MATERIALS IN EXTREMAL CONDITIONS

PACS numbers: 46.15.-x, 46.55.+d, 68.35.bd, 81.15.Pq, 81.40.Pq, 82.45.Bb

Effect of Incomplete Replacement of Cr for Cu in the Deposited Alloy of Fe-C-Cr-B-Ti Alloying System with a Medium Boron Content (0.5% wt.) on its Corrosion Resistance

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In this research, the corrosion behaviour of the Fe–C–Cr–B–Ti alloying system deposited alloys applied by flux-cored arc welding are studied. Samples of deposited alloy with a high content of chromium (13% by weight of Cr) received

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Citation: B. O. Trembach, M. G. Sukov, V. A. Vynar, I. O. Trembach, V. V. Subbotina, O. Yu. Rebrov, O. M. Rebrova, and V. I. Zakiev, Effect of Incomplete Replacement of Cr for Cu in the Deposited Alloy of Fe-C-Cr-B-Ti Alloying System with a Medium Boron Content (0.5% wt.) on its Corrosion Resistance, *Metallofiz.Noveishie Tekhnol.*, **44**, No. 4: 493–513 (2022). DOI: 10.15407/mfint.44.04.0493

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with self-shielded flux-cored wire electrode without exothermic additions are investigated. For comparison, the deposited alloy received from self-shielded flux-cored wire with exothermal addition (CuO-Al) introduced to the core filler is also analyzed. It provides a low content of chromium (4% wt.) and a high content of copper (7% wt. Cu). The corrosion resistance of the deposited alloys layers is measured based on the results of potentiostatic polarization testing. After comparison of the corrosion current density $I_{\rm corr}$ and the corrosion electrode potential value E_{corr} , measured for the 140Cr13Si1MnBTi and 110Cr4Cu7TiVBAl deposited alloys layers as found, these values varied from 1.525 mA/cm^2 to 0.166 mA/cm^2 and from 0.359 mV to 0.631 mV depending on the alloyed layers composition. Results of the studies are shown that the introduction of exothermic addition (CuO-Al) to the core filler of the flux-cored wire provides the highest resistance of the deposited alloy to corrosion due to additional alloving by copper. Thus, the proposed partial replacement of chromium with an equivalent amount of copper has a positive effect on the corrosion resistance increasing of Fe–C–Cr–B–Ti alloving system deposited alloy.

Key words: hardfacing, Fe-C-Cr-B-Ti alloys, self-shielded flux-cored arc welding, copper, exothermic addition, CuO-Al, SEM, corrosion resistance, potentiodynamic polarization.

У роботі представлено результати експериментальних досліджень корозійної поведінки натоплених стопів системи леґування Fe-C-Cr-B-Ti, нанесених із використанням самозахисного порошкового дроту. Досліджено зразки натопленого стопу з високим вмістом Хрому (13% маси Cr), одержаного із самозахисного порошкового дроту без екзотермічного додатку. Для порівняння також досліджували натоплений стоп, одержаний із самозахисного порошкового дроту з вмістом екзотермічного додатку (CuO-Al) до наповнювача, що забезпечило низький вміст Хрому (4% маси) та високий вміст Купруму (7% маси Cu). Корозійну стійкість леґованих шарів натопленого стопу оцінювали за результатами поляризаційних вимірювань. Порівнюючи густину струму корозії І_{согг} та величину електродного потенціялу корозії $E_{\rm corr}$, виміряних для шарів натоплених стопів 140Cr13Si1MnBTi та 110Cr4Cu7TiVBAl встановили, що ці показники змінювалися відповідно від $1,525 \text{ мA/см}^2$ до $0,166 \text{ мA/см}^2$ та від 0,359 мB до 0,631 мВ залежно від компонентного складу леґованих шарів. Результати досліджень показали, що введення екзотермічного додатку (CuO-Al) до наповнювача порошкового дроту забезпечує вищу корозійну стійкість натопленого стопу за рахунок додаткового його леґування Купрумом. Таким чином, запропонована часткова заміна Хрому на еквівалентну кількість Купруму чинить позитивний вплив на підвищення корозійної стійкости натопленого стопу системи леґування Fe-C-Cr-B-Ti.

