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Formation features of microstructure, elemental and phase compositions of the C-Cr-Mn-V-Fe coatings under conditions of electron beam (EB) Surfacing in vacuum

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ABSTRACT

The microstructure and interphase distribution of chemical elements in multilayer coatings made of white cast iron in Fe-Cr-V-C system additionally alloyed with manganese and obtained using electron-beam surfacing in vacuum have been investigated. It is shown that in deposited state the surface of Cr-V-Mn cast iron coating is represented by the composite structure of "austenitic manganese containing matrix - carbides V_2C, Me_7C_3 of variable composition" with high abrasive wear resistance (Ki = 9.4) similar to chrome vanadium cast iron coatings with an austenitic-martensitic matrix, but with significantly better abrasive wear resistance compared to cast iron coatings with an austenitic matrix stabilized by nickel.

KEYWORDS

white cast iron • layered electron beam (EB) surfacing • microstructure • carbides • matrix • vanadium manganese • wear resistance

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Introduction

Most equipment parts in mining, processing, metallurgical and other industries operate under intense abrasive and impact-abrasive wear conditions. The service life of heavily loaded parts directly depends on the wear resistance and hardness of their working surfaces, therefore its economically viable to develop new technologies of manufacturing parts with special hardening coatings that provide required operational reliability [1–8]. Therefore, the search for promising multi-component coating compositions and fundamentally new technological solutions for their production is of particular importance.

Recently, there has been a significant increase in practical application of technologies based on the highly concentrated energy sources (laser, electron beam (EB) surfacing, etc.) where the high surface and volume concentration of energy makes it possible to reduce the time of high-temperature exposure to materials tenfold, at the same time providing the low mixing ratio of coating materials with substrate materials and minimal deformations of hardening parts. Due to increased heating and cooling rate

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(~ 10^5 K/s), the formed coatings can demonstrate advanced strength and tribological characteristics due to formation of solid solutions supersaturated with alloying elements and separation of fine particles of reinforcing refractory compounds from these solid solutions [9,10].

To achieve these objectives the multicomponent alloys can be utilized as coating materials with abrasion resistance properties based on high-chromium high-carbon white cast irons exhibiting the structure of natural composites [11–16]. At the same time, one should take into account the important role of the matrix, which should combine such characteristics as high strength, high impact toughness, ability to wet the strengthening particles and the surface of parts to be hardened during surfacing, as well as have damping ability for effective relaxation of stress concentrators being developed during loading of heterogeneous coatings and have the ability to harden under plastic deformation [17,18].

The work objective was framed after the research study on excavator's teeth hardening with coatings from white chromium and chrome vanadium cast irons with an austenitic-martensitic matrix using EB surfacing method [19,20]. The field tests results showed the low abrasive resistance of coatings due to tendency to cracking and destruction. As a result, the objective was defined to develop and study composite coatings based on eutectic chromium cast iron, alloyed additionally with vanadium and manganese, with the purpose to obtain the austenitic strain-hardened 110G13 (Russian GOST) type matrix.

Considering the high physical and mechanical properties of the base materials of surfacing compositions and the unique capabilities of the EB surfacing technology, as well as the fact that no analogous research in this direction was found, it seemed relevant to conduct a systematic study of the patterns of formation of the structure and properties of coatings from white eutectic chromium-vanadium-manganese cast iron, obtained by layered EB surfacing method.

Materials and Methods

The initial material for the electron-beam surfacing of the coating was the mixture of industrial powders of hypereutectic chromium iron PG-S27, vanadium grade VAL-2 and ferromanganese FMn-78 (Russian GOST 4755-91) with the dispersion of 100-400 µm. To obtain the eutectic composition of the deposited layer, the industrial powders were mixed in the following ratio of the initial components: 65 % PG-S27 + 5 % V + 30 % FeMn (wt. %). The chemical composition of the surfacing powder is presented in Table 1.

