Proceedings of BALTTRIB’2024 edited by prof. J. Padgurskas
eISSN 2424-5089 (Online)

DOI: 10.15544/balttrib.2024.17

FORMATION OF WEAR- AND CORROSION-RESISTANT ARC SPRAY COATINGS FROM CORED WIRES

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Abstract. The two possible ways of improving the functional properties of arc spray coatings from cored wires (CWs) were analyzed. The first of them is associated with the addition of borax and boron oxide to the charge of CW 90Cr17B2MnSi to increase the homogeneity of the coating, and the second one – with the use of a technological factor of influence, such as the supersonic spraying mode using the increased pressure of the metal-air flow. The microhardness, structural and phase analysis, abrasive wear resistance under the conditions of rigidly fixed abrasive and corrosion resistance in 3% NaCl aqueous solution were used to certify the coatings. It was shown that both proposed approaches provide an opportunity to improve the properties of coatings from CWs. In particular, their homogeneity and microhardness, abrasive wear resistance under the conditions of rigidly fixed abrasive and corrosion resistance increased.

Keywords: arc spray coatings, cored wires, wear resistance, corrosion resistance.

1. INTRODUCTION

Arc spray coatings (ASCs) are usually inferior in hardness and wear resistance to coatings synthesized by plasma-electrolyte oxidation [1, 2]. However, the arc spraying method is the cheapest and technologically simplest method of gas thermal spraying, is easily implemented in manufacturing and does not require the expensive equipment. The use of cored wires (CWs) for arc spray coatings (ASCs) allows to use them for the restoration of various worked parts, such as various types of shafts for transport, agricultural machinery and utility purposes, compressors of the food processing industry, operating under conditions of the extreme friction and corrosive-abrasive wear [3–7]. Solid wires made of 40Cr13, 08Cr18Ni10Ti stainless steels are also often used as electrode materials for formation of the corrosion-resistant ASCs, which are relatively expensive and have a low hardness and wear resistance [8, 9]. CWs of the corresponding chemical composition are at least twice as cheap. However, coatings from CWs have increased chemical heterogeneity due to an incomplete fusion of chromium-containing charge and the shell of the unalloyed steel. As a result, galvanic couples appear in ASCs, and such coatings quickly fail due to galvanic corrosion. ASCs from CWs with a shell made of nickel or stainless steel are characterized by high corrosion resistance [10]. However, using a nickel or stainless-steel shell significantly increases the cost and complicates fabrication of CWs. Therefore, the purpose of this work is to increase the corrosion resistance of wear-resistant ASCs from CWs by adding elements to their charge that will contribute to the complete fusion of the charge and the shell and allow to spray the wear-resistant coatings with increased corrosion resistance.

2. EXPERIMENTAL

The shell of CW was made of unalloyed low-carbon steel, and 4 wt.% B_2O_3 or $Na_2B_4O_7$ was added (or not added) to their charge. Coatings made of CW 90Cr17B2MnSi and CW 90Cr6BMnSi were arc

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sprayed with the following parameters: arc voltage – 32 V, current – 150 A, distance from the arc to the specimen – 120 mm. In order to achieve the subsonic and supersonic speeds of the spray air flow, two variants of the air flow pressure were used – 0.6 and 1.2 MPa, respectively. To ensure a high wear resistance of ASC, a mixture of Cr, Ti and boron carbide (B_4C) powders was added to the composition of the CW charge.

To certify the coatings sprayed from the developed CWs, their structure and phase state were investigated, their microhardness and abrasive wear resistance were determined, and their corrosion and electrochemical properties were evaluated. A scanning electron microscope EVO 40XVP was used for metallographic studies. The phase composition of the coatings was studied using a DRON-3 X-ray diffractometer with Cu K_α radiation. The microhardness of the coatings was determined as the average value of 10–15 measurements by an PMT-3 device.

The scheme of the equipment for testing specimens with ASCs for the abrasive wear resistance under the conditions of rigidly fixed abrasive is shown in Figure 1. An electrocorundum disc with a diameter of 150 mm and a width of 8 mm was used, which rotated at a frequency of 2.7 s^{-1}. The load P in the zone of linear contact of the specimen with the disc was kept constant at 14.7 ± 0.25 N, and the path, along which they contacted was 1800 m. The abrasive wear resistance (1/W) of the coating was determined by the weight loss (ΔW) of the specimens after their tests. The value of ΔW was calculated from the difference in the specimen weight before and after its test. The specimens were weighed by a KERN ABJ 220 4M electronic analytical balance with an accuracy of 2×10^{-4} g.

