

This paper reports a study into the formation of the phase composition, structure, and properties of arc welding coatings by the flux-cored electrode materials from the Fe-Mo-B-C system. The welding alloys were applied using the flux-cored arc welding (FCAW) electrodes, which consisted of a shell made from the low-carbon steel filled with a reaction powder mixture that contained boron carbide and molybdenum in a ratio of 1:1.

The calculation of the phase composition of alloys that correspond to the surfaced layers by a CALPHAD method using the Thermo-Calc OpenCalphad software shows that under the equilibrium conditions the boride phases of molybdenum and ferrite cannot co-exist. The main phase of such alloys is a FeMo_2B_2 compound, which forms the eutectics with austenite. Given that the eutectic structures with borides are characterized by high brittleness, the introduction of components was conducted in the form of a reaction mixture in order to obtain the in situ formed boride phases in the form of separate structural components.

Analysis of the results of studying the microstructure and phase composition of coatings reveals that they consist of three main structural components: the eutectic (FeMo_2B_2 +ferrite) and the grains of molybdenum tetraboride MoB_4 . Thus, under the conditions of arc welding using the reaction mixture, an irregular structure is formed, which is favorable in terms of ensuring wear resistance due to the high microhardness of $\text{MoB}_4 > 27$ GPa.

The hardness of the coatings obtained is at the level of 63–65 HRC, and the wear resistance is higher compared to standard high-chromium alloys (grades T620 and T590) by 2–2.5 times. This makes it possible to recommend the coating of a given system for hardfacing the working surfaces of equipment in the coal, processing, woodworking industries, etc., where abrasive wear is the dominant type of surface wear

Keywords: powder wire, hardfacing, molybdenum borides, reaction synthesis, abrasive wear

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IN SITU FORMATION OF MOLYBDENUM BORIDES AT HARDFACING BY ARC WELDING WITH FLUX-CORED WIRES CONTAINING A REACTION MIXTURE OF $\text{B}_4\text{C}/\text{MO}$

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1. Introduction

Molybdenum borides (MoB_3 , $\text{Mo}_{1-x}\text{B}_3$, MoB_4 , Mo_2B_5 , MoB , MoB_2) are a group of superhard materials that are

promising in the application of wear-resistant coatings through a combination of hardness and ductility. According to data from the theoretical and experimental studies, the estimated chemical hardness and hardness at nano

indentation for the Mo borides are in the range from 26 to 38 GPa.

In addition, the compounds of molybdenum are characterized by the complete wetting by metals from the group of iron while the dissolution of Mo in small quantities contributes to the increased mechanical properties and heat treatment conditions for the low-carbon steels alloyed by boron [3].

Such a set of properties in the molybdenum borides makes them promising materials for the application of coatings intended for operation in an abrasive environment where the presence of dynamic loads is allowed. This is especially relevant for the working surfaces of equipment in the woodworking, brick and coal industries, earth digging equipment, etc.

The main factor that inhibits the obtaining of coatings based on the alloys of iron and molybdenum borides in the form of separate inclusions, similar to hardfacing alloys the Fe-Cr-C and Fe-W-C systems, is their low thermodynamic stability in the systems with iron. This is evidenced by the data given in work [4] that reports a study into the structure and equilibrium phase composition of alloys from the Fe-Mo-B system in a wide range of concentrations of B and Mo (to 32 and 34 at. %, respectively). The results from X-ray phase analysis and microscopic studies found no structure of the alloys of the Mo_xB_y type compounds over the entire concentration range. In this case, the main indicated phase of these alloys was a FeMo_2B_2 compound, which is mainly included in the composition of the ternary eutectics with Fe_2B and austenite.

Thus, the formation of Mo_xB_y in the iron-based coatings is possible only when using such application techniques that would provide for a composite-like structure. Among them, a promising method is the flux-cored arc welding (FCAW) by electrodes filled with a powder mixture of $\text{Me}+\text{B}_4\text{C}$, which was used previously for the *in situ* formation in the surface layer of TiB_2 and TiC [5].

