС-5 used by us is additionally alloyed by the manufacturer up to 0.5 ... 0.8 wt.% Co, which allowed to obtain a product with a hardness of up to 3100 MPa, with the following composition, wt. %: W 95.8-96.0; C 3.8-4.0; Fe <0.11; Co 0.5-0.8; C (free) 0.02-0.05, product fraction, Ø
0.25-0.5 mm.

The difficulty of obtaining monolithic coatings from high-chromium cast iron, when modified with tungsten carbide, using high-frequency technology, is explained by the existence of an objective technical contradiction between the working temperature of this process 1100 ... 1200 °C [3], the melting points of carbides 2500 ... 2800 °C, formed in the W-C system [16], as well as melting points of 1400 ... 1500 °C of ceramic materials of the BK type on a cobalt bond [1]. The large temperature difference and the short process time do not allow to obtain a high-quality, monolithic coating.

Trial experiments conducted by us on hardening ПГ-УС-25 with КВС-5 spherorelite alone, taken in an amount up to 5 wt. %, as expected, did not give the desired effect. In the coatings obtained, the tungsten carbide granules did not form a metal bond with high-chromium cast iron and were tinted from the layer even in the process of manufacturing isolated metallographic samples. In addition, due to a sharp difference in the mechanical properties, thermal expansion coefficients, and the melting point of spherorelite and hard alloys, cracks, pores, and other macrodefects formed in the coatings upon receipt.

It is known that the modification efficiency and the quality of coatings can be improved by increasing adhesion at the boundary of spherorelite granules with high-chromium cast iron at a melting temperature of 1100 ... 1200 °C. This problem can be solved by using tungsten carbide in coatings obtained by high-frequency technology not in pure form, but as part of special complexes – mixtures with substances capable of chemically interacting simultaneously with both the surface of the modifier and the binder material, and their activity it should appear at temperatures below 1100 ... 1300 °C. Boron carbide B₄C, can become such a component of the surfacing charge, which, under the conditions of high-frequency heating, as shown earlier [1, 17], reacts with the components of the hard alloy and the deposited steel surface, forming various products in the volume and at the phase boundaries: eutectic Fe-B, borides Fe₅B, FeB, carborbides Fe, Me(C,B)₆, boron austenite Fe, Me₂₃(C,B)₆ where: Me is the alloying metal (s), which is also confirmed by the data of [9, 18].

The high reactivity of B₄C under conditions of high-frequency heating and its introduction into the WC-W₂C+B₄C complex is also explained by the topochemical reaction between these substances and iron, steel with the formation of low-melting 960 ... 980 °C Fe-B eutectic [18]. These circumstances suggest that tungsten carbides WC, W₂C, which are part of spherorelite, are involved in physicochemical and adhesive processes at the phase boundaries.

Therefore, further modification of ПГ-УС25 cast iron coatings was already carried out by the КВС-5+B₄C complex, introducing its components into the finished charge for induction surfacing by reducing the ПГ-УС25 cast iron spherorelite content, and due to the flux for induction surfacing П-0,66 – boron carbide. The total number of components of the modifying complex in the mixture was 4 ... 12.5 wt. %, which, with the selected modification methodology, allows one to preserve the thickness, uniformity, quality, and optimal coating deposition regime in industrial conditions.

Figure 1 shows the structure of the coating obtained by modification of cast iron ПГ-УС25 complex: 3 ... 5 wt. % spherorelitis КВС-5 and 1 ... 1.5 wt. % boron carbide, with the main phases indicated on it (numbers).
As can be seen from the micrograph shown in figure 1, when modifying high-chromium cast iron with the KBC-5 + B₄C complex, in an amount of 4 ... 6.5 wt. % it was possible to obtain a monolithic coating in which spherorelite granules formed metal bonds with a matrix metal, are firmly held in the deposited layer and do not crumble during friction.