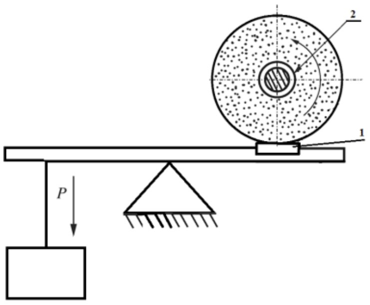


Figure 1. Scheme of equipment for studying abrasive wear resistance of ASC in contact with rigidly fixed abrasive: *1* – specimen; *2* – abrasive electrocorundum wheel; *P* – load

The corrosion-electrochemical properties of ASCs were investigated in 3% NaCl aqueous solution at a temperature of 20 ± 0.2 °C. The characteristics of corrosion processes were determined in the potentiodynamic mode using the SVA-1B-M voltammetric system. The scan rate was 2 mV/s. A three-electrode scheme was used: a working electrode (ASC, sprayed on a substrate made of steel 45), a reference electrode (silver chloride of the EVL-1M1 type), an auxiliary (platinum rod). The corrosion current density (i_{corr}) was determined from the polarization curves, and information on the nature of the corrosion was obtained. For electrochemical studies, a circular working cell with an area of 2 cm^2 was isolated on the surface of each specimen.

3. RESULTS AND DISCUSSION

During spraying of ASC, the CW components (shell and charge components) fused together and formed the coating that was relatively homogeneous in chemical composition. According to the reactions 1, 2 and 3, which proceeded with the release of a large amount of heat (Table 1), chromium and titanium interacted with boron carbide, forming borides and carbides, which were evenly distributed in the volume of the lamellae in the form of nanosized particles (Figure 2). Such dispersive strengthening of lamellae contributed to the increase of microhardness of ASC.

Table 1. Thermal effect of reactions with formation of carbides and borides.

Reactions of formation of carbides and borides	Enthalpy ΔH°_{298} of PW charge, kJ/g	Microhardness of borides ($HV_{0.3}$)
$7\,Cr + 2\,B_4C = 4\,CrB_2 + Cr_3C_2$ (1)	1.0	CrB_2 – 2200, Cr_3C_2 – 1700
$3Ti + B_4C = 2TiB_2 + TiC$ (2)	3.3	TiB_2 – 3500, TiC – 3000
$7Fe + B_4C = 4FeB + Fe_3C$ (3)	1.2	FeB – 1400

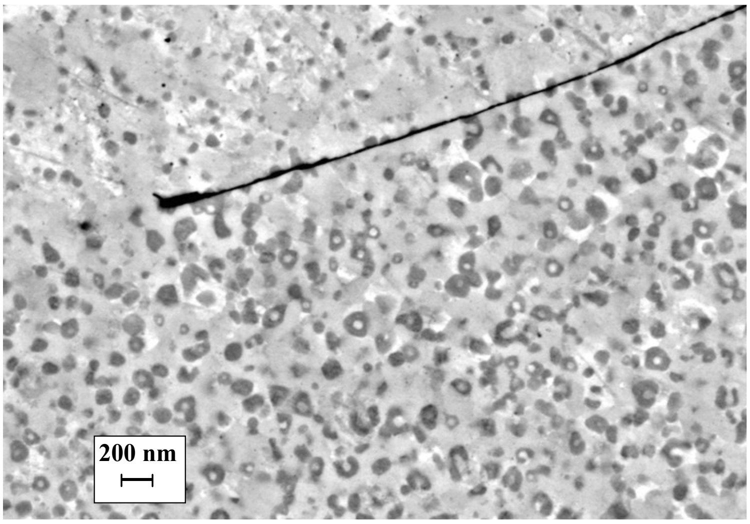


Figure 2. Dispersed particles of carbides and borides inside one of lamellae of coating sprayed from CW 90Cr17B2MnSi

During spraying of coatings, Ti actively interacted with oxygen during flight in the air flow, so a significant part of it did not react with B_4C. The desired hardness of ASC could not be achieved by adding only Cr and B_4C powders to the CW charge. The reaction (1) did not occurred to the full extent, due to which individual particles of B_4C did not take part in the formation of the coating, but, like oxides, were deposited in ASC in the form of the unchanged crystals. They formed protrusions on the polished surface, which became cutting edges, which caused the intensive wear of the counterbody (cast iron, bronze, babbitt) during friction in the coating counterbody tribo-pair.