Ключові слова: натоплювання, стоп Fe–B–C–Cr–Ti, самозахисний порошковий дріт, Купрум, екзотермічний додаток, CuO–Al, CEM, потенціодинамічна поляризація, корозійна стійкість.

(Received February 24, 2022)

1. INTRODUCTION

Critical components of machines used in the mining and mineral processing industries are subject to intensive wear in corrosive environments during operation in extreme conditions. Energy loss due to wear in mining comprises 43% of friction. Wear-related energy loss include energy used to produce new parts for the worn-out parts and spare worn equipment replacement [1]. The cost of worn parts in mining is approximately the same as the cost of maintenance. In addition, wearing of some equipment in mining industry can lead to catastrophic failures and emergency stops, which can have a bad influence to equipment efficiency and therefore to the cost. It even can cause non-fulfilment of customer's obligations.

There are many types of wearing, such as abrasive, impact, friction of metal with metal, corrosion, erosion, etc. Abrasive, corrosive, and abrasive-corrosive wear is a particularly important problem in the mining industry. In these conditions machines and machine parts are heavily scratched by the abrasives such as minerals and earth [2, 3]. Metal loss due to abrasive wear can be significantly increased in the presence of aggressively corrosive environment. Corrosive environment in the mining industry is defined by technological purposes due to the use of water or aqueous solutions, as well as due to high humidity of extracted, processed raw materials, or corrosive activity of raw materials.

The parts abrasion resistance can be increased due to the right selected materials. However, the parts of a wear-resistant alloy in the most cases are unreasonable because of two reasons. The first is its high cost. The second is the further machining process complication. Moreover, the working surface of the part is only partially destroyed. As the replacement of worn parts causes high operating costs, the service life can be extended by means of the process of the part working surface coating. In this case, it is more economically sufficient and technologically easier to use the wear-resistant coating locally. The use of surfacing technologies allows to combine rationally the properties of coating materials and bases [4–6], providing the necessary accuracy of the parts manufacture [7]. Coating materials are used to increase the wear resistance, corrosion resistance and crack resistance of products [8–10].

Different technologies are used for coatings application. Reinforcement of the parts working surfaces is carried out by friction [11] and ultrasonic impact treatment [12–14]. Chemical-thermal methods of hardening became widely used: sulfidation [15], boriding [16], ionic deposition [17–20], cementation [21] and eutectic coatings receiving [22]. Functional single-layer oxide coatings [23], double-layer [24–26], and multilayer oxide coatings [27], nanocomposite coatings with metal bond and diamond content [28], with non-metallic bond and diamond content [29], and nanooxides [30, 31], as well as discrete coatings are used [32]. Nowadays by means of electrospark deposition (ESD) [33–36], electrochemical chromium plating [37], thermal spraying [38–40], including the use of alloyed powders [41, 42], laser hardfacing [43], SHSprocess [44, 45], vacuum-arc hardfacing [46, 47], and electric-arc pulse hardfacing [48, 49] form coatings on the working surfaces of machine parts and equipment made of different metals and alloys.

The strategy of coatings development includes not only the choice of component composition and methods of application, but also the evaluation of the discrete atomic structure of the crystal lattice of materials [50, 51], corrosion and electrochemical properties [52-54] and stress-strain state to predict the bearing capacity. Methods for the layered coatings behaviour are subject to development under an influence of local loads [55-57] and non-stationary thermopower factors [58-60]. Engineering approaches for coatings and patches influence on the boundary balance of cracked plates [61-63] and shells [64-66] are worth of attention.

The use of hardfacing, which provides the formation of multilayer coatings with a thickness of 10-15 mm, is considered to be a progressive direction for the machine parts hardening. Prediction of the high entropy alloys phase composition perspective for wide application as a material for hardfacing coatings was performed in theoretical studies [67, 68]. Results of computer modelling of thermodynamic and mechanical properties of reinforcing phases in the deposited metals are provided in works [69-70].