The following main phases are formed in such a coating during induction surfacing: 1 – boron fine-dispersed eutectic from Fe and Cr carbides, with individual inclusions of crushed needle carbides Cr₇C₃, Cr₂₃C₇ with a hardness of up to 930 ... 950 HV₁₀₀; 2 – eutectic from Fe, Cr carbides, with inclusions at the fusion boundary with the base metal of primary and secondary boron dendrites, with hardness up to 850 ... 900 HV₁₀₀; 3 – spherical granules of carbide WC - W₂C, with a defined boundary, adhesive-bonded with a cast iron matrix, with a hardness of up to 1600 ... 1950 HV₁₀₀.

It is interesting to note that in the obtained coating, despite significant melting of the base metal, there are completely no dendritic structures typical for induction surfacing at the metal base / coating interface [1].

However, there are macroscopic defects in the coating: pores, cracks, the formation of which is associated with the presence of non-metallic inclusions (B₄C and products of its assimilation by surfacing material – graphite, soot).

To improve the quality of the coating, a softer material was additionally introduced into its composition – a thermostetting nickel powder clad with aluminum IIT-19H-01 in an amount of n. 2 ... 3 wt. % for the “healing” of cracks. In addition, the introduction of this component, theoretically, will increase the content of spherorelite in the material up to 8 ... 10 wt. % without deterioration of the quality of the coating [2, 4, 8].

Figure 2 shows the fine structure of the coating obtained by modification of cast iron ПГ-УС₂₅ complex: 8 ... 10 wt. % spherorelitis KBC-5; 1.5 ... 2.5 wt. % boron carbide and 2 ... 3 wt. % nickel powder IIT-19H-01. As can be seen from the figure, not only crack healing occurred in the coating material, but also a chemical interaction of boron carbide with the surface of spherorelite granules is observed, leading to the formation of a new phase at the interface – a tungsten-boride eutectic, which has a characteristic skeletal morphology, which leads to increase the adhesive interaction of the WC, W₂C modifier with the coating matrix.

In table 1, the results of a chemical analysis of the composition of the phases of the coating, modified by a complex of 3 ... 5 wt. % spherorelitis + 1 ... 1.5 wt. % B₄C, at control points (see figure 3), obtained by X-ray fluorescence microanalysis.

As follows from the data in table 1, the composition of the main phases of the obtained coating – boronated (point 1) and non-borated (point 2) eutectics from Fe, Cr carbides, does not differ significantly in the main and dissolved elements (Cr, Mn, Fe, Si). It can be seen that the boration of this phase of the material occurred mainly due to isomorphic substitution of part of the carbon in the eutectic Fe-Cr-C with boron, as evidenced by the fraction of this element reduced in 2 ... 3% in phase 1. But the introduction of B₄C into the material coating led to an increase in the eutectic content of silicon, and almost complete displacement of Nickel, which is confirmed by the data of [9].
**Table 1.** The results of a chemical analysis of the composition of the phases of the coating, modified by the complex composition, wt. %: 3 ... 5 - WC- W₂C + 1 ... 1.5 – B₄C.

| Spectrum point | Element, Kα line | Composition, % элемента, % | wt. | at. |
|----------------|------------------|----------------------------|------|-----|
| 1.             | C                | 08.91                      | 32.81|     |
|                | Si               | 02.24                      | 02.32|     |
|                | Cr               | 35.73                      | 26.56|     |
|                | Mn               | 02.39                      | 01.98|     |
|                | Fe               | 49.53                      | 34.29|     |
|                | Ni               | 00.09                      | 00.07|     |
|                | B                | 02.23                      | 01.53|     |
| 2.             | C                | 11.13                      | 35.81|     |
|                | Si               | 01.24                      | 01.71|     |
|                | Cr               | 33.37                      | 24.16|     |
|                | Mn               | 01.39                      | 00.98|     |
|                | Fe               | 42.53                      | 29.12|     |
|                | Ni               | 00.99                      | 00.65|     |
| 3.             | C                | 03.71                      | 16.26|     |
|                | Si               | 02.52                      | 05.07|     |
|                | Cr               | 24.84                      | 26.98|     |
|                | Mn               | 02.83                      | 02.91|     |
|                | Fe               | 59.38                      | 60.05|     |
|                | Co               | 00.55                      | 00.39|     |
|                | W                | 07.68                      | 02.36|     |
|                | B                | 01.17                      | 00.93|     |