The refractory oxide films were formed around all particles of the charge up to 150 μm in size. Thus, the melting temperature t_m of different films was, ºC: Cr_2O_3 – 2435, Al_2O_3 – 2050, SiO_2 – 1700, Fe_2O_3 – 1566, Fe_3O_4 – 1538, FeO – 1377. It is clear that such films prevented the fusion of the charge components between each other and the shell.

The analysis of Fe-Mn, Fe-Si, Fe-B, Fe-C state diagrams showed that to increase the activity of the interaction of the components of the charge between each other and the steel shell, it is necessary to add ferrosilicon, ferromanganese or ferrotitanium to the composition of the charge. During the interaction with the iron of the shell or with each other, they are prone to the formation of low-melting eutectics and thus can facilitate the interaction of Cr and B_4C between each other and the steel shell.

In addition, borax ($Na_2B_4O_7$) or boron oxide (B_2O_3) was added to reduce the melting temperature of the oxide films on the surface of the particles of the powder components of the CW charge. In the process of spraying of coatings, borax melted at a temperature of 741ºC and decomposed into sodium metaborate and boron oxide according to the reaction:

$$Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3. \quad (1)$$

Boron oxide interacted with metal oxides (Cr_2O_3 and Fe_2O_3) and formed metaborates ($CrBO_3$ and $FeBO_3$) with a low melting point:

$$B_2O_3 + Fe_2O_3 = 2FeBO_3, \quad (2)$$

$$Cr_2O_3 + B_2O_3 = 2CrBO_3, \quad (3)$$

In particular, for the $FeBO_3$ compound it was 800ºC, and $CrBO_3$ – 780ºC. The sodium metaborate easily neutralized the newly formed metaborates, quickly removing them from the zone of the molten metal, and new active boron oxide molecules took their place.

Due to the high ability of borax to dissolve oxides on the surface of the steel shell and particles of Cr powder, boron carbide interacted much more fully with Cr and Fe shells with the formation of nanosized boride particles (Figure 2). As a result, despite the increase of the microhardness of ASC due to the dispersion hardening of each of the lamellae, the abrasive wear resistance and corrosion resistance of the coating should also increase.

The formation of Fe-B, Fe–Si, Mn–Si, and Fe–Ti eutectics with a low melting temperature contributed to the formation of a low-melting melt, which dissolved the refractory components of the charge (Cr, B_4C, ferrochromium, ferrochromium boron) and the CW shell from inside. Due to the eutectic melting of the charge, it was almost completely fused with the shell to form a homogeneous melt, the dispersed droplets of which formed the coating.

The completeness of fusion of the charge materials between each other and the shell was determined by the value of the coefficient of microheterogeneity (K_{MH}) [11], according to the equation (7):

$$K_{МГ} = \left(\sum_{i=1}^{n} |c_{av} - c_i|\right) / \, n \times c_{av} \tag{4}$$

where n is the number of ASC areas, the composition of which was analyzed by micro-X-ray spectral analysis; c_i is the content of each of the alloying elements within each individual lamella; c_{av} is the average content of a certain element in the coating.

The scheme for determining the K_{MH} is shown in Figure 3. The K_{MH} coefficient characterized the deviation of the concentration of each of the alloying elements in each individual lamella from its average concentration c_{av} in the coating structure determined on 10 areas with an area of 0.5 mm^2 (typical spectrum 1, Figure 3). The local concentration of alloying elements c_i was determined on rectangular areas with an area of $1.2 \cdot 10^{-4}$ mm^2 ($i = 1...n$), which were comparable in size to the average area of the lamellae in the coatings (Figure 3). To determine the K_{MH} of the coatings, at least ten areas were analyzed, which were located at a distance of 5 mm across the spot of the spraying beam, which was 25...30 mm.