It should be noted that hardfacing is a key technology because it is more economically sufficient. Moreover, it allows to obtain surface layers of greater thickness compared to other methods of coatings formation. One of the most common among many hardfacing methods to increase wear resistance is the use of hardfacing with a self-shiealded fluxcored wire (FCAW-S) [71–74]. FCAW-S are characterized by simplicity of welding equipment, high hardfacing productivity, ability to achieve a high degree of alloying of the weld metal, the arc visibility [74].

However, the selected of deposited metal alloying system plays a significant role. Cast iron with a high content of chromium was used as the most widely used wear-resistant material, provided with a high content of hard carbides for a long time. However, despite its wide use in these alloys, there are some disadvantages, such as high cost, low ductility, and susceptibility to cracking of the weld metal [75]. In recent years, the innovation of Fe–B alloys is considered a break through due to their excellent wear resistance and good corrosion resistance with moderate impact strength, higher chemical and mechanical stability compared to alloy with high chromium content Cr [76]. However, the addition of boron instead of expensive alloying elements reduces the filler material cost [77]. Not with standing, it is unavoidable that boron-containing Fe–B alloys will be increasingly susceptible to localized corrosion due to the existence of numerous boride precipitates. Therefore, there is a great need in the alloy development to achieve high abrasion resistance and

corrosion resistance. Moreover, the corrosion resistance of Fe-B alloys will enlarge the further applications in various fields, increasing the resistance to abrasion and corrosion wear, hydroabrasive wear, corrosion wear and erosion wear.

In this case, this system alloying with elements improving its plastic properties and corrosion resistance is very interesting. Modern researchers mostly focused on alloying boron-containing alloys with a chromium [78], titanium [79-81], aluminium [76], vanadium and molybdenum [82–84]. However, the formation of chromium-rich borides, such as (Fe, Cr)₂B, reduces the content of corrosion-resistant alloying elements in the matrix, and therefore reduces corrosion resistance [85]. In this case, it will be interesting to add to the alloy of the Fe-C-Cr-B-Ti alloying system the alloying elements increasing the corrosion resistance and almost insoluble in borides, such as copper. Cu is a wellknown alloying element used to increase the overall corrosion resistance [86–90]. It is known the copper does not form compounds with boron (B) and remains mostly in the matrix [91], dissolving mostly in austenite [78]. Studies of alloys of the alloying system with a high boron content of 3.5% wt. [92] proved the efficiency of the copper introduction as an alloying element. However, today the use of alloys with lower boron content (up to 1% wt.) is more interesting. Yoo et al. [93] showed that steels with relatively low boron content (less than 0.6%) have better wear resistance. This is due to the formation of a brittle phase of FeB and a small amount of residual austenite [93].

Provision of required content of alloying elements in the weld metal is possible by introducing them into the alloy metal wire sheath or in powder form as the core filler. As known, during welding and hardfacing, as well as FCAW in general and FCAW-S particularly, there is irregular melting of the metal wire sheath and core filler. During the melting of flux-cored wires, due to the lag of the melting of the core filler from the metal wire sheath, a protrusion of the core filler is formed at the end of the fluxcored wire electrode [94]. These lags can be broken if they are formed in the form of large particles. If they fall into the molten welding pool, they can cause contamination of the weld metal with exogenous inclusions [94]. One of the ways to improve the uniformity of melting is to increase the contact tip work distance. This preheating enables the electrode to burn off faster and increases deposition rate. However, the excessive increase in contact tip to work distance (CTWD) is limited, due to the spin of the electrode resulting from the wire spooling [95].

The consequences are the unstable arc behaviour, increased spattering, or weld seam irregularities such as lack of fusion [96]. In this case, the introduction of an exothermic addition of CuO-Al system to the core filler of flux-cored wire electrode is more advantageous. According to our previous studies results [90, 97], the introduction of CuO-Al exothermic addition to the core filler provides the weld metal alloying with copper. In addition, the exothermic additions CuO–Al, caused grain fragmentation and an increase in the volume of ferrite in matrix of the deposited metal, increasing such mechanical properties as the elasticity modulus and microhardness [97]. Therefore, the wear resistance and corrosion resistance increasing at the stage of new parts manufacturing and during the worn parts restoration is an actual problem.