Table 1. Chemical composition of the surfacing material

Content, wt. %							
C	Cr	V	Mn	Si	Ni	W	Fe
2.5	17.0	5.0	23.0	1.5	1.1	0.2	base

* The eutectic composition was based on the data from study [3].

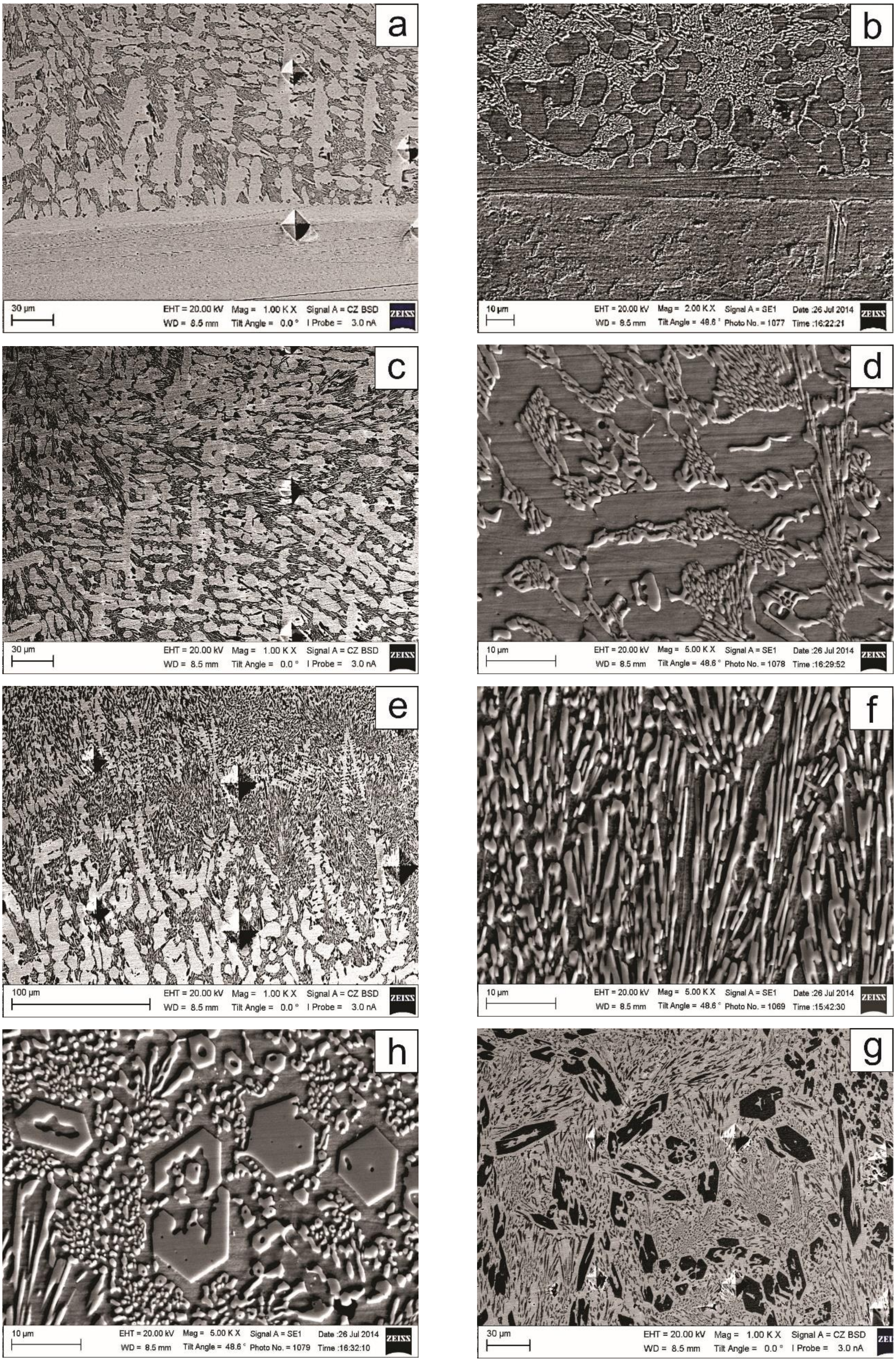

Fig. 1. Microstructure of electron beam (EB) coating along the depth of the layer of eutectic chromium-manganese-vanadium cast iron: (a, b) "substrate-coating" interface; (c, d) hypoeutectic structure; (e, f) eutectic structure; (g, h) hypereutectic structure

