

Corrosion properties of metal deposited by chromium flux-cored wire with boride-nitride-intermetallic alloying

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Abstract. The corrosion properties of the metal deposited with chromium flux-cored wire with boride-nitride-intermetallic alloying are investigated. It was established that the metal deposited with wire PP-Kh15+0.5%BN+1.25%TiB₂+0.5%ZrB₂ at the initial stage of corrosion behavior, estimated by the time until the first signs of corrosion appear, exceeds the metal welded with standard wire Sv-20Kh13 in 3.6 times, and long-term corrosion resistance 2.22 times. In this case, only a slight degree of etching of the matrix is observed in such a deposited metal, there is practically no dissolution of the boundaries of the boride eutectic, and the hardening phases do not undergo any changes, which determines the lower corrosion rate of such a coating. The powder wire PPKh15+0.5% BN+1.25% TiB₂+0.5% ZrB₂ can be recommended for surfacing wear-resistant coatings on parts of petrochemical equipment operating in an aggressive environment under abrasive wear.

1. Introduction

The durability of various equipment systems for the extraction, transport and storage of oil and gas is determined not only by the high wear resistance of its component parts, but also by their resistance to the corrosive effects of the corresponding medium. A significant role in improving these properties belongs to various methods of coating. Surfacing with Fe-15Cr system powder has great potential to create such corrosion coatings. However, such coatings have low wear resistance under abrasive wear.

At the same time, cored wires allow, due to the introduction of various alloying elements into their composition, to provide an increase in hardness and, accordingly, wear resistance of the weld coatings. It is known that high and stable mechanical and operational properties of steels can be obtained by combining solid solution hardening and hardening of second-phase particles (carbides, nitrides, borides, intermetallics) in an iron-based matrix [1, 2]. One of such effective methods of metal hardening is doping with boron [3-5]. When surfacing, boron compounds such as ferrobore, boron carbide, chromium diboride, and titanium diboride are used for this purpose [6-8]. Previously carried out studies of the authors established the positive effect of titanium and zirconium diborides on the wear resistance of nickel-chromium martensite-aging steels deposited with flux-cored wires [9-12]. Nitrogen is widely used for doping austenitic and austenite-ferritic corrosion-resistant steels [13-17]. It is noted that nitrogen improves the capacity for work hardening, significantly increases the ability to resist the propagation of cracks. Such steel turns out to be more durable than steel with carbon, while wear resistance indicators reach higher values. It should be noted that nitrogen is usually introduced into the melt through the use of nitrated chromium or ferrochrome.

At the same time, the use of boron nitride for these purposes, which is due to the similarity of a number of properties as an electronic analog of carbon, is of particular interest [18]. At the same time, boron nitride in the cored wires is used extremely rarely.

The authors showed the promise of using filler cored wire doped with the BN-TiB₂-ZrB₂ complex, which ensures high wear resistance [19].

At the same time, the transported media of oil fields are characterized by the presence of dissolved H₂S and CO₂ [20, 21]. Accordingly, another cause of the destruction of oil equipment is hydrogen sulfide and carbonate corrosion.

Therefore, to increase the operational durability of the metal deposited on the oil equipment parts, it is necessary not only to ensure its increased wear resistance, but also the corrosion resistance of such a metal.



At the same time, the corrosion resistance of the metal deposited by known cored wire has not been studied. In connection with the above, in the work investigated the corrosion properties of the metal deposited with flux-cored wire with boride-nitride-intermetallic doping.

2. Objects and research methods

The object of the study was the coating metal deposited by flux-cored wire PP-Kh15+0.5%BN+1.25%TiB₂+0.5%ZrB₂.

Surfacing was carried out on plates of steel St3 with a size of 200×50×10 mm using experienced flux-cored wire with a diameter of 2.4 mm in argon in three layers. Surfacing mode: current 230 A; voltage 24 V; surfacing speed of 20 m/h.