However, today the use of alloys with lower boron content (up to 0.6% wt.) is more interesting [93] due to the better wear resistance. The latter is explained by formation of FeB brittle phase and a small amount of residual austenite [93]. In this case, it is very interesting to study the effect of copper introduction in the boron-containing alloy Fe-C-Cr-

The name of the component		Content of the components in core filler of FCAW-S (% wt.)			
		FCAW-S 140Cr13Si1MnBTi	FCAW-S 110Cr4Cu7TiVBAl		
Gas slag- forming components	Fluorite concentrate ΓΟCT 4421-73	11	11		
	Rutile concentrate ΓΟCT 22938-78	7	7		
	Calcium carbonate ΓΟCT 8252-79	4	4		
	Ferromanganese ΦMH- 88A ΓΟCT 4755-91	6	5		
Alloying and deoxi- dizers	$\begin{array}{c} \text{Ferrosilicon} \Phi\text{C-92} \Gamma\text{OCT} \\ 1415\text{-}78 \end{array}$	2	4		
	Ferrovanadium ФВд-40 ГОСТ 27130-94	-	2		
	Metal Chrome X99 ΓΟCT 5905-79	40	10.4		
	Titanium powder ПТМ-3 ТУ 14-22-57-92	2	5		
	Graphite is silver	8	5.3		
	Boron carbide ΓΟCT 5744- 85	5	6.2		
Exothermic addition	Oxide of copper powder FOCT 16539-79	_	26		
	Aluminium powder ΠΑ1 ΓΟCT 6058-73	_	7		
Iron powder PZWR-1 FOCT 9849-86		15	7		

TABLE 1. Composition of core filler FCAW-S (diameter 4 mm) (% wt.).

B-Ti alloying system.

The purpose and objective of the research. The purpose of this work is to perform comparative testing of corrosion behaviour of boron-containing alloy Fe–C–Cr–B–Ti with high chromium content (Cr 13% wt.), and an alloy with equivalent substitution of chromium for copper (Cu 7% wt.). At that the required level of copper alloying, was received by recovery from the exothermic addition CuO–Al, which was introduced to the core filler.

2. EXPERIMENTAL PROCEDURE

Fe-C-Cr-B-Ti deposited alloys with a high chromium content (13% wt.) and a low chromium content (4% wt.) and a high copper content (7% wt.) were obtained in order to conduct comparative tests for corrosion behaviour in an industrial solution, flux-cored wire arc welding was used. The electrodes were coated with different compositions of the powder mixtures. A marble-fluorspar-rutile was used as the slag basis, the gas slag-forming component. For hardfacing, flux-cored wires electrode manufacturing of 08kn metal tape were used, the composition of the core filler was given in Table 1. The percent fill (or filling factor) of the flux-cored wire electrode is 0.35–0.36. Hardfacing was carried out with reverse polarity by A-874 automatic machine from a power source with rigid external characteristics. In Table 2 is shows the modes of hardfacing with self-shielding flux-cored wires electrode. At the same time, the process of hardfacing on metal plates from S235J2G2 EN10025-2 ($c\tau 3\pi c$) with dimensions $10 \times 100 \times 200$ mm was carried out in a flat position. After deposition, the welding samples were slow cooled in the drying box to 200°C and then cooled in the air.

In order to have the sufficient thickness of the layer and consider the

	Filler materials			
Parameters	FCAW-S 140Cr13Si1MnBTi	FCAW-S 110Cr4Cu7TiVBAl		
Average welding current, A	410	340		
${\rm Arc\ voltage}\ U_{\rm a}, {\rm V}$	32	28		
${\bf Travel speed, m/min}$	0.3			
Contact tip to work distance CTWD, mm	50	40		
Polarity	DCRP			
Preheating $T_{\rm p}$, °C	200			
Inter-pass temperature $T_{ m ip}$, °C	350			

TABLE 2. Hardfacing modes used in hardfacing process.

