1. Introduction

Currently, the greatest amount of materials for electric arc hardfacing is based on the alloys of the Fe–Cr–C system. These materials are characterized by high wear resistance under conditions of abrasive wear due to the existence in their structure of massive inclusions of the carbide phase of Cr$_7$C$_3$ and high-chromium eutectics. However, under working conditions, in which there are even minor dynamic and (or) cyclic loads, the use of such materials is limited due to the high fragility of coarse-grained metal carbide eutectic structure. For such conditions, it is rational to use electrode materials, the structure of which corresponds to the systems of alloying impact resistant steels [1–5]. The most common representatives of such steels are high-manganese (>13% by mass of Mn) austenitic steels, which are strengthened during
plastic deformation through twinning [6, 7]. Electrode materials of the Fe–Mn–C system demonstrate high performance under working conditions when there are significant dynamic loadings and are widely used in strengthening the parts of earthmoving equipment, milling facilities, mining equipment, etc. Their common drawback is low wear resistance at abrasive impact-free wear, in which the main mechanism of destruction of the surface layer is micro-cutting. Resistance to this type of wear can be ensured by extending the alloying system of Fe–Mn–C by adding carbide-forming elements of IV–VI groups of elements of the periodic system of elements by calculating the formation of the corresponding carbides, in the quantities required for indentation and further movement of abrasive particles in the surface layer by micro-cutting. In addition, the process of formation of carbide phases should affect as little as possible the composition of manganese austenite and, accordingly, the intensity of its deformation strengthening.

Taking into consideration that the use of serial impact-resistant coatings is limited under conditions of abrasive wear by the micro-cutting mechanism, the development of new impact-resistant materials with increased abrasive wear resistance is a relevant task for materials science and surface engineering.

2. Literature review and problem statement

The main directions of development of impact-resistant iron-based coatings are the use of alloys that are intensively strengthened during plastic deformation due to phase transitions or twinning and grain improvement due to dispersed insoluble phases.

The authors of paper [1] with the aim of improving the wear resistance of the rollers for cold rolling, studied the structure and the properties of the surface layers obtained using the flux-cored arc welding, which provides in a superficial layer of the austenite-martensite structure with the content of C ~0.35 %, Cr ~5.5 %, Mn ~1.5 %, Ni ~3 %, Mo ~3 %, W ~1.5 %. After cyclic deformation of coatings by compression at 1 GPa, it was recorded that their hardness increased from 50 to 56 HRC. Phase analysis and microstructural studies showed that such an increase in hardness was caused by the transformation of retained austenite into martensite. The effect of plastic deformation on the properties of the coatings of the Fe–W–C system, obtained by submerged arc welding, which contained additives of high-speed steel powder was studied in paper [2]. The results showed that plastic deformation of coatings with degrees of 35 and 55 % has a slight effect on the hardness of the surface layer, which is within 50–53 HRC, but significantly (by 1.7 times) increases wear resistance at friction on a fixed abrasive. The authors associate this character of the change in the properties with the existence of retained austenite.

To increase the impact toughness of electric arc coatings by grain refinement the microstructures, the authors [3] propose to introduce Ti and Nb additives allowing for the formation of appropriate carbide phases to the composition of coatings based on low-carbon high-chromium steel. Research results revealed that the addition of a total of ~0.16 % by mass of Nb and ~0.26 % by mass of Ti can increase impact toughness by 1.6 times, while the hardness of coatings does not change. In papers [4, 5], it is proposed to use for welding the high-alloyed alloys of Ti and V with the molybdenum additives instead of traditional chromic and tungsten materials. In the Fe–Ti–B–C system, the Mo supplement (8.5 % by mass) leads to an increase in the hardness of coating from 900 to 1,300 HV, of wear resistance by 1.2 times and a significant (almost by an order of magnitude) decrease in the size of solid phases. A similar tendency when adding Mo is observed in the Fe–V–B–C system, in which hardness increases from 1,000 to 1,300 HV, and wear resistance – by 5 times.