Figure 4 shows how K_{MH} changed depending on the content of alloying elements in the CW 90Cr17B2 charge. It is obvious that the addition of FeSi, FeMn, FeTi, FeP powders and eutectic alloy Ni-Cr-B-Si to the composition of the charge of this CW significantly reduced the K_{MH} coefficient, that is, increased the completeness of fusion of the components of the charge with each other and with a steel shell. Thus, at the coefficient $K_{MH} = 0.1$, the content of an element (for example, chromium) in different lamellas of the coating fluctuated within ± 10% of its average content in the coating.

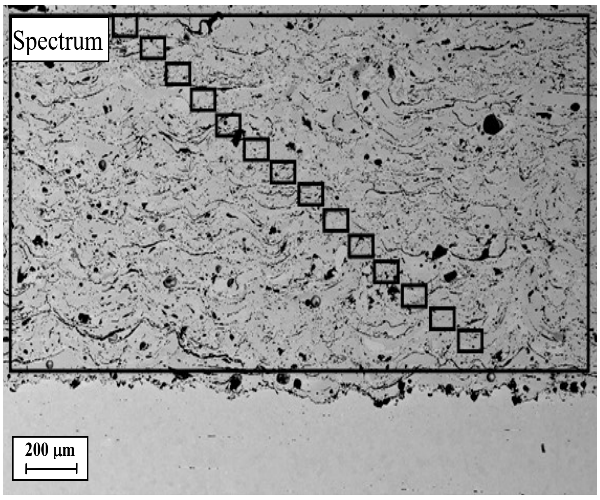


Figure 3. Scheme for determining local content of alloying elements in coating

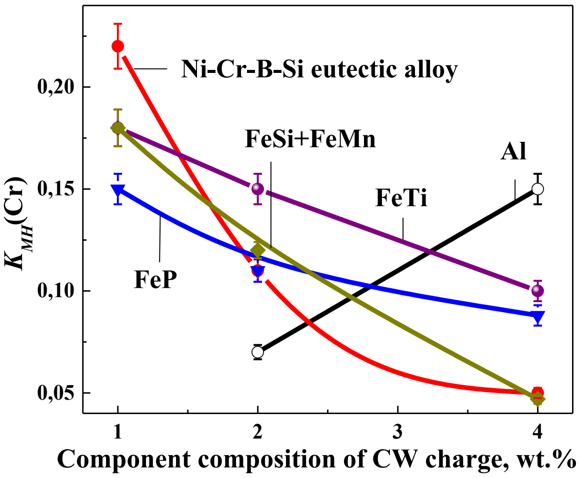
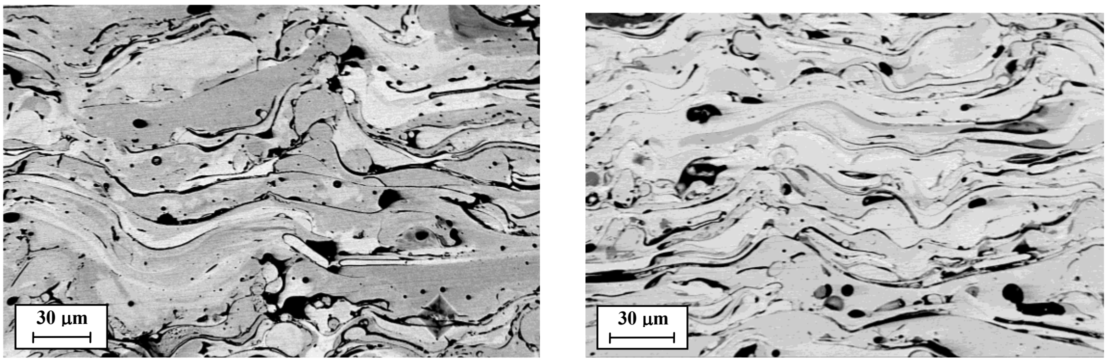


Figure 4. Influence of component composition of CW 90Cr17B2 charge on value of coefficient K_{MH}

The use of a supersonic air flow (at a pressure of 1.2 MPa) during the spraying of coatings made it possible to additionally reduce the size of the lamellae, the number of pores and oxide inclusions in the structure of the coatings (Figure 5).



a) b)

Figure 5. The structure of the CW 90Cr17B2MnSi coating with addition of $Na_2B_4O_7$ borax to its charge, sprayed using subsonic (*a*) and supersonic (*b*) air flow, formed at air pressure of 0.6 and 1.2 MPa, respectively

Table 2. Phase analysis of coatings sprayed from CWs with different content of B and Cr.