Matal	Content of alloying element in deposited metal, % wt.									
Metal	С	В	Cr	Cu	V	Ti	Mn	Si	S	Р
S235JRG2 EN 10025-94	0.17	_	_	_	_	_	1.55	0.55	0.045	0.045
140Cr13Si1MnB Ti	1.42	0.22	12.72	0.15	0.13	0.43	1.39	1.8,	0.037	0.016
110Cr4Cu7TiVB Al	1.08	0.45	3.51	7.2	0.26	1.49	1.18	1.23	0.031	0.017

TABLE 3. Chemical composition of substrate and hardfacing metals in $3^{\rm th}$ layers tested.

results shown previously, the samples were welded into two layers and have been used for testing. The chemical composition of both hardfacing layers and the substrate is presented in Table 3.

The potentiodynamic polarization tests were carried out at a scanning rate of 1 mV/s in a solution from -1.500 mV to +2.500 mV via standard calomel reference electrode (SCE) and graphite as the counter electrode. We used a solution corresponding to the chemical composition of technical water, used at the Central GOK (Kryvyi Rih) during iron ore grinding (in mg/l: 252 Ca, 281 Mg, 0.34 Fe, 672 Cl, 2366 SO₄, 13.5 nitrates, 225 bicarbonates, 4823 dry residue, total hardness— 36 mg-eq/l, pH = 7.7) to test the corrosion wear. The tests were carried out at atmospheric conditions (25°C) and humidity level of 31%. To optimizing the results each corrosion tests was repeated three times using the constant conditions such as solution pH = 6. The values of the corrosion current (I_{corr}) and the corrosion potential (E_{corr}) were determined by extrapolating the anodic and cathodic Tafel regions to the results of potentiodynamic studies.

The characteristics of corrosion processes were investigated in the potentiodynamic mode, using the voltammetric system CBA-1B-M. The reference electrode is \Im BJ-1M1 type silver chloride.

3. RESULTS

3.1. Open Circuit Potential Curves

The change in open circuit potential (OCP) can indicate the corrosion behaviour of the samples surface. EOCP measured in an ionic solution is an equilibrium potential of anodic and cathodic reactions. The measured OCP of a deposited metal in a corrosive solution can be regarded as its corrosion potential. The more negative the potential, the lower the



Fig. 1. Open circuit potential versus time plots deposited metal hardfacing: FCAW-S 140Cr15Si1TiMnB(*a*), FCAW-S 110Cr4Cu7Ti1VB(*b*).

corrosion resistance of the surface.

Open circuit potential potentiodynamic polarization measurements were made in solution corresponding to the chemical composition of technical water, to compare the corrosion performances of the test specimens (Fig. 1).

When the open-circuit potentials of the samples were compared, it is seen that the open circuit potentials of the samples deposited metal by FCAW-S 110Cr4Cu7TiVBAl are positioned (-0.62 V) at more stable values compared to deposited metal by FCAW-S 140Cr15Si1MnBTi at around -0.375 V (Fig. 1).

Sample deposited metal with high content chrome (12% wt.), which does not fit the general trend, displays a stable value during the first 1000 s, while the average value of the corrosion potential is -404 mV. However, in the time period of 1000-1500 s there is an increase in initial in open circuit potential from -0.404 to -0.355 V, followed by a steady increase to wards -0.377 V. The increasing OCP after some exposure after immersion is due to the growth of the corrosion film. At the same time, the subsequent increase in the potential indicates the formation of a less stable oxide film on the surface of the sample with a low content of chromium (4% wt.) and a high content of copper (7% wt.), which is destroyed, exposing the underfilm surfaces of the alloy. This tendency to change the corrosion potential persists with continued testing.

According to Figure 1, an alloy with a low content of chromium (4% wt.) and a high content of copper (7% wt.) has a very stable curve of corrosion potential change. The curve has a gradual curve of potential change with a slight angle of inclination, which indicates the passivation of the surface of the samples and the slowing down of corrosion processes. Thus, the relatively stable value of OCP is a consequence of



Fig. 2. Polarization curves of deposited metal hardfacing by FCAW-S 140Cr13Si1TiMnB.

the dynamic balance between the advance of corrosion and the deposit of corrosion products.