The high microhardness of molybdenum borides and their positive influence (at a slight dissolution) on the properties of steels make their application promising as the components of hardfacing materials. The study of such materials implies the development of new wear-resistant coatings with a composite structure, which is relevant for materials science and tribology.

2. Literature review and problem statement

Among the compounds of refractory metals, obtained *in situ* from the powder mixtures of $\text{Me}+\text{B}_4\text{C}$, the Ti- B_4C system has remained the most studied one until now. The result of the components' interaction in the specified system comes down to obtaining the grains of TiB_2 and TiC in pure form or in the form of inclusions in the matrix from the selected alloy. Paper [6] demonstrated the possibility of forming a surface layer, strengthened *in situ* by the particles of TiB_2 and TiC during a reaction welding by friction at stirring by adding B_4C to the weld zone. The hardness of the titanium alloy after such treatment increases by almost 2 times. TiB_2 and TiC , synthesized *in situ*, were also found at the laser cladding of coatings from a mixture of Ni, Cr, Ti powders and B_4C . The coating has a distinct heterophase structure and a microhardness of ~12 GPa [7]. The similar character of the formation of titanium compounds is also observed

at the electric arc deposition of coatings by a non-fusible (tungsten) electrode of the preliminary applied Ti and B_4C mixtures with a different component ratio (5:1, 3:1, and 3:2) [8]. In this case, the ratio of the components does not affect the fundamental possibility of the formation of titanium compounds but only the quality of the bonding between the coating and the base. The bond quality between the coating and the base is improved while increasing the Ti content and the abrasion resistance is naturally increased by increasing the B_4C content. Study [9] investigated composites with a titanium matrix produced by a hot-pressing method from a mixture of fine powders TiC and TiB_2 and obtained *in situ* from the reaction mixture of Ti and B_4C . It is important to note that the comparative analysis of the composites' properties, obtained at the same phase ratio, shows that the abrasive durability of composites, obtained *in situ*, is higher by ~1.5 times.

Other refractory metals (except Ti) in the mixtures with boron carbide are used primarily to produce the composites and pure compounds *in situ*. The authors of [10] obtained ZrB_2 , ZrC , and a ternary boride phase of ZrCo_3B_2 from a mixture of powders of Co, Zr, and B_4C by the method of reaction combustion synthesis at the temperatures of ~1,200 °C. The results of the X-ray phase analysis revealed no traces of the starting B_4C among the products of interaction, indicating the completeness of the reaction course. Similarly, the course of the self-propagating high-temperature synthesis in the Cu-Zr-B-C system produced the particles of ZrB_2 and ZrC in the copper matrix [11]. The *in situ* formed VB_2 and $(\text{Ti,V})\text{B}_2$ were found by the authors of [12] when obtaining the B_4C -based composites, by the hot-pressing method involving the powders of B_4C , TiH_2 , and VC at 2,200 °C. In [13], VB_x and VC were obtained in the structure of coatings with a microhardness of ~12 GPa, due to the interaction between ferrovandium and B_4C . The authors of [14] investigated the influence exerted by adding Nb and B_4C in the same quantity (~5 %) on the structure and wear resistance of coatings made from high-chromium Fe alloys obtained by laser cladding. The results showed that only the carbide phase of Nb forms in the interaction between Nb and B_4C , and, instead of the predicted NbB_2 phase, a Fe_2B -based phase is formed.

There are no literary data on using the Mo- B_4C system in a pure form for arc welding coatings. According to [14], when obtaining coatings from the Fe-Ti-Mo-B-C system by using a method of the laser application of a mixture of powders of ferroalloys and B_4C an increase in the Mo content results in a significant refinement of the grain structure. When one increases the content of Mo up to ~8 % of weight the grain sizes of $(\text{Ti, Mo})\text{B}_2$ and $(\text{Ti, Mo})\text{C}$ are reduced from ~100 to ~10 μm , while the coating hardness increases from 900 to 1,300 HV. One of the arguments confirming the possibility of the formation of molybdenum borides of various composition from the reaction mixture of $\text{Mo}+\text{B}_4\text{C}$ is given in work [15], which shows the fundamental possibility of obtaining a series of Mo_xB_y compounds by heating the $\text{Mo}/\text{B}_4\text{C}$ mixture over a temperature range of 1,273–1,673 K.