The surfacing was carried out on the substrates made of low carbon steel C1030 200 × 30 × 5 mm in size.

The process of layered surfacing of a wear-resistant coating using the EB surfacing method was carried out in a vacuum chamber with 5×10^{-1} Pa pressure. During surfacing, an electron beam of 1 mm in diameter and 3 kW of power was deployed in a line with a size of 5×1 mm with a scanning frequency of 50 Hz, forming a melt pool with a size of 5 × 5 mm on the surface of the steel substrate.

The structure of the coating was analyzed using a Carl Zeiss Axio Observer A1m optical microscope (Fig. 1) after etching in a Marble reagent and Rigaku SmartLab X-ray diffractometer (Cu Kα radiation). The chemical composition of the metal base was determined at local points on carbides and inside eutectic colonies using X-ray spectral microanalysis (MRSA) on a Zeiss Merlin Compact scanning electron microscope, and hardness was tested using Instron RB2000 hardness tester and PMT-3 microhardness tester. Wear resistance tests were carried out in laboratory conditions with a non-rigidly fixed abrasive material made of silica sand with a fraction of < 300 μm, a hardness of 1000-1200 $HV_{0.1}$ in accordance with GOST 23.208-79.

Results and Discussion

After multilayer (6 passes) electron-beam surfacing of 65 %PG-S27 + 5 % V+30 % FeMn (wt. %) powder on a low-carbon steel substrate, a 3.5 mm thick coating was obtained. It is clear that with each successively applied layer a decrease in the crystallization rate occurs due to heating of the substrate, leading to the change of the composite structure over the depth of the coating, as well as the chemical composition and dispersion of the structural components. The metallographic analysis indicated (Fig. 1) that the coating is characterized by a gradient structure caused by dilution of surfacing material by substrate material (Iron) and uneven crystallization of microvolumes of the material due to different cooling rates of the layer-by-layer deposited metal.

The distribution curves of the main alloying elements over the thickness of the deposited layer, shown in Fig. 2, indicates their gradual increase in concentrations from the interface to the surface of the coating.

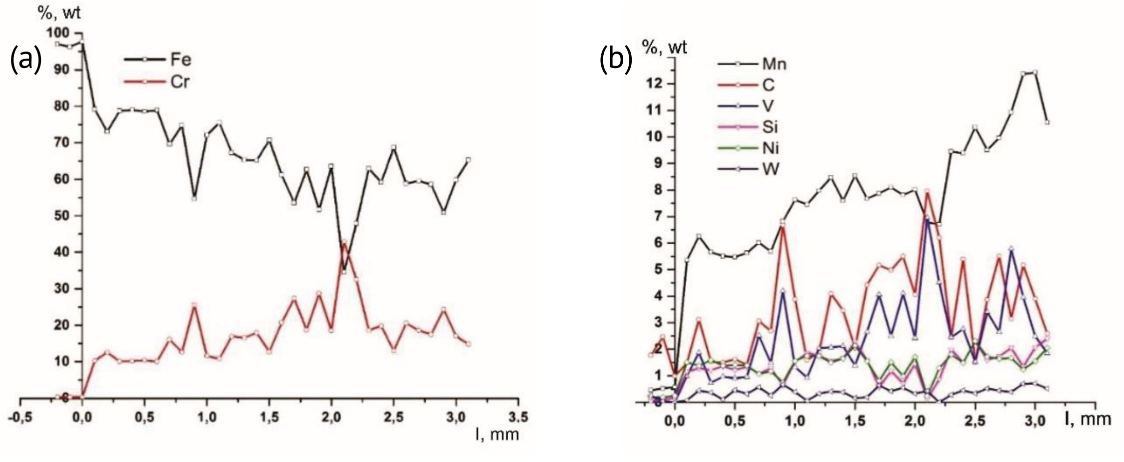

Fig. 2. Chemical elements distribution over the thickness of CR-V-MN cast iron coating (a; b) obtained using electron beam (EB) surfacing method

