Increase in corrosion resistance of carbon steel surface due to plasma surface modification with powder mixtures of NiCrBSi alloy and chrome carbide

Van Chie Nguyen1, A E Balanovskiy1, A N Baranov1, E A Guseva1, V V Kondrat'ev1, M G Shtayger2 and A I Karlina1

1 Irkutsk National Research Technical University, 83, Lermontova Street, Irkutsk, 664074, Russia
2 MC Mechel Steel, 1, Krasnoarmeysky Street, Moscow, 125167, Russia

E-mail: karlinat@mail.ru

Abstract. The studies assess the possibility of increasing the corrosion resistance, wear resistance of the surface of steel St3 using the method of plasma surface modification. The addition of OK 84.78 electrode coating powder in mixtures containing NiCrBSi leads to the increase of surface hardness. It is shown that the higher the content of OK 84.78 coating powder in the modifying mixture, the higher the probability of occurrence of defects in the fused surface layer (cracks, pores, heterogeneity). Studies of corrosion processes in a 3% NaCl solution show that coatings containing alloyed elements Cr, Ni have a higher passivation in a corrosive environment. NiCrBSi + 20% OK 84.78 coating is considered to be high corrosion-resistant.

1. Introduction
In recent years, the type of hardening of corrosion-resistant coatings based on Ni alloy has been well studied [1, 2]. In order to achieve the expected coating properties, there has been a trend towards adding other additional components like WC, TiC, SiC, which are successfully used in various surface treatments to obtain multicomponent coatings. [3-6]. Chromium carbides (CrxCy) advantages are chosen due to their popularity, low cost and high hardness. Chromium carbide is a potentially suitable ceramic phase for use in cermet due to the excellent oxidation resistance of its three polymorphs - cubic (Cr23C6), hexagonal (Cr7C3) and rhombic (Cr3C2).

Considering that the radius of chromium and iron is almost the same, therefore it diffuses more easily into steel. The combination of Ni-based alloy and CrxCy additive is found in the using of laser cladding [5], vacuum brazing [7], plasma spraying [8], HVOF [9]. NiCrBSi is a self-fluxing nickel-based alloy that is widely used for surface modification using highly concentrated sources of heating [10-12]. The presence of alloyed elements Ni, Cr leads to passivation in corrosive environments due to the formation of their oxides.

Several studies have noted that the coatings of the NiCrBSi system have high corrosion resistance [13, 14]. In their work [15], Shabana and his colleagues obtained two types of NiCrBSi, Cr3C2-NiCr coatings by thermal spraying (HVOF). Corrosion tests carried out in a 3.5% NaCl solution showed that the corrosion resistance of NiCrBSi was slightly higher than coating Cr3C2-NiCr. The authors believe that Cr3C2-NiCr can be used for applications where corrosion and wear are of paramount
importance. In an environment with a 5% solution of H$_2$SO$_4$, Cr$_3$C$_2$-NiCr, the coating showed better corrosion resistance behavior than NiCrBSi [16]. Corrosion study [17] in 3.5% NaCl solution showed that using the HVAF-Sprayed method, the resulting NiCr coating has a more negative potential than the Cr$_3$C$_2$-NiCr coating. The pores and carbides inherent in Cr$_3$C$_2$-NiCr coatings significantly reduce corrosion resistance, the former by providing preferred paths for ion diffusion, and the latter by the formation of cathode sites in galvanic vapors (between NiCr and Cr$_3$C$_2$).

Previously, coatings were obtained in the heating of modification mixtures containing NiCrBSi by an electric arc in a protective gas [18]. It is shown that high-quality coatings are obtained with a thin powder pre-layer and only in the mode of reflow of the main substrate, but their hardness is not very high. The method of surface modification of metals using plasma heating has long been used in many industries [19, 20]. In this method, successful, coatings are obtained by chromium plating, carburizing and chromium-nickel plating, but the production of plasma coatings based on a mixture of NiCrBSi and chrome carbide has not yet been sufficiently studied. It is known that the OK 84.78 welding electrode is widely used for surfacing of hardening layers operating under conditions of intense abrasive wear. Its matrix is made of austenitic cast iron saturated with coarse chromium carbides. The weld metal also has high corrosion resistance in contact with corrosive media and scale resistance.

The purpose of this work is to evaluate the corrosion resistance of a plasma coating made of powder mixtures of alloy NiCrBSi and an OK 78.84 electrode coating.