Our analysis of the scientific literature reveals that the main issue in the formation of coatings based on iron strengthened by Mo_xB_y in the form of separated inclusions, similar to TiB_2 [6–9], is the interaction within the Fe- Mo_xB_y system. Its result is the formation of a FeMo_2B_2 phase, which is part of the eutectics with iron, thereby forming a structure that is not optimal in terms of wear resistance,

compared to composite [11–13]. Therefore, the conventional methods of hardfacing involving electrode materials in the form of master alloys or ferroalloys, which imply the complete melting and recrystallization of the alloy, are not rational for coatings from the Fe-Mo_xB_y system. A composite structure can be obtained, in particular, by combining the *in situ* formation and arc welding implying the use of the reaction mixtures of Mo and B₄C. Under such conditions, given the high rate of the structure-forming processes, the interaction degree in the Fe-Mo_xB_y system is considerably minimized and, accordingly, the diffusion interaction, which is undesirable for such coatings, slows down. In addition, the hardness and wear resistance of the coatings containing hard refractory compounds synthesized *in situ*, are substantially higher compared to conventional coatings based on the alloys from the Fe-Cr(B)-C system. The abrasion resistance of the composites containing the *in situ* formed compounds is substantially higher compared with the composites of a similar phase composition obtained with the use of ready-made compounds. This predetermines the development of new chromium-free materials for hardfacing with the relatively high hardness, crack resistance, and cyclic stability, which could be applied by electric arc methods based on simple technology.

3. The aim and objectives of the study

The aim of this study was to develop new flux-cored electrode materials for hardfacing by arc welding based on the Fe-Mo-B-C alloying system by using the Mo/B₄C reaction mixture intended for the *in situ* formation of molybdenum compounds with boron with enhanced microhardness.

To accomplish the aim, the following tasks have been set:

- to assess, by using the Fe-Mo-B-C system thermodynamic analysis, the phase composition of alloys in the concentration and temperature ranges that correspond to the formation of FCAW coatings from the Mo/B₄C mixtures;
- to establish the phase composition, structure, and mechanism of the structure formation of a surface layer at FCAW with a reaction mixture of Mo/B₄C;
- to determine the hardness and wear resistance of coatings and provide practical recommendations regarding their use.

4. The materials and procedure to study the structure and properties of arc welding coatings applied by electrodes with a reaction mixture of Mo/B₄C

The flux-cored electrodes were fabricated at a machine designed at the Institute of Electric Welding named after Paton in the form of single-core powder wire made from the low-carbon steel of brand 08kp GOST 3559-75, filled with a mixture of the powders of Mo (grade MPCh) and B₄C (brand 2V ISO 9001:2008) with an average particle size of ~5 and ~20 μm, respectively. The powders of Mo and B₄C were blended in a drum mixer of inertial type at ratio 4:1 for 24 hours. Upon mixing, the mixture was plasticized using a solution of pulver bakelite in alcohol. Next, the mixture was dried at 150–200 °C for 2 hours; it was granulated by rubbing through a sieve with a size cell of 1 mm. To improve the technological properties of the arc welding process (the arc protection from the atmosphere, the stability of arc

burning), the mixture was additionally supplemented with rutile (TiO₂) and fluoride calcium (CaF₂) in the proportion 1:2 and in the amount of 20 % of the mixture mass. The fill factor of the ready-made flux-cored electrodes (the ratio of a charge weight to the weight of an electrode) was at the level of 0.4. Thus, the calculated elemental composition of the surface layer was as follows, % by weight: Mo – 35 %; B – 4 %; C – 1 %. Arc welding was performed at a direct current of reverse polarity (the current magnitude is 160 A, voltage – 30 V).

