JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **15** No 5, 05031(5pp) (2023)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **15** № 5, 05031(5cc) (2023)

Structure and Protective Properties of Complex Chromosilicide Diffusion Coatings on Steel 20

I. Pohrebova[1], K. Yantsevych[2], T. Loskutova[1], N. Kharchenko[3], T. Hovorun[3]

[1] *National Technical University of Ukraine "I. Sikorsky Kyiv Polytechnic Institute", 37, Beresteiskyi ave, 03056, Kyiv, Ukraine*
[2] *E.O. Paton Electric Welding Institute, 11, Kazymyr Malevych st., 03150 Kyiv, Ukraine*
[3] *Sumy State University, 2, Rimsky Korsakov st., 40007 Sumy, Ukraine*

(Received 05 August 2023; revised manuscript received 18 October 2023; published online 30 October 2023)

The paper presents the results of studies of the structure, chemical composition, microhardness, heat, and corrosion resistance of multicomponent coatings obtained during diffusion chromosiliconizing of steel 20. The coating was applied in a specially designed reaction chamber at a temperature of 1050 °C for 6 hours to the surface of carbon steel 20 in a closed reaction space at a reduced pressure of the active gas phase, for the formation of which rational amounts of silicon and chromium were used, as well as carbon tetrachloride as an activator. It was established that the obtained coatings consist of carbides of chromium $Cr_{23}C_6$, Cr_7C_3 doped with silicon and a zone of solid solution of chromium and silicon in iron. The maximum amount of silicon is observed in the inner area of the coating (2.82 – 3.89 wt. %) at a depth of 15-50 microns. The total thickness of the coating is 110 μm, and the microhardness of the surface layers is 19.5 GPa. The surface layers of coatings, based on chromium and silicon, lead to the formation of protective films Cr_2O_3, Al_2O_3, which ensures their high heat resistance in the air atmosphere and corrosion resistance in oxidizing acids. The possibility of increasing the corrosion resistance of coatings by introducing inorganic oxidants into aggressive solutions has been established.

Keywords: Diffusion coatings, Microhardness, Chromosiliconizing.

DOI: 10.21272/jnep.15(5).05031 PACS numbers: 61.46. – w, 62.20.Qp, 62.20. – x, 68.55N

1. INTRODUCTION

Multilayer film materials [1, 2] and diffusion coatings based on carbides and silicides of transition metals [3-5] have a high complex of physicochemical properties, and their application on the surface of steels makes it possible to significantly improve the operational characteristics of machine parts and tools [6, 7]. Diffusion layers formed when steel is saturated with silicon are protective coatings with high heat and corrosion resistance [3, 5]. However, silicide coatings obtained by modern technologies are not used in industry due to their high fragility, porosity, and low adhesion to the matrix of the base material. It is possible to eliminate the disadvantages of silicon-based diffusion layers by alloying them with chromium, which can be achieved by complex saturation of carbon steels with silicon and chromium [3].

The work aims to study the phase, chemical composition, structure, and protective properties of coatings on steel 20 after complex chromosiliconizing.

2. MATERIALS AND METHODS

Chromosiliconizing was carried out by the gas method in a specially developed installation at National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", which had a unique reaction chamber of a new design [8]. The reaction chamber allows for a reduction of the consumption of silicon and chromium powders (by 25 – 30 % wt) to eliminate the possible alloying of carbide phases with elements included in the material used to manufacture the chamber, as well as the need to introduce solid carbon-containing substances into the starting reagents. Diffusion coatings were applied to the surface of carbon steel 20 in a closed reaction space under reduced pressure of the active gas phase, for the formation of which rational amounts of silicon and chromium were used, as well as carbon tetrachloride as an activator [3]. The carbon source was a bottom with an area of 0.06 m^2, made of graphite. The chromosiliconizing process was carried out at 1050 °C for 6 hours.

X-ray structural analysis was performed on the DRON UM-1 installation in copper monochromatized radiation with the processing of the results in the Powder Cell 2.2 program. The chemical composition of the coatings was determined by micro-X-ray spectral analysis using the Energy 200 energy dispersive attachment to the CamScan 4D scanning electron microscope with the INCA 200 result processing program. Microstructural studies were performed on the CamScan 4D electron microscope after etching the samples with Murakami's reagent, followed by etching with a 3 % solution of nitric acid in ethyl alcohol. Measurement of microhardness and refinement of the thickness of the diffusion layer, as well as its separate phases, were performed on the PMT-3 device.