In addition, the comparative values of the potentials of the samples can be concluded about a much higher OCP (-0.625 V) of the alloy with partially substituted chromium for copper (110Cr4Cu7TiVBAl), compared with the OCP (-0.35 V) of alloy with high content chrome (140Cr15Si1TiMnB).

3.2. Potentiodynamic Polarization Test

But to determine the corrosion resistance is not enough to consider the potential of the open circuit mainly after a short time of immersion in the solution. Therefore, in the second stage of the study, anode-cathode potentiodynamic curves were recorded. Analysis of polarization curves obtained in potentiodynamic tests allows assessing the material's corrosion behaviour. Figures 2 and 3 shows the Tafel plots derived from the potentiodynamic polarization curves of deposited metals.

The curve is nonlinear at low currents as the current flowing consists of both anodic and cathodic components, but it starts to behave linearly at high currents on a semi-logarithmic plot. This is due to the predomination of cathodic current (or anodic current) to the other one at high current density and the corresponding hydrogen evolution. This linear region is referred to as the Tafel region [98]. Tafel region, characterized by a slope, which contains mechanistic information about the corrosion reaction.

Detailed analysis of anode-cathode potentiodynamic curves allowed the determination of the electrochemical parameters, which are



Fig. 3. Polarization curves of deposited metal hardfacing by FCAW-S 110Cr4Cu5Ti1VB.

summarized in Table 4.

Analysis of the sample surface with a high content of chromium 140Cr13Si1MnBTi showed the area in which a sudden change in the slope of the cathodic polarization curve occurs with a plateau in the cathodic current, this may be attributed to the growth of the film previously formed [99]. This behaviour of the Tefal curve may be indicative of the possibility of the separation of the protective layer from the surface.

Analysis of the received polarization curves showed that the alloy with a low content of chromium (4% wt.) and a high content of copper (7% wt.) has the equally changing curves (Fig. 3). This type of the curve shows the stable growth of the oxide film, which gradually increases its thickness and reduces the corrosion rate. This means that the oxide film on the sample surface during corrosion testing is dense.

The stable potential $(E_{\rm corr})$ reflects the thermodynamic properties of the material and the surface state of the electrode. According to the principle of thermodynamics, the lower $E_{\rm corr}$ indicates the greater corrosion tendency, while the higher $E_{\rm corr}$ indicates the lower corrosion tendency. According to the calculated values, the corrosion potential $(E_{\rm corr})$ of deposited metal with a high content of chromium (13% wt. Cr) is

TABLE 4. Average electrochemical parameters obtained from the linear polarization curves for each of the coatings: current corrosion (I_{corr}), corrosion potential (E_{corr}), and the anodic (β_a) and cathodic (β_c) Tafel slopes.

Type of filler materials	$E_{\rm corr}$, mV	$j_{ m k}$, $\mu { m A/cm^2}$	$b_{\rm c}$, mV	$b_{\rm a}$, mV
FCAW-S 140Cr13Si1MnBTi	-359	0.524807	-358	119
FCAW-S 110Cr4Cu7TiVBAl	-631	0.165959	-146	120



Fig. 4. SEM image of the deposited metal following the corrosion test hadfacing by: FCAW-S 140Cr15Si1MnBTi (*a*), FCAW-S 110Cr4Cu7TiVBAl (*b*).

-359 mV whilst, a nobler $E_{\rm corr}$ of -631 mV determined for the alloy with a low content of chromium (4% wt.) and a high content of copper (7% wt. Cu).

3.3. Macroscopic and Microscopic SEM Examination of the Surface after Electrochemical Corrosion Tests

Figure 4 presents the SEM image of the surface morphologies after potentiostatic tests at the applied potential of -1.5 and 0.5 V SCE of the deposited metal sample of hardfacing by FCAW-S 140Cr13Si1TiMnB and the experimental FCAW-S 110Cr4Cu5TiVBAl with the introduction of exothermic addition (CuO-Al) in the core filler.