2. Materials and methods of study

2.1. Materials and methods

The chemical composition of steel St3 consists of C (0.14-0.22%), Si (0.05-0.17%), Mn (0.4-0.65%), Ni, Cu, Cr (≤ 0, 3%), As (≤ 0.08%), S, P (≤ 0.05%). For preparing the paste, the following powders were used: alloy PR-N80X13S2R with granules of 40-100 microns; electrode OK 84.78; office glue (silicate). The chemical composition of the alloy PR-N80X13S2R, OK 84.78 and their content in the initial compositions are shown in Table 1.

| el. | NiCrBSi | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 |
|-----|---------|---------|----------|---------|----------|---------|----------|---------|----------|---------|----------|
|     |         |         |          |         |          |         |          |         |          |         |          |
| Ni  | 80      | 90      | 100      | 80      | 90       | 100     | 80       | 90      | 100      | 80      | 90       |
| Cr  | 14      | 20.87   | 27.74    | 34.61   | 41.48    | 48.35   | 48.35    |         |          |         |          |
| Fe  | 1.8     | 1.62    | 1.44     | 1.26    | 1.08     | 0.9     | 0.9      |         |          |         |          |
| B   | 1.5     | 1.35    | 1.2      | 1.05    | 0.9      | 0.75    | 0.75     |         |          |         |          |
| Si  | 2.4     | 2.36    | 2.32     | 2.28    | 2.24     | 2.2     | 2.2      |         |          |         |          |
| C   | 0.3     | 1.4     | 2.5      | 3.6     | 4.7      | 5.8     | 5.8      |         |          |         |          |
| Mn  | 0.38    | 0.76    | 1.14     | 1.52    | 1.9      |         |          |         |          |         |          |

The preparation of the surface coating consisted of applying a paste from the mixtures according to Table 1 using glue, drying at 50-60 °C for 1 hour. After drying, the coating thickness of all samples was about 0.25 mm. Plasma treatment modes: current 140A, consumption of argon 10 l/min; the gap between the tungsten electrode and the surface of substrate is 5 mm; the moving speed of the samples is 2.7 mm/s.

The samples processed after plasma modification were cut using a "Polilab P100A" machine and then pressed using a "Polilab S50A" press. The surface of the plasma samples was polished on a "Polilab P12M" machine to shine, after that, they continued to poison in a 1% solution of nitric acid with ethanol. Observing their microstructure using an optical microscope MET-2. The microhardness was measured on a device of hardness testers of the HMM - G series.
2.2. Corrosion control method
To control the corrosion behavior of the test samples, a 3% NaCl solution was used. The steel was preliminary etched in hydrochloric acid to a pure metal, then washed in distilled water and degreased with ethyl alcohol 99%. The coated samples were polished with 1000 grit Eagle waterproof abrasive paper, then washed with distilled water and finally ethyl alcohol. Before measurements, the area of one cm$^2$ was fixed on the surface. The remaining surface was covered with insulating tape and waterproof glue so that the shielded surface were not exposed to the electrolyte. The prepared samples were placed in a 500 ml beaker so that the selected area was completely immersed in the working solution. Used potentiostat-galvanostat "PI-50-Pro" for corrosion control. Operating mode: Starting potential -1400 mV; Maximum potential 100 mV; Minimum potential -1500 mV; final potential 100 mV; current range 2000 mA; potential range 50 V; sweep speed 26.932 mV/s. Work with the PS_Pack2 program according to the "Linear sweep" experiment type.

3. Results and its discussion
3.1. Study of the microstructure and microhardness of the obtained coatings
After plasma treatment of the samples, the cross-sectional views of the surface coating are shown in Table 2.

It can be seen that high-quality coatings are No. 1, 2, 3, 6, and No. 4, 5, which have several defects (cracks, pores, heterogeneity). Coating No. 1 has a great depth, the others have a depth of about 850-900 microns. The large difference in depth between coating No. 1 and the rest is explained by the fact that the NiCrBSi alloy is more ductile than the OK 84.78 powder alloy, which has more hard phases (carbides). This prevents heat transfer to the inner sublayers, because of which the substrate dissolves less and the bath has a small volume.