The heat resistance of diffusion coatings was studied with the help of a differential thermal analyzer "Q-1500 D" derivative [3] and by the change in the mass of the samples after their oxidation at a temperature of 800 – 1000 °C for 6 hours.

Corrosion studies were carried out for steel 20 and steel with coatings at a temperature of 20 °C under conditions of natural aeration. Research was carried out in industrially important aggressive environments: 15 % HCl, 15 % H_2SO_4, 10 % HNO_3, 10 % CH_3COOH, 10 – 15 % H_3PO_4, technical water, 3 % NaCl. The duration of the corrosion tests was chosen depending on the research material and the aggressive environment. For steel samples in nitric acid solutions, it corresponds to

2 hours; for other solutions – 24 – 144 hours; for samples with diffusion coatings, the time of corrosion tests varied from 24 to 720 hours. The corrosion resistance of steel and coated samples was evaluated by the massometric corrosion index Km (g/m²h), the protective effect of the coatings by the corrosion inhibition coefficient (γ), and the degree of their protection (Z, %) [3].

3. RESULTS AND DISCUSSION

It was established by X-ray structural analysis (Fig. 1) that on the surface of steel 20 after its chromosiliconizing, layers are formed consisting of chromium carbides $Cr_{23}C_6$ (a = 1.0628 nm), Cr_7C_3 (a = 0.6999 nm, b = 1.2185 nm, c = 0.4545 nm) and a solid solution of chromium and silicon in α-iron. The BCC period of the α-iron lattice does not change significantly in the depth of the studied samples and is within the range from a = 0.2866(3) nm at a depth of 50 μm to a = 0.2869(1) nm at a depth of ~ 100 μm.

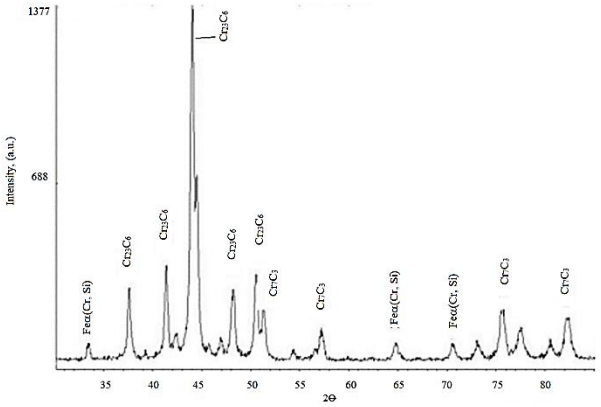

Fig. 1 – Diffractogram of steel 20 after chromosiliconizing: T = 1050 °C, τ = 6 h (surface). $CuK_{\alpha 1}$ radiation, λ = 0.1541841 nm

As the microstructural analysis showed, the resulting coatings have two zones parallel to the diffusion front, with a clearly defined boundary of the coating-substrate separation (Fig. 2). The first outer zone of the coating based on $Cr_{23}C_6$ and Cr_7C_3 carbide, with a thickness of 18 – 20 μm, appears as a light gray band after etching. The second zone is a solid solution of silicon and chromium in α-Fe. The thickness of this zone can reach 80 – 100 microns. The total thickness of the coating is 110 – 120 microns [3]. Our results are consistent with X-ray structural analysis of chromosilicide coatings obtained by the powder method in a container [3, 9].

The chemical composition of the obtained chromosilicide coating was studied by micro-X-ray spectral analysis (Fig. 2, Table 1). It was established that the outer layer (spectrum 1, spectrum 2) contains chromium and carbon in the amount of 71.14 – 69.96 % by mass, 25.74 – 25.13 %. Respectively and corresponds to chromium carbides $Cr_{23}C_6$ and Cr_7C_3. In addition, this layer contains silicon and iron in the amount of 0.15 – 0.26 wt. % and 2.95 – 4.65 wt. %, respectively. Directly below it is a layer of a solid solution of chromium and silicon in α-iron (spectrum 3, 4). The concentration of silicon and chromium in this layer is relatively high and is 3.89 – 2.82 % by mass and 16.06 – 14.95 % by mass, respectively.