The phase structure of coatings was determined based on the method of X-ray diffraction (XRD) phase analysis using the diffractometer DRON-3M in filtered CuK_α radiation. The microstructure of coatings was determined by the method of scanning electron microscopy (SEM); the distribution of chemical elements in the structural components – by the method of energy dispersion X-ray spectroscopy (EDS) using the electron microscope Carl Zeiss EVO 40XVP, equipped with the spectrometer INCA ENERGY 350. The grain sizes were determined according to the procedure described in work [16]. The macro hardness of coatings was determined by the Rockwell method (scale C); the microhardness – by the Vickers method while loading the indenter with 50 g. The wear resistance of coatings was determined by rubbing the cylindrical samples against a monolithic abrasive (carborundum grinding wheel) at a load of 5 kN, a slide speed of 3 m/s, and a friction path of 500 m. For a comparative analysis of the properties of the examined materials and standard ones, we selected electrode materials from the Fe-Cr-C-B and Fe-Cr-C-B-Ti systems of brands T520 and T690, produced by the Institute of Electric Welding named after Paton.

The thermodynamic analysis of the phase equilibrium in the Fe-Mo-B-C system's polythermal cross-sections, corresponding to the coatings' composition, was performed using the Thermo-Calc and OpenCalphad software [17]. The modeling was carried out by extrapolating the thermodynamic functions of the lower order systems, specifically Fe-Mo-C [18], Fe-B-C [19], Fe-Mo-B [4], as well as the data given in work [20].

5. Results of studying the formation of the structure of arc welding coatings from flux-cored electrodes with a reaction mixture of Mo/B₄C

5.1. Thermodynamic analysis of alloys enriched with iron from the Fe-Mo-B-C system

The polythermal cross-section of Fe-Mo-B-C (Fig. 1, a) in a concentration range that is typical for alloys from the Fe+B₄C system, which can be obtained by arc welding with flux-cored electrodes, belongs to the eutectic type. The stable phases in a given system are as follows: melt (L), compound FeMo₂B₂ (τ), the high- and low-temperature ferrite (F and F^{HT}), austenite (A), the lower iron boride (Fe₂B), and cementite (Cem). The compound τ is a dominant phase of the examined alloys; it is a part of all alloys containing Fe-MoBC_{0,25} from 0 to 30 at. % only in the form of the eutectic with austenitic, or in a pure form. The full-eutectic structure corresponds to composition ~10 at. % and temperature ~ 1500 K. The crystallization process of a typical hypo-eutectic alloy (Fig. 1, b) begins with the crystallization of high-temperature ferrite and its subsequent transformation to austenite. It exists in equilibrium with a melt

to a temperature of ~1,500 K, at which a eutectic decay of the melt occurs according to the following scheme: $L \rightarrow A + \tau$. Such eutectics exist in equilibrium with the melt to a temperature of 1,400 K, at which the formation of the ternary eutectics $A + \tau + Fe_2B$ occurs. This structure is stable over a sufficiently wide temperature range up to the temperatures of 1,100 and 1,000 K, at which austenite transforms to ferrite followed by its eutectic decay, respectively. The eutectic decomposition of austenite is accompanied by the disappearance of the Fe_2B phase.

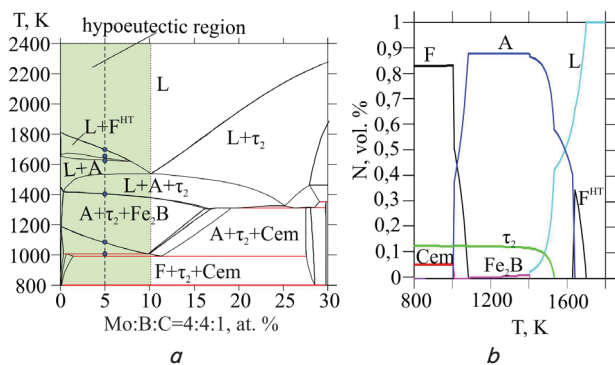


Fig. 1. Results of calculating the phase equilibrium of the Fe–Mo–B–C system over the following range: *a* – a fragment of the polythermal cross-section of the Fe–Mo–B–C system for alloys enriched with iron along the Fe–MoBC_{0,25} line; *b* – temperature dependence of the equilibrium amount of phases of a typical hypo-eutectic alloy