Type of CW	Phase composition of coating	Lattice parameter, Å			SG	Microhardness o coating $HV_{0.3}$	Phase conten in coating, wt. %
		a	*b*	*c*			
CW 90Cr17BMnSi	α-Fe martensit	3.4784(8)	3.4784(8)	3.4784(8)	*Fm-3m*	600–700	50
	γ-Fe(Cr)	2.9056(3)	2.9056(3)	2.9056(3)	*Im3m*		25
	$Fe(Cr)_2B$	5.1887(7)	5.1887(7)	4.0277(1)	*I4/mcm*		25
CW 90Cr6BMnSi + $Na_2B_4O_7$	α-Fe martensit	3.5927(1)	3.5927(1)	3.5927(1)	*Fm-3m*	700–750	30
	γ-Fe(Cr)	2.8640(9)	2.8640(9)	2.8640(9)	*Im3m*		50
	$Fe(Cr)\ _2B$	5.1107(9)	5.1107(9)	4.3226(2)	*I4/mcm*		20
CW 90Cr17B2MnS	α-Fe(Cr) ferrit	3.6062(3)	3.6062(3)	3.6062(3)	*Fm-3m*	670–970	15
	γ-Fe (Cr)	2.8663(1)	2.8663(1)	2.8663(1)	*Im3m*		68
	$Fe(Cr)_2B$	5.1908(6)	5.1908(6)	4.1496(4)	*I4/mcm*		17
CW 90Cr17B2MnSi $Na_2B_4O_7$	α-Fe(Cr) ferrit	2.9439(6)	2.9439(6)	2.9439(6)	*Im3m*	750–980	13
	γ-Fe(Cr)	2.8781(4)	2.8781(4)	2.8781(4)	*Im3m*		67
	$Fe(Cr)_2B$	5.1607(5)	5.1607(5)	4.2979(4)	*I4/mcm*		20

X-ray diffraction analysis revealed the presence of a continuous Fe-Cr substitution solid solution with a small homogeneity region in the structure of the sprayed ASC from the analyzed CW (Table 2). At the incorporation of chromium atoms into the γ-Fe crystal lattice, an increase of the crystal lattice parameter was observed from a = 2.8617 Å for γ-Fe to a = 2.9386 Å for Fe-Cr compounds. A comparison of the crystal lattice periods for $Fe(Cr)_2B$ compounds also indicated a slight incorporation of chromium atoms into the structure of the Fe_2B compound. In addition to the main phases (α-Fe, γ-Fe(Cr) та $(Fe,Cr)_2B$), when borax was added to CW, the traces of iron oxide Fe_3O_4 were also found in the structure of the coating. In general, because of a more complete interaction of the components of the charge and the shell of the analyzed CW, there was an increase of the microhardness of the ASC (Table 3).

Table 3. Electrochemical parameters of coatings from CW 90Cr17B2MnSi and 08Cr18Ni10Ti steel in 3% NaCl aqueous solution.

Type of CW, which was used to spray coating with thickness of 1 mm	Corrosion potential E_{corr}, mV	Corrosion current density I_{corr}, mA/cm^2
CW 90Cr17B2MnSi (without addition of 4 wt.% $Na_2B_4O_7$ to CW charge)	480	0.0015
CW 90Cr17B2MnSi (with addition of 4 wt.% $Na_2B_4O_7$ to CW charge)	–450	0.0006
For comparison: 08Cr18Ni10Ti steel	–350	0.0003

The corrosion resistance of coatings sprayed CW 90Cr17B2MnSi with the addition of $Na_2B_4O_7$ to its charge was found to be at the level of 08Cr18Ni10Ti stainless steel in 3% aqueous NaCl solution, which was used to simulate the effect of sea water. The corrosion currents of coatings sprayed with CWs slightly exceeded those of 08Cr18Ni10Ti steel, but this is due to a significantly larger area of the interaction of the porous coating with the environment compared to the surface of solid steel. In particular, no traces of corrosion were found on the polished surface of the CW 90Cr17B2MnSi coating, even after it was kept for 124 hours in this environment. This gave reason to claim that coatings sprayed from CW 90Cr17B2MnSi with the addition of $Na_2B_4O_7$ to its charge can be used to protect against the corrosion of metal structures during their exploitation under the influence of salt solution or its vapours (Table 3).