The transformations occurring at the interface between spherorelite granules and high-chromium cast iron (point 3) also change the composition of the base material, and the degree of boron assimilation here is higher than in case of point 1, since almost the entire amount of carbon determined at point 3 corresponds to a stoichiometric fraction of this element in the carbide eutectic WC-W₂C [16].

However, the X-ray phase analysis of this coating did not reveal new phases of individual or mixed borides in it, which once again confirms the main form of boron in modified materials – in the composition of the eutectic Fe-C-B, Fe-Me-C-B, where: Me is the alloying metal (s) where it replaces part of the carbon. While the formation of special carbides W₂Fe₂C₆, W₂Co₄C in the coating of new phases (figure 3), indicates the occurrence of surface chemical reactions due to the participation of the low-melting Fe-B eutectic and redistribution of carbon from the carbides and 3, 4 component eutectics Fe-Cr-C- (B) [10, 17].

![Figure 3](image-url) **Figure 3.** A fragment of an x-ray of the coating modified by the complex: 3 ... 5 wt. % spherorelitis + 1 ... 1.5 wt. % B₄C.
The absence of peaks of FeB and Fe₂B in the X-ray diffraction pattern, for example, is similar to coatings that we obtained earlier by high-frequency heating of 65Г steel in a charge containing 80 ... 85 wt. B₄C [18], as well as the absence of peaks of Cr, W borides, can be associated with a small total share of boron both in the introduced complexes (1 ... 2.5) and in the charge as a whole (0.8 ... 2 wt. %).

The conducted studies allowed us to develop two optimized composition of the charge for industrial induction surfacing of high-chromium cast iron ПГ-УС25 hardened with spherorelite, the compositions and some properties of which are shown in table 2.

| Charge | Ingredient | Composition, wt. % | HRCэ |
|--------|------------|--------------------|------|
| 1.     | ПГ-УС25    | 80...85            |      |
|        | KBC-5      | 3...5              | 60...65|
|        | B₄C        | 1...1.5            |      |
|        | Flux II-0,66| the rest           |      |
| 2.     | ПГ-УС25    | 75...78            |      |
|        | KBC-5      | 8...10             | 50...55|
|        | B₄C        | 1.5...2.5          |      |
|        | IIT-19H-01 | 2...3              |      |
|        | Flux II-0,66| the rest           |      |

According to table 2, you can issue the following production recommendations. To obtain thin wear-resistant coatings on the cutting edges of parts and hardening, for example, heat-treated knives of agricultural machines, it is preferable to use composition No. 1, since the hardness of this material is 1.2 ... 1.4 times higher than the hardness of the base metal (65Г steel), which provides the blade with a self-sharpening effect and increases the service life [1]. To obtain thicker coatings (lancet paws, crusher hammers, etc.), as well as in other cases, composition No. 2 can be recommended.

4. Conclusion

It has been proposed to increase the wear resistance of Fe-Cr-C coatings obtained by induction surfacing of ПГ-УС25 high-chromium cast iron and their modification with the WC-W₂C+B₄C complex.

It is shown that the introduction of the specified complex into the basic industrial charge for induction surfacing of the complex allows to increase wear resistance by 3.1 times (with respect to the base metal) and 1.3 times (with respect to the base, unmodified material), depending on the mass fraction spherorelitis in the charge.

The detected changes in the structure and properties of the coatings are explained by various processes: the formation of new phases; Charpy effect; grinding and dispersion hardening of the eutectic Fe-Cr-C during high-frequency boronation and modification.

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