Tests for general corrosion were carried out in a salt fog chamber (SFC) at a temperature of 50±1 °C while spraying copper-acetic acid salt solution (neutral brine with the addition of dihydrated copper chloride (CuCl₂+2H₂O) and crystalline acetic acid) for 3 hours every 1 hour, which provides 1.5-2 ml/h of precipitation of salts. The concentration of the solution is 0.26±0.02 g/l, pH from 3.1 to 3.3. The duration of stay in the conditions of the influence of copper-acetic salt fog was 2400 hours.

The following characteristics were evaluated:

- the average and maximum rates of general corrosion, which were determined by the weight loss of the metal;
- average and maximum local corrosion rates, which were evaluated by the depth of corrosion ulcers.

The evaluation of the corrosion behavior in a salt fog chamber of the metal deposited by flux-cored wire PP-Kh15 was carried out in comparison with the metal deposited by standard wire Sv-20Kh13.

Metallographic studies of the deposited metal were carried out on an optical microscope Axio Observer A1m (Carl Zeiss).

3. Results of the experiments and discussion

The results of the evaluation of the initial stage of corrosion behavior in the chamber of the salt mist of the metal of the investigated compounds in comparison with the metal surfacing by standard wire are shown in Table 1.

Table 1. Evaluation of the corrosivity of the investigated coating compositions

Composition	The time of the first signs of corrosion, h
PP-Kh15+0.5%BN+1.25%TiB ₂ +0.5%ZrB ₂	432
Sv-20Kh13	120

From table 1 it can be seen that the metal obtained by wire PP-Kh15+0.5%BN+1.25%TiB₂+0.5%ZrB₂ at the initial stage of corrosion behavior, estimated by the time until the first signs of corrosion appear, exceeds the metal welded with standard wire Sv-20Kh13 3.6 times.

The overall corrosion resistance of the investigated coating compositions at the time of removal from the tests (2400 hours) is given in Table 2

Table 2. The results of the weight loss of metal samples of the investigated compositions after corrosion tests

Composition	Weight loss, g	Relative Corrosion Resistance ϵ_{tot}
PP-Kh15	0.6039	2.22
+0.5%BN+1.25%TiB ₂ +0.5%ZrB ₂	1.3392	1

From table 2 it follows that the weight loss of the metal obtained by surfacing PP-Kh15+0.5%BN+1.25%TiB₂+0.5%ZrB₂ and as a result of long-term tests is significantly less than that of the metal obtained by surfacing Sv-20Kh13. Resistance to general corrosion can be expressed as the coefficient of relative corrosion resistance ϵ_{tot} , numerically equal to the ratio of the weight loss of the coating taken per unit metal obtained by welding Sv-20Kh13 to the test metal with borides for the same test time. In this case, the metal with borides in long-term corrosion resistance 2.22 times greater than the metal of the coating obtained by welding Sv-20Kh13. As can be seen, the reduced corrosivity in the initial test period for the metal of the coating doped with boride compounds is maintained in the future. Apparently, the presence of boride compounds in such a metal compensates for the negative effect of carbon, especially on local corrosion resistance, due to the formation of a passivating film on the surface, inhibiting the corrosion process [22]. The number of compounds of chromium and boron in corrosion products increases with increasing test time, which causes a decrease in the rate of corrosion damage.

After soaking in the salt fog chamber for 2400 hours, the surface of the metal without borides was covered with a continuous layer of corrosion products. At the same time, on the surface of the metal with borides, these corrosion products were significantly smaller (Fig. 1, 2).



Figure 1. Sample (a) and the surface of the metal (b), deposited by Sv-20Kh13 after 2400 hours of testing for general corrosion