The results of tests of coatings sprayed from CW 90Cr6BMnSi (without and with the addition of $Na_2B_4O_7$ and B_2O_3 to its charge) on their abrasive wear resistance under the conditions of rigidly fixed abrasive were compared with the results obtained on hardened U12 steel with different hardness, which was taken as a reference specimen for comparison (Figure 6). The results of abrasive wear resistance of coatings sprayed at subsonic and supersonic air flow modes were also compared.

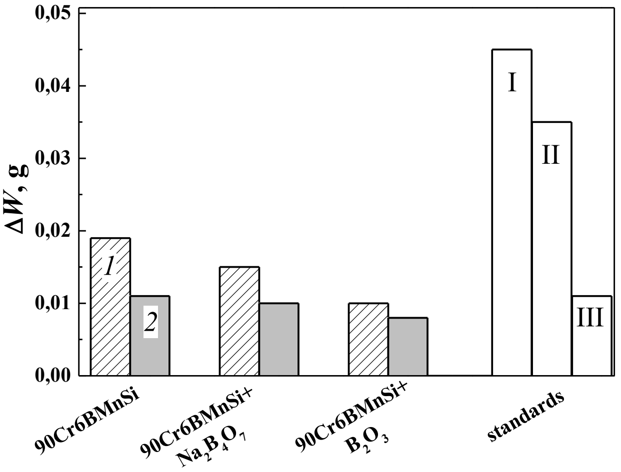


Figure 6. Weight loss of coatings sprayed from CW 90Cr6BMnSi (without and with addition of borax $Na_2B_4O_7$ and boron oxide B_2O_3 to its charge) under subsonic mode of their application at pressure of 0.6 MPa (1), supersonic at pressure of 1.2 MPa (2) and reference specimens made of U12 steel heat-treated to hardness of 460 $HV_{0.3}$ (I), 640 $HV_{0.3}$ (II) and 830 $HV_{0.3}$ (III)

In general, increasing the air pressure during spraying of the CW 90Cr6BMnSi coating reduced the weight loss of the coating after abrasive wear tests (Figure 6). Moreover, this happened even without adding borax or boride to the charge, but after their addition, the positive effect of the increase of the pressure of the spraying air flow on the wear resistance of the obtained coatings increased due to the increase of their homogeneity. In general, the addition of borax to the charge of CW 90Cr6BMnSi increased the wear resistance of coatings by 25% at both subsonic and supersonic spraying modes. And the addition of CW B_2O_3 to the charge increased additionally the wear resistance of the coating by 20%. But it is important to note that compared to reference specimens heat-treated to different hardness (I, II and III), the wear resistance of ASC from CW, to which B_2O_3 was added to the charge, even exceeded the wear resistance of high-carbon U12 stee after its hardening.

4. CONCLUSIONS

The obtained results proved the legality of using supersonic air flow speed during arc spraying of the coatings from cored wires, and the modifying the composition by adding borax and boron oxide to their charge in order to increase the homogeneity of their structure, hardness, abrasion resistance and corrosion resistance in 3 % NaCl aqueous solution. It was shown that under the conditions of the rigidly fixed abrasive, the abrasive wear resistance of the coating with CW 90Cr6BMnSi with modifying additives to its charge was not worse than high-carbon U12 steel after its hardening. Concerning corrosion resistance in 3% NaCl aqueous solution, the coating sprayed from CW 90Cr17B2MnSi with the addition of borax reached the level of 08Cr18Ni10Ti stainless steel.

ACKNOWLEDGEMENTS

This research was carried out with financial support of the National Research Foundation of Ukraine within the framework of the project No. 2022.01/0005 "The concept of restoring and extending exploitation resource of equipment of the most important branches of the national economy of Ukraine".

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