Consequently, the equilibrium structure of the hypo-eutectic alloys in the Fe–MoBC_{0,25} system consists of the eutectic F+ τ (at the moment of formation of A+ τ), the eutectoid (F+Cem), and ferrite F. Because of the τ phase, Mo borides are not stable over the entire considered range of concentrations, so it is impossible to obtain, when using the traditional methods of arc welding, a structure with the inclusion of molybdenum borides in the ferrite or austenite matrices.

5.2. The structure and phase composition of arc welding coatings of the Fe–Mo–B–C system obtained from the reaction mixture of B₄C/Mo

An analysis of the microstructure of a surface layer obtained by FCAW using the electrodes with a powder mixture of B₄C/Mo (Fig. 2, *a*) shows that it has a heterophase structure. The main structural components of the coating are the faceted grains with a cross-section of the triangular, rectangular, hexagonal shape, the lamellar eutectics that surrounds the specified grains, and a single-phase alloy matrix. The shape of the grains' cross-sections is typical for the compounds forming a hexagonal syngonium. The morphological features of the eutectic correspond to the eutectic (FeMo₂B₂+austenite) identified in study [4] in the Fe–Mo–B alloys. Based on the results of XRD phase analysis, three main phases were identified:

Mo₃B_{0,91} with a hexagonal lattice, low-temperature ferrite, and FeMo₂B₂. the phases' lattice parameters are as follows: Mo₃B_{0,91} – $a=5.317$ and $c=6.103$ Å–(P6₃/mmc space group); ferrite – $a=2.842$ Å (Im-3m space group); FeMo₂B₂ – $a=5.76$ and $c=3.198$ Å (P4/m3m space group). In addition, minor traces of cementite were found, as well as of the Fe₂B and Mo₂CB compounds. An analysis of the distribution of chemical elements over the area (Fig. 3) shows that the faceted grains (white phase) contain both a high content of Mo and B in the almost complete absence of Fe traces. This, together with the results of XRD phase analysis, and the analysis of the grains' shapes, makes it possible to identify the specified phase as molybdenum tetraboride MoB₄. The eutectics around the MoB₄ grains contain the high content of Fe, Mo, and B at the same time. Taking into consideration the nature of the phase equilibrium in the Fe–Mo–B–C system and the results from XRD phase analysis, it is a eutectic mixture of FeMo₂B₂ (τ) and ferrite. The matrix of the alloy is ferrite with the increased lattice parameter due to the dissolution of Mo and C.

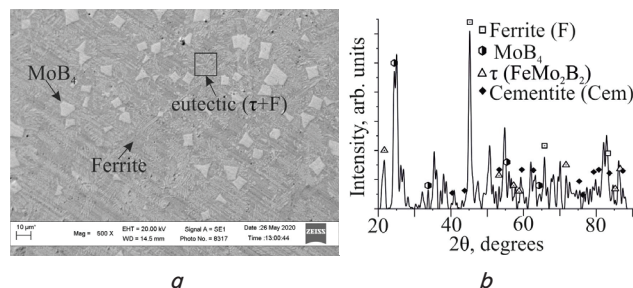


Fig. 2. Results from an analysis of the structure and phase composition of a coating with electrodes with the reaction mixture of B₄C/Mo: *a* – the microstructure of a surface layer (x500); *b* – X-ray diffraction pattern of the coating