Microscopic examination of the surface of samples conducted after electro-chemical tests showed that initiated corrosion leads to local changes (Fig. 4). Some residues have appeared on the surfaces of Fig. 4. This can be explained that the fluctuations in the anodic parts of the Tafel curves occur due to the separation of the protective layer from the surface.

3.4. Examination of Corroded Surfaces

After corrosion tests, the corrosion surfaces of 140Cr15Si1MnBTi alloys with high chromium content (13% wt. Cr) and experimental alloy 110Cr4Cu5TiVBAl with low chromium content and high copper content were subjected to SEM and EDS analyses, the results of which are presented in Figs. 5 and 6.

Analysis of the chemical composition of FCAW-S 140Cr15Si1MnBTi deposited metal surface after corrosion testing (Fig. 5) proved that this

surface is not uniform. We can determine three specific areas on the surface.

The first areas (Fig. 5, Spectrum 1) corresponded to Fe_2B borides. It should be noted that these areas were additionally doped with chromium, including their chemical formula corresponding to (Fe, Cr)₂B. The area (Fig. 5, Spectrum 2) corresponded to the eutectic of chromium carbides with a corroded matrix ($Cr_2C_3 + Fe_2O_3$). Areas with pits formed as a result of corrosion and flat areas were revealed at the surface. The barrier compound chemical composition of which is similar to the magnetite (oxidation of $Fe(OH)_2$ to Fe_3O_4) enriched with chromium



Fig. 5. SEM image and EDS analysis of the sample hardfacing by FCAW-S 140Cr15Si1MnBTi following the corrosion test.

compounds, is formed at higher potentials (E > 0.7 V). It is notable that on the surface of the sample applied with FCAW-S 140Cr13Si1MnBTi flux-cored wire electrode, enrichment of the end surface oxide by Cr was not observed. We suppose that the Cr₂O₃ layer does not increase the corrosion resistance of these alloys, the concentration of Cr in the matrix reached 13% wt.

Addition of big enough quantity of Cu to the Fe-C-B-Cr-Ti system alloy significantly changed the corrosion film properties. The rate and homogenization of corrosion film formation, consisting of iron oxides and chromium oxides, was increased by introduction of copper. This increasing can be explained by copper oxides appearance.



Fig. 6. SEM image and EDS analysis of the sample hardfacing by FCAW-S 110Cr4Cu7TiVBAl following the corrosion test.

4. DISCUSION

The oxidation reaction is an anodic reaction in which metal lost occur and the renewal reaction is a cathodic reaction take place. Both of these reactions are electrochemical in nature and are necessary for corrosion [100]. The aqueous environment in the corrosion process is an electrolyte, therefore the electrons move from the anode to the cathode. The corrosion process involves metal electrons removal (oxidation). The part with negative potential serves as an anode to initiate reaction of the metal solution. Part with a positive potential serve as a cathode for cathodic reactions, such as renewal of water or hydrogen and renewal of oxygen.

In process solutions, the cathodic process is mainly the depolarization process of oxygen [101]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, \tag{1}$$

$$2\mathrm{H}_{2}\mathrm{O} + 2e^{-} \rightarrow \mathrm{H}_{2} + 2\mathrm{OH}^{-}.$$
 (2)

The main electrochemical reaction that is expected in the matrix structure is the oxidation reaction, and the corrosion reactions of ironbased alloys at pH containing dissolved oxygen, almost neutral, can be written as:

$$Fe \rightarrow Fe^{2+} + 2e^{-}.$$
 (3)

In process solutions, Fe^{2+} continues to react with OH and O_2 in the soil to form insoluble hydroxides:

$$Fe^{2+} + 2OH \rightarrow Fe(OH)_2,$$
 (4)

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3.$$
(5)

The following anodic reaction expected for the high chromium alloy:

$$Cr \to Cr^{3+} + 3e^{-}.$$
 (6)

In case of low-chromium alloy with high content of copper (7% wt.) on anode the following reaction (7) will take place:

$$Cu \to Cu^+ + e^-. \tag{7}$$

In the case of an alloy with a high copper content the main anodic reactions are as follows:

$$2\mathrm{Cu}^{+} + 2\mathrm{OH} \rightarrow 2\mathrm{Cu}(\mathrm{OH}) \rightarrow \mathrm{Cu}_{2}\mathrm{O} + \mathrm{H}_{2}\mathrm{O}.$$
 (8)