Metallographic studies of the cross-section showed that with the change of chemical composition along the coating depth, the number of characteristic structures was formed, as shown in Fig. 1. Once crystallization of the first layer was complete, a narrow zone (8–10 μm) at the "substrate-coating" interface was formed in the shape of a non-etched strip (Fig. 1(a,b)) with composition of a high-alloy steel (Table 2). This is followed by the next ~ 1000 μm section of the structure - a transition zone, consisting of excessive austenite dendrites, formed from the interface, which are surrounded by a rarefied skeletal austenite-carbide eutectic (Fig. 1(c,d)).

Table 2. The analysis of distribution of alloying elements along the depth of the coating

Layer	Thickness of deposited layers, μm	Chemical Elements Content						
		C	Cr	V	Mn	Si	Ni	W
Layer 1	10	1.1 ± 0.1	8.3 ± 0.3	0.6 ± 0.2	4.3 ± 0.2	1.0 ± 0.1	-	-
Layer 2	1,000	1.8 ± 0.7	10.6 ± 0.9	1.1 ± 0.4	5.6 ± 0.3	1.3 ± 0.1	1.4 ± 0.1	0.3 ± 0.2
Layer 3	200-300	4.0 ± 1.6	19.8 ± 7.2	1.5 ± 0.6	8.6 ± 1.8	1.5 ± 0.6	1.5 ± 0.5	0.4 ± 0.2
Layer 4	2,000	5.4 ± 0.8	21.0 ± 2.6	4.47 ± 0.6	10.2 ± 1.8	1.2 ± 0.5	1.21 ± 0.6	0.18±0.2

During the subsequent deposition of layers an eutectic-type 200-300 μm structure was found with high density distribution of carbide in eutectic colonies. The carbide phase in the form of plates or needles grows in fan-like manner in the outward direction from substrate to surface (Fig. 1(f)), which indicates directional solidification in the process of electron-beam surfacing. Spheroidal carbide particles (1, 2 μm) are relatively evenly distributed on and between the plates, most of which have a somewhat elongated shape with a ratio of dimensions along the axes in the range of 1-2 and with average size of 1-5 μm.

The final surfacing resulted in the formation of the thickest ~ 2000 μm fourth layer of hypereutectic cast iron. The structure is characterized by the presence of large primary hypereutectic carbides of hexagonal shape in the austenite-vanadium-carbide eutectic (Fig. 1) and the highest content of the main alloying elements - chromium, vanadium and manganese (Table 2).

The analysis of distribution of alloying elements along the depth of the coating, as shown in Fig. 2 and Table 2, showed that the chemical composition of the coating has changed compared to the estimated one, which is attributed to the intrinsic specifics of the electric beam (EB) surfacing technology.

The temperature of the melt pool must be at least 2000 °C to ensure the complete melting of the surfacing powder 65 % PG-S27 + 5 % V + 30 % FeMn that contains vanadium with the melting point of 1920 °C. Among the main alloying elements present in the coating, manganese has the lowest melting point of 1245 °C and lowest boiling point of 2080 °C. Therefore, at 10^{-1} Pa pressure in the vacuum chamber and ~ 2000 °C melt bath temperature in the electron beam zone, the manganese begins to actively evaporate. As a result, the loss of manganese relative to the calculated content was 56 %. According to MRSA data (Table 2), the manganese content in the coating after surfacing decreased relative to the calculated composition from 23.0 to 10.2 wt. %, which with the existing ratio of alloying components turned out to be sufficient to form a composite coating with an austenitic matrix. The presence of austenite is confirmed by diffractogram of the coating surface, with diffraction maximas corresponding to g-Fe, vanadium carbide V_2C and trigonal carbide Me_7C_3 (Fig. 3). The combination of the detected phases stipulates the formation in the coating of double eutectics of inverted type - based on vanadium carbide (g-Fe - V_2C) and chromium carbide - g-Fe - Me_7C_3 [1,4].