Alloys of the Fe–Mn–C system, which make it possible to obtain manganese austenite in the structure of the surface layer, are most versatile and widely represented in the market of materials for hardfacing by such manufacturers as Lastek (Belgium) and ESAB (Sweden), etc. The hardness of serial coatings after hardfacing is ~21–25 HRC and after the operation at impact loads ~45 HRC. An increase in wear resistance of such coatings can be achieved by insignificant ~1.2 % by mass of V [6], which ensures an increase in initial hardness up to 35 HRC. In paper [7], the effect of alloying on hardness and impact wear resistance of electric arc coatings based on the Fe–Mn–C system was studied. The results showed that during the transition from the doping system Fe–Mn–C to the Fe–Mn–W–C system (the content of W is 19 % by mass), the hardness of coatings increases from 11 HRC to 36 HRC. The coating consists of austenite and carbides (of cementite type, tungsten and MnC type). After adding ~4 % by mass of Mo to the alloys of the Fe–Mn–W–C system, the hardness increases up to 44 HRC, in this case, the appearance of new phases on the diffractogram was not detected.

Analysis of the above literary data shows that when creating impact-resistant coatings based on alloys, capable of deformation strengthening, the main problem is to ensure their resistance to impact-free abrasive wear. An effective way of enhancing the mentioned characteristic is alloying of the alloys of the Fe–Mn–C system with carbide-forming elements allowing for the formation of carbide phases with high micro-hardness in the structure. However, the unresolved problem at present is a reasonable choice of carbide-forming components that ensure the existence of stable carbide phases in the structure. The results obtained by now, are based on empirical data related to the components (Mo, W, etc.), which ensure the formation of complex carbides of the MnC and M2C. That is why there arises the need to study the systems of alloying high-manganese alloys, in which the existence of carbide phases of the MC type is thermodynamically advantageous.

Taking into account the experience of development of impact-resistant coatings, it can be concluded that the rational way for their creation is to combine simultaneously several approaches for providing impact resistance, specifically, to modify the structure by weakly soluble phases and to ensure deformation strengthening. This implies the expansion of the conventional alloying system Fe–Mn–C due to the addition of the components that form the compounds that are resistant in electric arc welding, such as Nb [8], Ti [9] or at the interacting with the melt, form complex carbide phases of the Mn3C, M23C6 type [10].

3. The aim and objectives of the study

The aim of this study was to establish the nature of the formation of phase composition, structure and proper-
ties of electric-arc coatings based on the alloying system Fe–Mn–C at the addition of niobium and titanium carbides. It will enable obtaining the surface layers with high performance due to the combination of high impact and wear resistance in the abrasive medium.

To accomplish the aim, the following tasks have been set:
- to establish diffusive redistribution of the elements in the alloys based on the Fe–Mn–C system at cooling speeds, which are typical of electric arc welding;
- to assess the impact of additives of titanium and niobium carbides on the equilibrium phase composition of high-manganese steels in the temperature range characteristic of electric arc welding;
- to establish the shape, size, and character of the mutual location of the carbide structural components of the coatings of the high-manganese steel – TiC(NbC) system;
- to determine the hardness of coatings of the high-manganese – TiC(NbC) system before and after plastic deformation, as well as their wear resistance under conditions of friction on a non-fixed abrasive compared with serial coatings.

4. Materials and methods to study the structure and properties of electric arc coatings of the system high-manganese steel – TiC (NbC)

The samples for research were made by flux-cored arc welding with electrode materials of coatings on the steel St. 3 base. Powder electrode materials were produced in the form of single-core powder tape, consisting of a shell made of steel 08kp GOST 3559-75 and a filler – mixtures of ferro siliconomanganese MNS17 GOST 4756-91, graphite C-354 GOST 3559-75, niobium carbide NbC TU 6-09-03-363-74, molybdenum carbide Mo2C TU 6-09-03-6-75, niobium carbide NbC TU 6-09-03-6-75, niobium carbide NbC TU 6-09-03-6-75, molybdenum carbide Mo2C TU 6-09-03-363-74, to improve the protection of the arc from the atmosphere and to enhance the technological properties of electrode materials, rutile, and calcium fluoride were additionally introduced to their composition. Hardfacing was performed in the manual mode with the use of welding rectifier VDU-506. Hardfacing modes were: descending volt-ampere characteristic, current 160–170 A, voltage 30–32 V, inverse polarity.