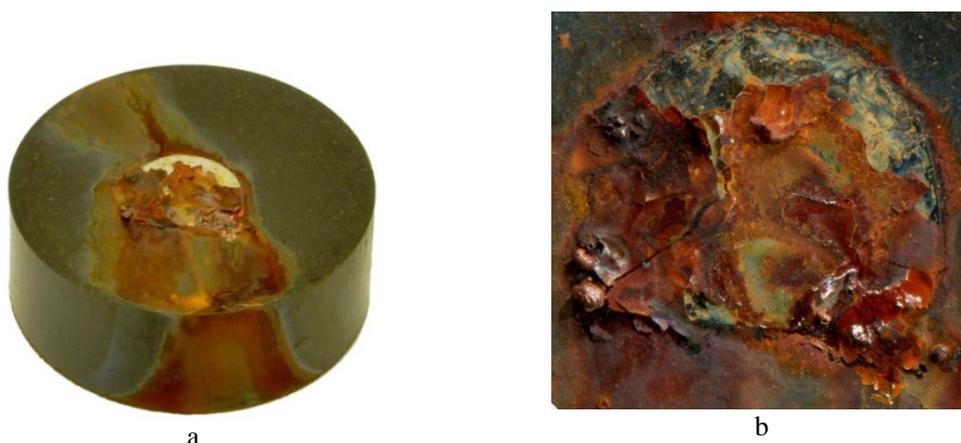


Figure 2. Sample (a) and the surface of the metal (b), deposited by PP-Kh15+0,5%BN+1,25%TiB₂+0,5%ZrB₂ after 2400 hours of testing for general corrosion

Corrosion spots with cavities were observed over the entire surface area of the samples. The depth of corrosion damage for the metal deposited by wire Sv-20Kh13 was greater and reached 0.85 mm, while for metal with borides it was smaller and reached 0.34 mm. The greatest inhibition of the corrosion rate occurs in the largest ulcers. This is probably due to the fact that in larger ulcers, the protective boron-containing layer of corrosion products is more concentrated, blocking

or slowing the development of local damage. The boron-containing amorphous phase has a lower electrical conductivity than the chromium-containing amorphous phase and suppresses electrochemical processes leading to ulcer corrosion. In addition, the boride phase is characterized by ionic selectivity of Cl^- , CO_3^{2-} , and HCO_3^- ions to the surface of corrosive steel. Cl^- ions do not accumulate at the metal-corrosion interface and the destruction of steel slows down.

A higher tendency to general corrosion of the metal deposited with wire Sv-20Kh13 can be explained not only by the absence of boride compounds, but also by an increased concentration of carbon and a lower concentration of chromium [23].

Differences in the corrosion resistance of the investigated coatings can also be attributed to the difference in their microstructures [24].

Metallographic studies have established that on the metal surface of the studied compounds after the removal of corrosion products there is a different degree of etching of the microstructure (Fig. 3, 4).

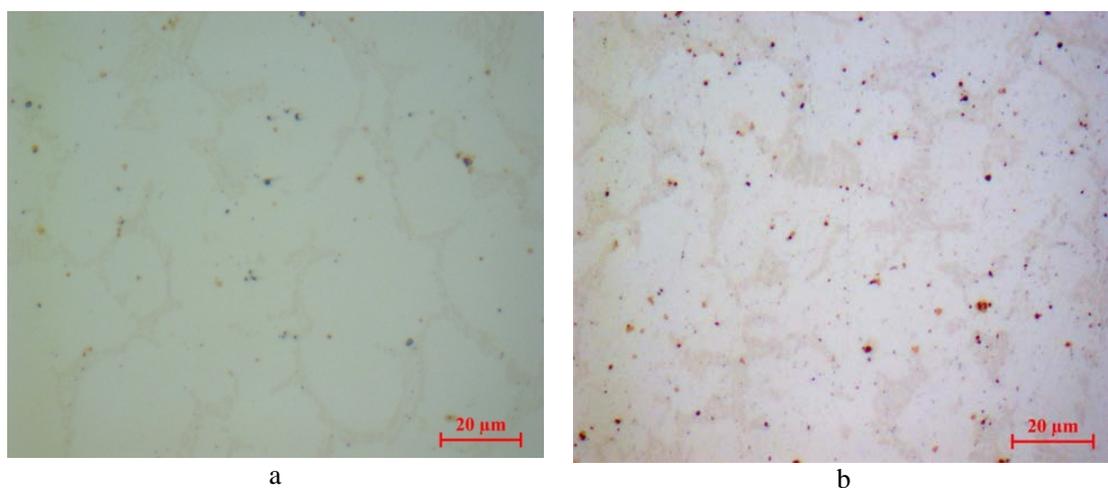


Figure 3. Microstructure of the coating's metal deposited by wire PP-Kh15+0.5%BN+1.25%TiB₂+0.5%ZrB₂ before the test (a) and after the test (b) for general corrosion