At the same time, the coating with a high chromium content (48.35%) in the original composition No. 6, having the radius of chromium and iron is almost the same, therefore, the composition of OK 84.78 is more saturated in the steel substrate. Other coatings containing the compositions OK 84.78 and NiCrBSi bring inhomogeneous matrices of coating than single alloys (NiCrBSi or OK 84.78), even the presence of NiCrBSi still adds various elements, and therefore these compositions complicate the dilution of the substrate and the diffusion of alloyed elements. As a result, it is obvious that thin sublayers appear on the surface in coatings No. 1, 2, and cracks in others. The microhardness values of the coatings are presented by their distribution in Figure 1.
| №  | Initial composition | Type of coatings | Note |
|----|--------------------|-----------------|------|
| 1  | NiCrBSi            | Uniform weld pool | Homogeneous layer Depth 1300 microns |
| 2  | NiCrBSi + 10% OK 84.78 | Uniform weld pool | Homogeneous layer Depth 900 microns |
| 3  | NiCrBSi + 20% OK 84.78 | Uneven weld pool | Homogeneous layer Depth 850 microns |
| 4  | NiCrBSi + 30% OK 84.78 | Pores, Cracks | Inhomogeneous layer |
| 5  | NiCrBSi + 40% OK 84.78 | Pores | Inhomogeneous layer |
| 6  | OK 84.78           | Homogeneous layer | Depth 910 microns |
Coatings No. 2, 3 have thin sublayers (thickness about 50 microns). In these sublayers, the structure differs from the rest of the coverage areas. If the first points of hardness measurement on coatings No. 2, 3 (199 HV and 303 HV) are not counted, then the dispersion of the microhardness values of the main coating zone is presented by the diagram in Figure 2. It can be seen that in coating No. 2 the range of the confidence interval of measurement errors is narrow, i.e. the microhardness values are concentrated, and the average measurement values coincide with the median and close to the average value of the microhardness of coating No. 1.

This can be explained by the fact that the addition of 10% OK 84.78 does not increase the hardness, but with an increase in the chromium and carbon content and a corresponding decrease in the nickel content, which leads to a decrease in the formation of the γ-Ni phase, the hardness of which is lower than that of other phases in the coating. At the same time, the concentration of hardness values of coating No. 3 is lower, but most of its values (75%) are higher than the maximum for coating No. 2. All hardness values of coating No. 3 are distributed with a similar concentration as for coating No. 1, but more than 50% of the value is higher than the maximum for coating No. 1. This means that an increase in the weight of OK 84.78 by another 10% can noticeably increase the hardness of the surface coating, i.e. the role of chromium and carbon in the formation of harder phases with an increase in their content was confirmed. When using only the coating composition of OK 84.78, the resulting coating has high microhardness values in the range of 300-650 HV. Low values (297 and 426 HV) at
the last points near the coating / substrate boundary may be caused by insignificant diffusional carbon. Because of these points, the concentration of microhardness values becomes the lowest.

![Figure 2](image1)

**Figure 2.** Dispersion of microhardness values of the cross-section of coatings: No. 1 - NiCrBSi; No. 2 - NiCrBSi + 10% OK 84.78; No. 3 - NiCrBSi + 20% OK 84.78; No. 6 - OK 84.78.

3.2. Study of corrosion behaviour in 3% NaCl solution

For each alloy and St3 steel, the corrosion control was repeated 6 times. The dependences of the current (mA) on the potential (mV) relative to the silver chloride reference electrode are shown in Figure 4. The experimental error for St3 steel is from 1.0 to 10.3%, for NiCrBSi, OK 84.78, NiCrBSi + 10% OK 84.78, NiCrBSi + 20% OK 84.78 coatings from 0.32 to 9.03%, and for NiCrBSi coatings + 30% OK 84.78, NiCrBSi + 40% OK 84.78 from 0.4 to 15.5%. The dependence lines for all coatings have a section in the middle, parallel to the horizontal axis, and then the corrosion current sharply increases for St3 steel at a potential of -500 mV, for the rest, the potential increases to -300, -200 mV. The shape of these lines proved that all coatings have a higher corrosion resistance and the highest resistance for the alloy NiCrBSi + 20% OK 84.78.

![Figure 3](image2)

**Figure 3.** Dependencies of the current (mA) on potential (mV) relative to the silver chloride reference electrode for NiCrBSi, NiCrBSi-10% OK 84.78, NiCrBSi-20% OK 84.78, NiCrBSi-30% OK 84.78, NiCrBSi-40% OK 84.78, 100% OK 84.78 and steel St3.
Typical polarization curves are shown in Figure 4. This graph gives examples of the line of voltage versus logarithm of current density for St3 steel and NiCrBSi + 10% OK 84.78 coating. It can be seen that the coating based on a mixture of NiCrBSi and 10% OK 84.78 is more passive against the corrosive environment than steels. The coating passivation line will extend from -1000 to -300 mV, and for steel, it slopes earlier from the horizontal. A typical graph represents the role of alloying elements, especially chromium. Its presence leads to an increase in corrosion resistance due to the formation of oxides, and so will greatly reduce the current density. However, for a significant comparison between them, the construction of an approximating curve with the value of the reliability of the approximation gives the current and the corrosion potential. The result is shown in Table 3.