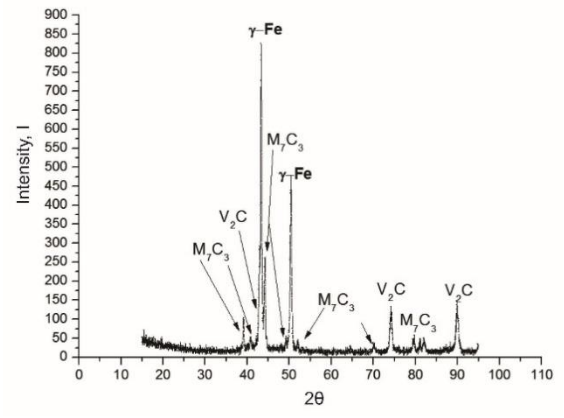

Fig. 3. X-ray diffraction pattern of coating made from powder mixture with composition 65 % PG-S27 + 5 % V + 30 % FeMn (wt. %) formed by EB surfacing in vacuum

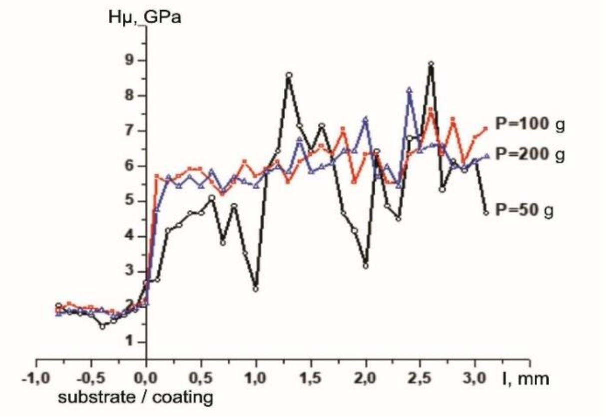

Fig. 4. Microhardness distribution in the system "low-carbon steel substrate - coating of eutectic chrome-vanadium cast iron" at loads of 50, 100 and 200 g

Composition analysis of Me_7C_3 carbides showed that complex alloying leads to formation of carbides $(Cr\text{-}Fe\text{-}V\text{-}Mn)_7C_3$ of variable composition, in which chromium is partially replaced by iron, and manganese and vanadium are present in approximately equal concentrations. It is shown that carbides $(Cr\text{-}Fe\text{-}V\text{-}Mn)_7C_3$ differ slightly from each other in chemical composition, staying within the following concentration of alloying elements: Cr - 43.58 ÷ 45.43; Fe - 29.9 ÷ 32.55; V - 7.18 ÷ 8.45; Mn - 7.29 ÷ 8.17.

Microhardness measurements on a sample cross section under various loads (200, 100, 50 g.) showed a gradual increase in microhardness from substrate to coating surface due to increase in the degree of alloying of the material and increase of dispersion of the structural components of the composite structure in the formed layer (Fig. 4).

As can be seen from the graphs the microhardness along the depth of the coating changes in accordance with the layer-by-layer structures formed during crystallization process. Thus, the average microhardness of the hypoeutectic cast iron section of the coating structure at indenter load of 200 g is 5.5 GPa, of the eutectic cast iron section is 6.1 GPa, and of the hypereutectic cast iron section is 6.5 GPa. A gradual increase in hardness from substrate to working surface in accordance with the gradual change in chemical composition along the depth of the deposited layer may indicate decrease of the gradient of properties and stresses between the coating and the substrate, and reduction of the tendency of the entire "substrate-to-coating" system to cracking.