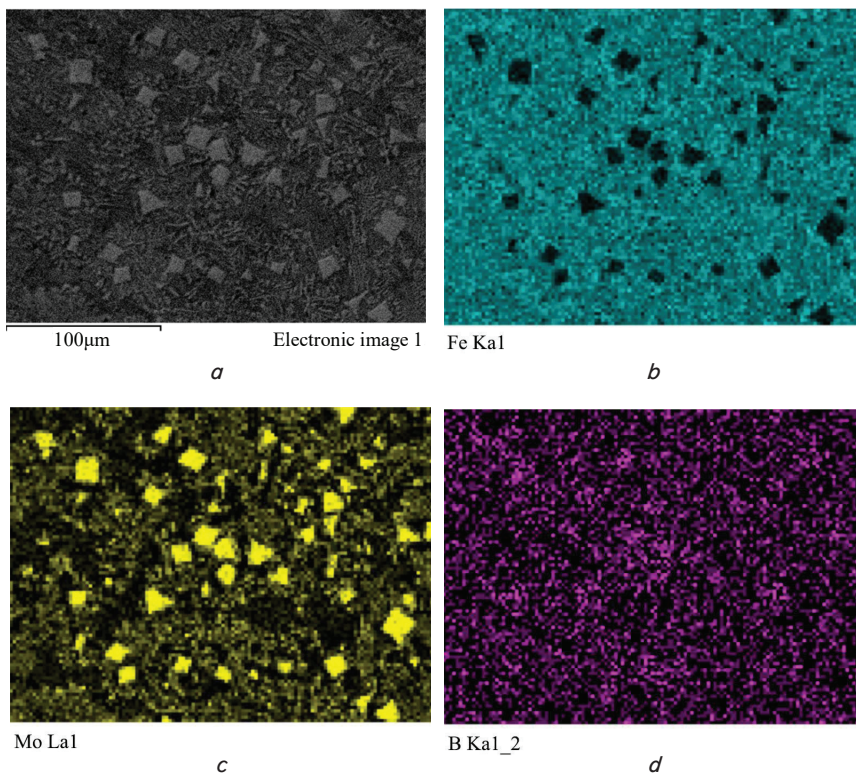


Fig. 3. Results of EDS analysis of the coating of the Fe–Mo–B–C system: *a* – the area of analysis; *b* – the distribution of Fe; *c* – the distribution of Mo; *d* – the distribution of B

The presence of ferrite in the form of a separate structural component (matrix) of the coating assumes the presence of a ductility reserve, and, consequently, promotes the increase of its impact stability.

5.3. The hardness and wear resistance of FCAW coatings made from flux-cored electrodes filled with a reaction mixture of B_4C/Mo

The results of measuring wear resistance of the obtained coatings show that their resistance when rubbing against a fixed abrasive is substantially (by 2–2.5 times) higher compared with standard high-chromium materials for arc welding (Fig. 4).

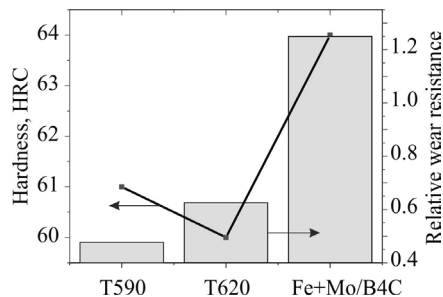


Fig. 4. Results of a comparative analysis of wear resistance of electrode materials with a reaction mixture of B_4C/Mo and standard materials for arc welding

The high wear resistance of the obtained coatings is primarily due to the higher microhardness of molybdenum borides compared to the boride and carbide phases of chromium, as well as a finer eutectic structure and the presence of a ferrite matrix that strongly holds carbide grains.