![Figure 4. Voltage dependencies on logarithm of current density for anodic and cathodic polarization curves for a St3 steel sample and a NiCrBSi coating + 10% OK 84.78 in a 3% NaCl solution.](image)

Table 3. Average value of current and corrosion potential for different compositions and steel St3.

| Val. | NiCrBSi | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 | NiCrBSi | OK 78.84 | OK 78.84 |
|------|---------|---------|----------|---------|----------|---------|----------|---------|----------|---------|----------|----------|
|      | 100%    | 90%     | 10%      | 80%     | 20%      | 70%     | 30%      | 60%     | 40%      | 100%    |          |          |
| I, A/m² | 1.082   | 1.167   | 1.180   | 1.420   | 1.776   | 1.258   | 1.304   |
| E, mV  | -985    | -957    | -952    | -931    | -950    | -1014   | -1088   |

First, with an increasing in the content of OC 84.78, i.e., a corresponding increase in the content of chromium in the coatings, the corrosion potential moves in a more positive, but from 30% to 100% in a more negative value. For coatings No. 2, 3, the current and corrosion potential does not differ much, but diverges for coating No. 4, 5. A strong change can be caused by defects, including pores, cracks and heterogeneity, because of which it leads to pitting corrosion. Coating No.1 has the lowest current, but the corrosion potential is more negative than multicomponent coatings.
Figure 5. Distribution of average values of corrosion current and potential by composition: 1 – NiCrBSi; 2 – NiCrBSi/OK 84.78 (90%-10%); 3 – NiCrBSi/OK 84.78 (90%-10%); 4 – NiCrBSi/OK 84.78 (80%-20%); 5 – NiCrBSi/OK 84.78 (70%-30%); 6 – NiCrBSi/OK 84.78 (60%-40%); 7 – St3.

4. Conclusion
The formation of coatings from a series of mixtures NiCrBSi and OK 85.78 in the plasma-heating mode was established: power 140 A, sample speed 2.7 mm / s, gas flow rate 10 l / min). The depth of the NiCrBSi coating is 1300 µm, the others have a thickness of about 800-900 µm.

The study of the microstructure has shown that for the same coating thickness, single alloys are more saturated inside the steel. With the increase in the content of OK 85.78, i.e. chromium, carbon, defects (pores, cracks, heterogeneity) appear in the coatings, especially with compositions of 30, 40%.

Microhardness measurements showed that there is a possibility of increasing the hardness of the NiCrBSi coating with the addition of OK 84.78. The spread of microhardness values with a composition of 10% OK 84.78, the values of hardness are more concentrated near the average value, and with its 20% in the composition, it is much higher than that of the coating NiCrBSi and (NiCrBSi + 10% OK 84.78).

When studying corrosion in a 3% NaCl solution, the addition of OK 84.78 to the main mixture leads to a decrease in the corrosion current, except for coatings that have defects. With compositions having 10, 20% OK 84.78, the difference in the corrosion current between them and the NiCrBSi coating is not large. According to the value of the microhardness of the cross-section and the corrosion current strength, the coating of the mixed composition (NiCrBSi + 20% OK 84.78) is more corrosion-resistant.

References
[1] Jing Yu and Bo Song 2018 Friction and wear behavior of a Ni-based alloy coating fabricated using a multistep induction cladding technique Results in Physics 11 105-111. DOI: https://doi.org/10.1016/j.rinp.2018.08.049
[2] Wen Sun, Ayan Bhowmik, Adrian Wei Yee Tan, Fei Xue, Iulian Marinescu, Feng Li and Erjia Liu 2019 Strategy of incorporating Ni-based braze alloy in cold sprayed Inconel 718 coating Surface & Coatings Technology 358 1006-1012. DOI:
[3] Saeddi R, Shoja-Razavi R, Bakhshi S-R, Erfanian mesh M and Ahmadi-Bani A 2020 Optimization and characterization of laser cladding of NiCr and NiCr–TiC composite coatings on AISI 420 stainless steel Ceramics International DOI: https://doi.org/10.1016/j.ceramint.2020.09.284.