Abrasive wear resistance tests of coatings made using EB surfacing method in vacuum showed the following results (Fig. 5): the studied coating made of chromium-vanadium-manganese cast iron with an austenitic matrix (composition 1), with abrasive wear resistance of *Ki* = 9.4, is practically not inferior in abrasive wear resistance to the coating of chrome vanadium cast iron with an austenitic-martensitic matrix (composition 2) (*Ki* = 10), but significantly surpasses the wear resistance of the cast iron with an austenitic matrix coating stabilized by nickel (composition 3) (*Ki* = 4.5) [4,5]. The hardness of the coating surface was 50 ± 1 HRC on Rockwell scale.

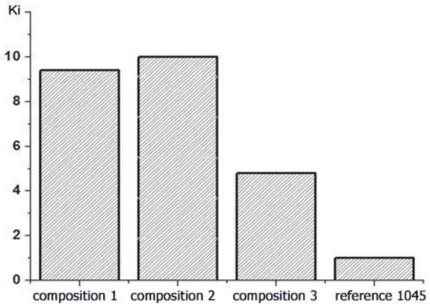

Fig. 5. Abrasive wear resistance of coatings made of white high-chromium high-carbon cast irons alloyed with vanadium, nickel and manganese obtained using EB surfacing method in vacuum (Cr20Mn10V5 (composition 1); Cr19V5 (composition 2); Cr20NiV5 (composition 3))

Conclusion

1. It was shown that functional alloying with vanadium and manganese during layered electron beam (EB) surfacing of the powder composition 65 % PG-S27 + 5 % V + 30 % FeMn wt. % leads to formation of coatings with gradient structure along the depth of the layer. There is a sequential formation of layers within the coating structure of high-alloy steel (Cr_8Mn_4V), hypereutectic ($Cr_{10}Mn_5V$), eutectic ($Cr_{18}Mn_8V_2$) and hypereutectic ($Cr_{20}Mn_{10}V_4$) white high-alloy cast irons.

2 It was found that the loss of manganese during electron beam (EB) surfacing at 10^{-1} Pa pressure in vacuum chamber was 56 % from calculated chemical composition. The residual content of manganese after surfacing of 10.2 wt. % in the coating, contributed to the formation of a composite coating based on austenitic strain-hardened matrix.

3. It was shown that complex alloying leads to formation of carbides of two types: spheroidal V_2C based on vanadium and trigonal carbides $(Cr\text{-}Fe\text{-}V\text{-}Mn)_7C_3$ of variable composition, where the content of the main alloying elements was within the following concentration limits: Cr – 43.58 ÷ 45.43; Fe - 29.9 ÷ 32.55; V - 7.18 ÷ 8.45; Mn - 7.29 ÷ 8.17.

4. Comparative studies have shown that coating obtained in this work from chromium-vanadium-manganese cast iron with an austenitic matrix of $Cr_{20}Mn_{10}V_5$ (composition 1) composition, with abrasive wear resistance coefficient of *Ki* = 9.4, is practically not inferior in abrasive wear resistance to chrome-vanadium cast iron $Cr_{19}V_5$ (composition 2) coating with austenitic matrix of *Ki* = 10, but significantly surpasses the wear resistance of the $Cr_{20}NiV_5$ (composition 3) coating with an austenitic matrix stabilized by nickel (*Ki* = 4.5).