The composition of the studied electrode materials is shown in Table 1. The microstructure of applied coatings was studied by the method of electron microscopy using electron microscope Carl Zeiss EVO 40XVP in the mode of electron backscatter diffraction (EBSD). The element composition of the structural components of coatings was studied by the method of energy-dispersive X-ray spectroscopy (EDS) using the spectrometer INCA ENERGY 350. The hardness of the obtained coatings was determined by the Rockwell method (scale C) with the use of the hardness meter TK-2M. To establish the ability of the coatings for deformation strengthening, the indentation of the coatings with the hard-alloyed ball of 10 mm in diameter at the load of 29.4 kN was carried out with the use of Brinell press by measuring hardness in the deformed areas. Distribution of stresses and deformations during the indentation infiltration was calculated using the procedure proposed in paper [11]. Microhardness of coatings in the zone of the thermal influence was determined with the use of the microhardness meter PMT-3, equipped with the digital camera-eyepiece oTREK UCMOS 5100 at the load of the indenter of 200 gr. Wear resistance of coatings was determined in accordance with the ASTM standard by the scheme of friction of a rubber roller on the samples in the medium of quartz sand. The calculation of phase equilibrium in the multi-component system was performed based on a database of the thermodynamic function of phases, created with the use of the data given in paper [12]. The temperature-concentration dependences of free energy of the system were determined using the software module of Gibbs energy module system version 5.2. The character of the formation of the phase composition under non-equilibrium conditions was established using the software module TC DICTRA and the MOB2 database.

Table 1

| No. of sample | Fe  | Mn  | C   | Si  | Nb | Ti | Mo |
|---------------|-----|-----|-----|-----|----|----|----|
| E1            | 77.2| 17.6| 1.2 | 4.0 | –  | –  | –  |
| E2            | 68.08| 18.30| 2.37| 4.22| 7.03| –  | –  |
| E3            | 68.71| 19.74| 2.61| 4.56| –  | 4.38| –  |
| E4            | 67.46| 18.54| 1.96| 4.28| –  | 7.76| –  |

To conduct the comparative analysis of the properties of the research materials and the serial ones, the electrodes for impact-resistant hardfacing based on high-manganese steel, produced by Lastek (Belgium) – Lastek 22 and ESAB (Sweden) – OK 86.28 (OK 14MnNi), were selected.

5. Results of studying the composition, structure, and properties of electric arc coatings of the high-manganese steel – TiC (NbC) system

5.1. Formation of the phase composition of alloys based on high-manganese steel under non-equilibrium conditions

In a general case, when applying coatings based on high-manganese alloys, it is necessary to ensure the existence of the non-equilibrium structure of manganese austenite. According to the calculated polythermal section of the Fe–Mn–Si–C system on the line FeMn0.22Si0.05 – C, which corresponds to the ratio FeMnSi in the experimental alloy E1, it can be seen in Fig. 1 that under the equilibrium conditions, a single-phase austenite structure is not a stable phase at temperatures below 800 K. According to this temperature, depending on the concentration of carbon, the stable phases are austenite (A), ferrite (F), carbide phase of cementite type (M(C), higher carbide phases of the M2C2 and M2C3 types, Cr, Mo, V carbonide (SiC). An increase in the content of C in the alloys of this system leads to a decrease of the stability of austenite and, consequently, to narrowing the single-phase austenite area and areas of its coexistence with other phases. Analysis of the diagram shows that in order to create impact-resistant coatings, carbon dioxide content in coatings should be in range I (Fig. 1). This is due to the fact that the increase in the carbon content of more than 2.1 % leads to the eutectic reaction of the type: L → A+M2C, the product of which is the brittle eutectics of the rod type, and at the content of C of less than 1 %, there is a decrease in the energy of packaging defects that are necessary to ensure the deforma-tion strengthening by the twinning mechanism characteris-tic of TWIP steels [13].
Analysis of calculated equilibrium content of phases (Fig. 2, a) and the element composition of austenite (Fig. 2, b) in the process of cooling the alloy of E1 composition shows that the alloy crystallization starts with the crystallization of austenite at temperature of ~1,600 K, which takes place in a narrow temperature range of ~50 K. After the completion of crystallization, there is a fairly wide (~1,500–1,220 K) temperature range of the existence of austenite, the composition of which is most favorable to ensure impact resistance. Further cooling below 1,220 K leads to the beginning of the release of cementite, the number of which reaches ~20 vol. % at 800 K. The process of cementite release is accompanied by a decrease in the number of Mn in austenite by 4 % by weight. In parallel with the cement formation at the temperature of ~900 K, there begins an intensive ferrite release from austenite, in this case, the amount of ferrite reaches 60 vol. % at the temperature of 800 K. Thus, the equilibrium phase composition of the E1 alloy at the temperature of 800 K and below does not imply the ability to deformation strengthening due to significant reduction in the amount of dissolved carbon in austenite and the existence of the significant amount of ferrite and cementite.