It is possible that Cu_2O further reacts with O_2 and H_2O , in the environment:

$$2\mathrm{Cu}_{2}\mathrm{O} + \mathrm{O}_{2} \to 4\mathrm{Cu}\mathrm{O}, \tag{9}$$

$$H_2O + O_2 + Cu_2O \rightarrow Cu(OH)_2.$$
(10)

Notably, the enrichment of Cr in the outermost surface oxide was not observed on the surface of the sample deposited with flux-cored wire electrode FCAW-S 140Cr13Si1MnBTi. This indicates that the Cr_2O_3 layer does not contribute to the corrosion resistance of these alloys, although the Cr concentration of the matrix was as high as 13% mass (Table 1). The latter can be explained by the fact that greater part of the chromium forms own carbides and replaces Fe in borides (Fe, Cr)₂B. In corrosion film, it's not enough for the chromium oxides Cr₂O₃ formation, which increase the corrosion resistance. In addition, the places of the alloy matrix around the carbides are even more exhausted by Cr and serve as the local corrosion places. Such microscopic separation, according to Chaker [102] promotes the formation of anodes and cathodes between the exhausted matrix and hardening particles. Therefore, causing the corrosion inside the grains plays a dominant role in corrosion of the alloys subject to study [103]. Thus, the corrosive wear will be described according to the microcorrosion cell mechanism.

Corrosion rate decrease with increasing Cu concentration may be connected with precipitation of renewed Cu on the steel surface, which forms a protective barrier against further steel oxidation. Oxidation-reduction reaction with a presence of Cu^{2+} on the steel surface was proposed by Mobin and Shabnam [104]:

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}.$$
 (11)

The amount of Cu in the matrix is increased [91] with the addition of Cu, as an anodes substance during corrosion, because the standard potential for the redox couple Cu^{2+}/Cu is positive. Cu alloy elements are separated on the sample surface and formed a compact Cu-rich passive film [105] in the atomic scale. This effect is connected with the presence of cathode element Cu dispersed in the ferrite matrix, stimulating the anodic polarization of the ferrite, and increasing the passivation process. Probably some atoms of Cu are also oxidized to Cu^{2+} , while the most part of dissolved Cu^{2+} is precipitated on outer surface, forming a compact layer of Cu [106]. The latter will help to increase the corrosion resistance of deposited alloy. Rapid formation, increased by a higher content of copper 110Cr4Cu7TiVBAl, led to formation of more homogeneous crystalline layer of the corrosion product (except iron oxides and chromium oxides) enriched additionally by copper oxides CuO. Thus, the partial replacement of Cr with copper (Cu) contributes to the

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increase of the copper content in the oxide film on the alloy surface after corrosion tests, which can be explained by the formation of a more continuous oxide film CuO. This film effectively protects alloy surface and reduces the corrosion rate.

5. CONCLUSIONS

The main purpose of this work was to explore the effect of partial replacement of Cr on Cu during FCAW-S process on corrosion behaviour of deposited metal of the boron-containing alloy Fe-C-Cr-B-Ti alloying system. The following conclusions were drawn from this investigation: 1. The results of our experiments showed that, despite the high content of Cr (13% wt.), boron-containing high-carbon alloy without Cu have a marked tendency to corrosion in industrial solution. However, on the sample thedeposited metal FCAW-S surface of \mathbf{the} of 140Cr13Si1MnBTi typical Cr_2O_3 film, which usually implements passivity in these alloys, often do not work effectively.

2. Potentiodynamic polarization curves revealed lower $I_{\rm corr}$ values for 140Cr15Si1MnBTi alloy having a high content of chromium (Cr 13% wt.) compared to 110Cr4Cu7TiVBAl alloy with a low content of chromium (4% by weight) and a high content of copper (7% by weight of Cu). 3. In addition, a small increase in the copper amount in solid solution in the remelted layer can also play a moderate but useful role, forming more corrosion-resistant protective films.

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