[4] Bhosale D G, Rathod W S and Rukhande S W 2020 Effect of counter faces on sliding wear behavior of WC-Cr3C2-Ni composite coating deposited by high velocity oxy fuel Materials Today: Proceedings In press DOI: https://doi.org/10.1016/j.matpr.2020.08.466

[5] Peng Wang, Shuang Li, Xin Geng, Jipeng Zhang and Chuncheng Wei 2020 Microstructure, surface stress and surface temperature response of ZrB2–SiC based coatings J. of Alloys and Compounds 843 156084 DOI: https://doi.org/10.1016/j.jallcom.2020.156084

[6] Mao-Sheng Yang, Xi-Bo Liua, Ji-Wei Fan, Xiang-Ming He, Shi-Hong Shi, Ge-Yan Fu, Ming-Di Wang and Shu-Fa Chen 2012 Microstructure and wear behaviors of laser clad NiCr/Cr3C2–WS2 high temperature self-lubricating wear-resistant composite coating Applied Surface Science 258 3757-3762. DOI: https://doi.org/10.1016/j.apsusc.2011.12.021

[7] De Wang, Yujiang Xie, Yanhong Yang, Mingsheng Wang, Wenqin Wang, Xiangping Cheng and Deping Lu 2016 Influence of Cr addition on microstructure of vacuum brazed NiCr – Cr3C2 composite coatings Materials Characterization 115 46-54. DOI: https://doi.org/10.1016/j.matchar.2016.03.016

[8] Liu Q, Wang Y, Bai Y, Li Z D, Tan G L, Bao M Y, Li X J, Zhan H, Sun Y W, Chong N J, Wang R J and Ma Y S 2020 Formation mechanism of gas phase in supersonic atmospheric plasma sprayed NiCr-Cr3C2 cermet coatings Surface & Coatings Technology 397 126052. DOI: https://doi.org/10.1016/j.surfcoat.2020.126052

[9] Shankar R, Balasubramanian K R and Sivapirakasam S P 2020 Hot corrosion behavior of nanostructured and conventional HVOF Cr3C2 – NiCrBSi coatings on super alloy Materials Today: Proceedings In press, corrected proof. 1-8. DOI: https://doi.org/10.1016/j.matpr.2020.04.005

[10] Meng J, Shi X, Zhang S, Wang M, Xue F, Liu B, Cui W and Bian L 2019 Friction and wear properties of TiNi-TiB2-Ni based composite coatings by arc argon cladding technology Surf. Coat. Technol. 374 437-447

[11] Makarov A V, Soboleva N N, Malygina I Yu and Kharanzevskiy E V 2019 Improving the properties of a rapidly crystallized NiCrBSi laser clad coating by high-temperature processing J. of Crystal Growth 525 125200. DOI: https://doi.org/10.1016/j.jcrysgro.2019.125200

[12] Rachida Rachidi, Bachir El Kihel and Fabienne Delaunois 2019 Microstructure and mechanical characterization of NiCrBSi alloy and NiCrBSi-WC composite coatings produced by flame spraying Materials Science & Engineering B 241 13-21. DOI: https://doi.org/10.1016/j.mseb.2019.02.002

[13] Zhaia L L, Bana C Y and Zhang J W 2019 Microstructure, microhardness and corrosion resistance of NiCrBSi coatings under electromagnetic field auxiliary laser cladding Surface & Coatings Technology 358 531-538. DOI: https://doi.org/10.1016/j.surfcoat.2018.11.034

[14] Serres N, Hlava F, Costil S, Langlade C and Machi F 2011 Corrosion properties of in situ laser remelted NiCrBSi coatings comparison with hard chromium coatings J. of Materials Processing Technology 211 133-140. DOI: https://doi.org/10.1016/j.jmatprotc.2010.09.005

[15] Shabana, Sarcar M M M, Suman K N S and Kamaluddin S 2015 Tribological and Corrosion behavior of HVOF Sprayed WC-Co, NiCrBSi and Cr3C2-NiCr Coatings and analysis using Design of Experiments Materials Today: Proceedings 2(4-5) 2654-2665

[16] Sidhu T S, Prakash S and Agrawal R D 2007 A Comparative Study of Hot Corrosion Resistance of HVOF Sprayed NiCrBSi and Stellite-6 Coated Ni-Base Super alloy at 900°C Materials Science & Engineering A 210-218

[17] Sadeghimresht E, Markocean N and Nyle´n P 2017 Microstructure Effect of Intermediate Coat Layer on Corrosion Behavior of HVAF-Sprayed Bi-Layer Coatings J. Therm. Spray Tech. 26
243-253

[18] Nguyen Van Trieu 2020 Increasing the hardness of the surface layer of low-carbon steel due to plasma treatment of the modifying coating *ISTU Bulletin* **24**(1) 52-63

[19] Balanovskii A E 2019 New mechanism of interaction between a welding-arc discharge of reverse-polarity direct current and an aluminum surface *High Temperature* **57**(6) 784–797

[20] Balanovskii A E and Vu V H 2017 Plasma surface carburizing with graphite paste *Letters on materials* **7**(2) 175-179