The formation of the phase composition of electric arc coatings occurs under non-equilibrium conditions due to a high rate of cooling of the surface layer. In this case, the phase composition will be determined by the degree of completeness of the diffusion redistribution of elements. The temperature mode of cooling of the face-hardening metal to the full extent corresponds to the heat treatment, which involves heating above critical points and further cooling by air. Under these conditions, the cooling rate is within 0.1–10 K/s. That is why to establish the maximum possible amount of cementite, which can be formed at the application of electric arc coatings, the kinetics of cementite release in the range of 920–1,220 K was calculated at the cooling rate of 0.1 K/s. The results of modeling show that under such conditions the amount of cementite in the system will make up 0.19 % by mass. Taking into consideration the morphological features of cementite release in high-manganese steel and the results of calculation of diffusion redistribution of chemical elements (Fig. 3), it can be concluded that at the cooling rate of 0.1 K/s along the boundaries of austenite grains, a layer of cementite (Fe, Mn) C of the thickness of 0.1 microns, and depletion of austenite by carbon and manganese will take place only in a thin (0.2 microns) diffusion layer. Such character of redistribution of elements almost will not affect the properties of austenite. That is why under the actual conditions of the application of electric arc coatings of the proposed composition, the ability of the coating to deformation strengthening will be almost fully preserved.

The influence of TiC and NbC additives on the phase composition of high-manganese steel

Analysis of temperature dependences of the quantitative phase composition of alloys E2 and E3, corresponding to the Fe–Mn–Nb–Si–C and Fe–Mn–Ti–Si–C systems (Fig. 4), shows that they are almost identical. In both cases, crystallization begins with the release of MC-type carbide (NbC or TiC) at ~2,400 K and finishes at ~1,500 K. In the solid state, it has no noticeable transformations and its number is at ~8–9 vol. %. This suggests that NbC and TiC carbides demonstrate high thermodynamic stability in the interaction with high-manganese steel in the liquid and solid state, so they do not actually affect its chemical and phase composition.
5.3. The structure of coatings of the system high-manganese steel – TiC (NbC)

Analysis of the microstructure and distribution of chemical elements in the coating of the Fe–Mn–Nb–Si–C system (Fig. 5) shows that the coating is a steel layer with the high and uniform content of manganese, in which dispersed (dimensions of 1–2 μm) inclusions of the carbide phase (NbC) in the form of faceted grains of the shape that is close to the cubic are evenly distributed. This is evidenced by the existence of a white phase with a faceted shape (Fig. 5, a) and the existence of the local areas of enriched Nb, which are highlighted on the distribution map by dark color (Fig. 5, b). The fusion zone is characterized by a smooth change in the Mn concentration, which indicates the presence of the diffusion zone and implies a strong bonds between the coating and the base. At the boundary with the base, there is a thin (~10 μm) layer with a needle structure, which is typical of the coatings, the application of which is accompanied by intense heat removal [14]. The microstructure areas are enriched by Ti (highlighted dark on the distribution map (Fig. 6, c) that correspond to the carbide phase have distinct contours that indicate low mutual solubility of carbide phase and steel. The microstructure areas are enriched by Ti (highlighted dark on the distribution map (Fig. 6, c) that correspond to the carbide phase have distinct contours that indicate low mutual solubility of carbide phase and steel. The microstructure areas are enriched by Ti (highlighted dark on the distribution map (Fig. 6, c) that correspond to the carbide phase have distinct contours that indicate low mutual solubility of carbide phase and steel. The microstructure areas are enriched by Ti (highlighted dark on the distribution map (Fig. 6, c) that correspond to the carbide phase have distinct contours that indicate low mutual solubility of carbide phase and steel. 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The microstructure areas are enriched by Ti (highlighted dark on the distribution map (Fig. 6, c) that correspond to the carbide phase have distinct contours that indicate low mutual solubility of carbide phase and steel.

Thus, the two-phase layer of the alloy is found during the electric arc application of coatings of the system of high-manganese steel – NbC (TiC) after cooling the surface layer. This condition corresponds to the A+MC areas of the corresponding diagrams of phase equilibrium in the temperature range (~1,300–1,500 K).