6. Discussing the results of forming the structure of arc welding coatings from flux-cored electrodes with a reaction mixture of Mo/B_4C

Our generalization of the results of the thermodynamic analysis (Fig. 1), the structure and phase composition (Fig. 2, 3), shows that, when applying coatings of the Fe-Mo/ B_4C system, one observes three main zones: reaction, melting, and solidification (Fig. 5). In the reaction zone, under the influence of an electric arc, there is the reactive combustion synthesis similar to the type of self-propagating high-temperature synthesis, ending by the *in situ* formation of MoB_4 . Given the low thermodynamic stability of Mo carbides, they do not form under these conditions, the free carbon is released instead, which partially interacts with atmospheric oxygen forming CO_2 , which serves as the arc protection function. In the zone of melting, there is a partial dissolution of Mo and B from MoB_4 in iron. This leads to that the melt composition acquires such a concentration that corresponds to the hypo-eutectic alloys (Fig. 1). This leads to that in the next zone of solidification there is the crystallization of phases in the following sequence: high-temperature ferrite, austenite, eutectic (austenite+ $FeMo_2B_2$). Following the process of the eutectic austenite decomposition, the structure consists of three phases: ferrite, $FeMo_2B_2$ and MoB_4 .

The structure, obtained as a result of the proposed process of arc welding, is favorable in terms of ensuring the abrasive wear resistance since it represents an inclusion of

the superhard compound (MoB_4) in a ductile matrix. The materials obtained could be used to replace standard electrode materials from the Fe-Cr-C system for severe operating conditions, in particular, when hardfacing the working surfaces of equipment for mining and processing coal, in the brick industry, earth digging equipment, etc.

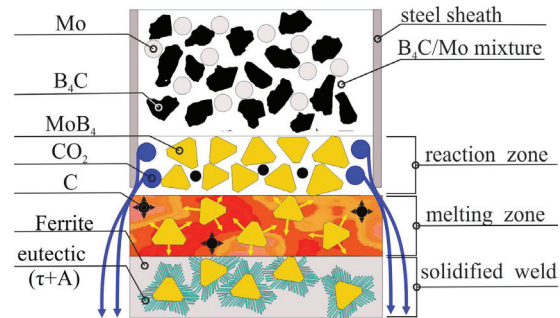


Fig. 5. Schematic formation of a surface layer when welding with flux-cored electrode materials with a reaction mixture of Mo/B_4C

The main restriction for the application of the developed coatings is the inadmissibility of re-melting the applied layer or its operation at elevated temperatures. Such exposure would lead to the transition of the structure into an equilibrium state with the eutectic structure as a result of dissolving the grains of MoB_4 in ferrite. In addition, when applying powders with a reaction mixture, it is necessary to specially prepare the powders, which implies providing for their flowability by introducing polymeric binders.

Further studies need to investigate the impact of other refractory metals that form the solid boride phases, such as Ti, V, Zr in the mixtures with Mo and B_4C . The main difficulty in the subsequent development of such coatings is the complete elimination of the ferrite-boride eutectics by rationally selecting the composition of powdered mixtures (starting reagents).

7. Conclusions

1. Based on the calculated polythermal cross-section of alloys in the Fe-Mo-B-C system along the Fe- $MoBC_{0.25}$ line, the main structural component of such alloys, which ensures wear resistance, is the eutectics ferrite+ $FeMo_2B_2$. Dissolving molybdenum borides in ferrite under conditions of arc welding leads to the formation, in a surface layer, of the hypo-eutectic alloy structures.

2. When applying coatings of the Fe-Mo-B-C system by the method of FCAW using flux-cored electrode materials containing a reaction mixture of B_4C/Mo , there is the *in situ* formation of the inclusions of a metastable superhard phase of MoB_4 . Its morphology represents the uniformly spaced faceted grains, which coexist with the pre-eutectic alloys, rich in iron, of the Fe-Mo-B-C system.

3. The hardness of coatings made from flux-cored electrodes containing the *in situ* formed MoB_4 is at the level of 63–65 HRC. Their wear resistance, when rubbed against a monolithic abrasive, exceeds the wear resistance of standard alloys from the Fe-Cr-C and Fe-Cr-B-C systems by 2–2.5 times. Such coatings are recommended for use when hardfacing parts operated under the conditions of enhanced abrasive wear, in particular in the coal mining, brick, and processing industries.

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