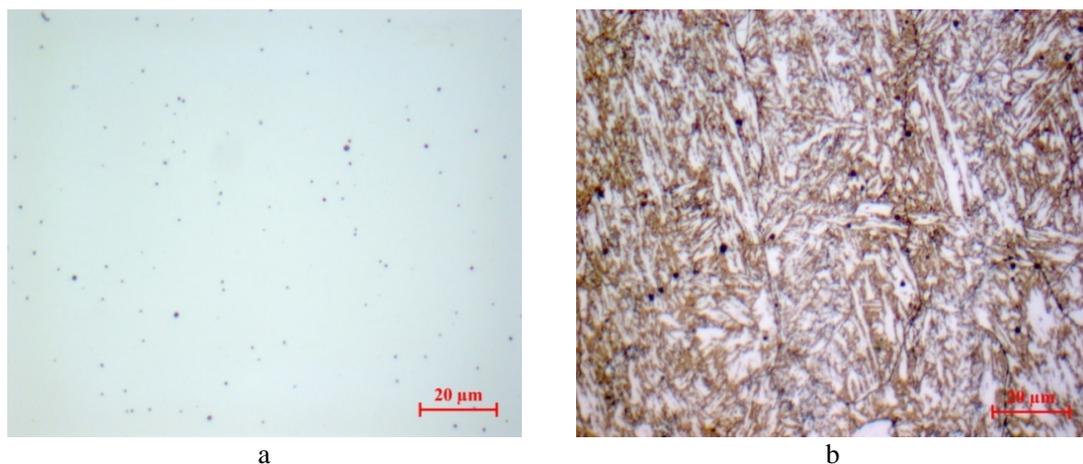


Figure 4. Microstructure of the coating's metal deposited by wire Sv-20Kh13 before the test (a) and after the test (b) for general corrosion

Corrosion dissolution usually begins with grain boundaries [25]. Micrographs show the dependence of total corrosion on the difference in corrosion rates in areas of grain boundaries. A uniform etching of all structural components of the metal of the coating is observed in the metal deposited with the wire Sv-20Kh13.

In the coating metal obtained by surfacing PP-Kh15 with borides, there is only a slight degree of etching of the matrix, while the dissolution of the boundaries of the boride eutectic is practically not observed, and the reinforcing phases do not undergo any changes. Apparently, this is due to the transition of a significant part of chromium into the eutectic and its binding to borides and nitrides. The hardening of the metal of such a coating is due to the formation of a eutectic component based on chromium and iron borides, which has a frame structure and a large number of dispersed particles of titanium and zirconium nitrides up to 2.5 μm in size [26]. In such a structure, there are fewer interfacial surfaces. As a result, the number of microgalvanic pairs between the island phases and the matrix decreases, respectively, increasing the corrosion resistance.

The positive effect of nitrogen in the presence of titanium and zirconium on the corrosion resistance of the metal is also explained by the formation of nitrides, creating a protective layer. According to the theory of dissolution, nitrogen, dissolving in an acidic medium with the production of ammonium ions, raises the pH of the solution, thereby passivating the nascent pittings [25]. On the other hand, nitrates and nitrites formed as a result of dissolution act as inhibitors of anodic dissolution processes. In addition, relaxation of structural stresses occurs as a result of dispersion hardening. Taking into account ideas about the formation of passivating mixed oxides of elements with high affinity for oxygen, it can be assumed that in this case titanium and zirconium inhibit the active dissolution of the solid solution, facilitates its passivation and increases the resistance against pitting corrosion.

The described processes determine the high corrosion resistance of the coating obtained by welding with flux cored wire with boride-nitride-intermetallic doping.

4. Conclusion

Thus, flux-cored wire PP-Kh15+0.5%BN+1.25%TiB₂+0.5%ZrB₂ provides the surfacing metal not only with high wear resistance, but also corrosion resistance. Such cored wire can be recommended for surfacing wear-resistant coatings on parts of petrochemical equipment operating in aggressive environments under abrasive wear.

Acknowledgments

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