5.4. Properties of coatings of the system of high manganese steel – TiC (NbC)

Comparative analysis of hardness and wear resistance of coatings E1, E2 and E3 with serial coatings based on high-manganese steel produced by Lastek (Belgium) and ESAB (Sweden) (Fig. 7) shows that the use of ferro silico-manganese (E1 material) in the charge enables obtaining the coating with almost similar level of properties. Additional alloying of the charge with Ti and Nb carbides leads to a significant increase in hardness both in the welded (12–13 HRC), and deformed state (6–8 HRC). This increase in hardness due to the appearance of carbide phases in the structure leads to a natural increase in abrasive wear resistance by 1.6–1.8 times. An increase in hardness and wear resistance when adding NbC is more expressive than when adding TiC, even though the hardness of TiC is higher by 6 GPa.

Such an increase in hardness of coatings is caused by the fact that faceted carbide grains act as stress concentrators in the process of plastic deformation of the surface layer, which leads to the intensification of deformation strengthening. During abrasive wear, carbide grains block submerging the abrasive particles into the surface and inhibit the micro-cutting processes due to their high micro-hardness of >20 GPa.
6. Discussion of results of studying the character of the formation of phase composition, structure, and properties of electric arc coatings of the system of high-manganese steel – TiC (NbC)

An important advantage of the developed electrode materials of the Fe–Mn–Ti (Nb)–Si–C system over the existing ones is that they combine abrasive wear resistance and the ability to intensive deformation strengthening. This is accomplished by the fact that their phase composition includes metastable manganese austenite and carbide phases with high microhardness.

The reason for the existence in the hardfacing layer of a large amount of metastable austenite phase, capable of cold hardening, instead of equilibrium ferrite-carbide structure of the alloy into the equilibrium state. In addition, the deformation strengthening up to its full loss, due to the transition of the alloy into the equilibrium state. In addition, the application of the developed coatings is irrational in chemically active aggressive media.

Given the high level of abrasive resistance along with the ability to deformation strengthening, the proposed electrode materials can be successfully applied to replace the serial materials of the Fe–Mn–C system. The main areas for their application are the working surfaces of the digging equipment, crushing equipment, as well as parts of coal combine and drilling equipment.

The obtained results are based on the study of the interaction of high-manganese alloys with refractory carbides when obtaining ceramic composites. Their analysis shows that the electric-arc coatings of the Fe–Mn–Ti(Nb)–Si–C system are also characterized by the composite structure, where the role of the matrix is performed by manganese austenite, and the role of strengthening inclusions is played by the MC-type carbides. This structure makes it possible to ensure an increase in operational indicators by combining the dispersion and deformation mechanism of strengthening the surface layer.

A further increase in the properties of electric-arc coatings based on high-manganese steel implies alloying by several carbides at the same time allowing for the formation of inclusions of complex carbides of MC types with increased microhardness in the structure of steel. At the same time, the combination of carbides of transition metals of the IV–VI group of the periodic system of elements, such as Mo2C, WC, VC and others are promising for alloying high-manganese steel.

7. Conclusions

1. Conditions of coating cooling of at electric arc welding ensure the existence of almost completely single-phase austenite structure due to the impossibility of intensive diffusion redistribution of carbon. The amount of cementite that can be released from austenite at cooling is ≤0.19 % by weight and the thickness of the corresponding carbide layer is 0.1 microns. Such amount of cementite is insufficient to influence the ability of austenite to deformation strengthening.

2. The additives of Nb and Ti carbides in the amount of ~9 vol. % to high-manganese steel do not significantly affect the nature of phase transformations associated with the austenite phase. The carbide phase of the MC type crystallizes at 2,400 K and does not undergo any transformations in solid phase under equilibrium and non-equilibrium conditions, showing high thermodynamic stability.

3. The microstructure of coatings of the alloying the Fe–Mn–Ti(Nb)–Si–C system is a layer of manganese austenite, in which carbide inclusions of dimensions of up to 2 µm are evenly distributed. They have a faceted shape (close to the cubic one), and their amount is ~9 vol. %.

4. Alloying the coatings based on high-manganese steel by Nb and Ti carbides allowing for the formation of ~9 vol. % of carbides of the MC type leads to an increase in hardness after welding (by 50 %) and after cold plastic deformation (by 15 %) compared to serial materials for hardfacing the Fe–Mn–C system. At the same time, the abrasive wear resistance of coatings with the structure of austenite +MC is by 1.6–1.8 times higher than that of the coatings with the single-phase austenite structure in the non-deformed state.
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