References

1. Garber ME. *Wear-resistant white cast irons: properties, structure, technology, operation.* Moscow: Mechanical Engineering; 2010. (In Russian)

2. Tenenbaum MM. *Wear resistance of structural materials and machine parts under abrasive wear.* Moscow: Mechanical Engineering; 1966. (In Russian)

3. Tsypin II. *Wear resistant white cast irons. Structure and properties.* Moscow: Metallurgy; 1983. (In Russian)

4. Pawar S, Jha AK, Mukhopadhyay G. Effect of Different Carbides on the Wear Resistance of Fe-Based Hardfacing Alloys. *International Journal of Refractory Metals and Hard Materials*. 2019;78: 288–295.
5. Gunther K, Bergmann JP. Influencing Microstructure of Vanadium Carbide Reinforced FeCrVC Hardfacing during Gas Metal Arc Welding. *Metals*. 2020;10(10): 1345.
6. Gunen A, Kalkandelen M, Karahan İH, Kurt B, Kanca E, Gök MS, Serdar Karakaş M. Properties and Corrosion Behavior of Chromium and Vanadium Carbide Composite Coatings Produced on Ductile Cast Iron by Thermoreactive Diffusion Technique. *J. Eng. Mater. Technol.* 2020;142(4): 041008.
7. Dampilon BV, Durakov VG. Features of structure formation of coatings from eutectic chromium vanadium cast iron obtained by electron beam surfacing. *Perspektivnye Materialy*. 2012;1: 87–91. (In Russian)
8. Durakov VG, Dampilon BV. Influence of heat treatment on the structure and abrasive wear resistance of coatings from eutectic chromium vanadium cast iron. *Perspektivnye Materialy*. 2012;4: 82–86. (In Russian)
9. Valkov S, Ormanova M, Petrov P. Electron-beam surface treatment of metals and alloys: Techniques and trends. *Metals.* 2020;10(9): 1–20.
10. Konovalov S, Ivanov Y, Gromov V, Panchenko I. Fatigue-induced evolution of AISI 310S steel microstructure after electron beam treatment. *Materials*. 2020;13(20): 4567.
11. Krushenko GG, Taldykin YA, Uskov IV. Steel castings with a surface-alloyed wear-resistant layer. *Liteinoye Proizvodstvo*. 2000;3: 21–22. (In Russian)
12. Liu K, Wang F, Li C, Su L. Influence of Vanadium on Microstructure and Properties of Medium-Chromium White Cast Iron. *Iron and Steel*. 2005;40: 207–211.
13. Krolicka A, Szczepanski L, Konat L, Stawicki T, Kostencki P. The Influence of Microstructure on Abrasive Wear Micro-Mechanisms of the Claddings Produced by Welding Used in Agricultural Soil. *Materials*. 2020;13: 1920.
14. De Mello JDB. Abrasion Mechanisms of White Cast Iron II: Influence of the Metallurgical Structure of V-Cr White Cast Irons. *Mater. Sci. Eng*. 1986;78(2): 127–134.
15. Qi X, Jia Z, Yang Q, Yang, Y. Effects of vanadium additive on structure property and tribological performance of high chromium cast iron hardfacing metal. *Sur. Coat. Technol*. 2011;205(23-24): 5510–5514.
16. Radulovic M, Fiset M, Peev K. The influence of vanadium on fracture toughness and abrasion resistance in high chromium white cast irons. *J. Mater. Sci*. 1994;29: 5085–5094.
17. Efremenko VG. Effect of vanadium and chromium on the microstructural features of V-Cr-Mn-Ni spheroidal carbide cast irons. *International Journal of Minerals, Metallurgy and Materials*. 2014;21: 1096–1108.
18. Filipovic M, Romhanji E, Kamberovic Z, Korac M. Matrix microstructure and its micro-analysis of constituent phases in as-cast Fe-Cr-C-V alloys. *Mater. Trans*. 2009;50(10): 2488–2492.
19. Kawalec M. The spheroidization of VC carbides in high-vanadium cast iron. *Archive of Foundry Engineering*. 2011;3: 111–116.
20. Dampilon BV. *Structure and properties of coatings based on nitrogen-containing chromium-manganese steel with carbonitride strengthening, obtained by electron-beam surfacing. Thesis for the Degree of Cand. Eng. Sci.* Tomsk: ISPMS SB RAS; 2003. (In-Russian)

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