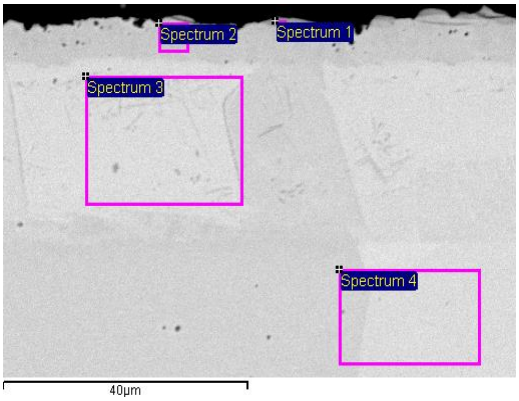

Fig. 2 – Microstructure of steel 20 after chromosiliconizing; snapshot in backscattered electrons

Thus, it was established that on the surface of steel 20 after chromosiliconizing, coatings consisting of chromium carbides and a solid solution of silicon and chromium in α-iron are formed. At the same time, the maximum amount of silicon is observed in the inner zone of the coating at a depth of 15 – 50 μm from the surface (3.89 – 2.82 wt. %), namely in a solid solution of silicon and chromium in α-iron.

The distribution of the microhardness of chromosilicide coatings, obtained along the cross-section of the diffusion layer, was studied (Fig. 3). The obtained results are consistent with the layer-by-layer X-ray structural analysis data. The microhardness of the surface layer based on chromium carbides $Cr_{23}C_6$ and Cr_7C_3 is relatively high and is 19.5 – 19.0 GPa.

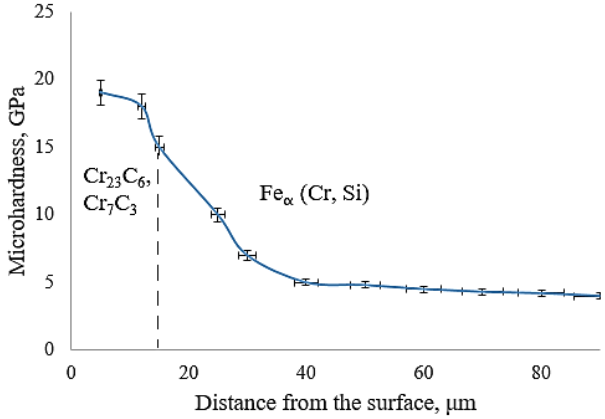

Fig. 3 – Distribution of microhardness across the cross-section of steel 20 coating after chromosiliconizing

The higher microhardness of the resulting layer compared to pure chromium carbides [3] is due to doping the latter with silicon. The decrease in microhardness begins at a depth of 15 μm, which is explained by the strengthening of the interference maxima of α-Fe and the gradual disappearance of peaks from chromium carbides. It should be noted that this distribution of microhardness across the cross-section of the coating should lead to a decrease in internal stresses in the coating and contribute to an increase in its adhesion to the base [3, 4].

Applying 20 complex chromosilicide coatings to the surface of steel increases its heat resistance and corrosion resistance in various aggressive environments.

Studies of the heat resistance of samples made of steel 20 with chromo-silicide coatings on a derivatograph showed that the resulting coatings have high heat resistance in the entire investigated temperature range for one hour (Fig. 4). It was established that during heating in the temperature range of 150 – 200 °C, the course of only one chemical reaction associated with heat absorption is observed. At the same time, despite the significant exothermic effect in the specified temperature range, no significant changes are marked on the curves of mass change (2) and rate of mass change (4). The lack of change in the mass of samples with a chromo-silicide coating when heated to 1000 °C may indicate that it is in this interval that a dense oxide film of chromium and silicon, possibly small in mass and thickness, is already formed on the surface of the coatings, which protects the diffusion layer from further oxidation. The obtained coatings practically do not oxidize up to 1000 °C, while single-component chromium coatings have mostly low heat resistance at temperatures above 900 °C [3, 4].

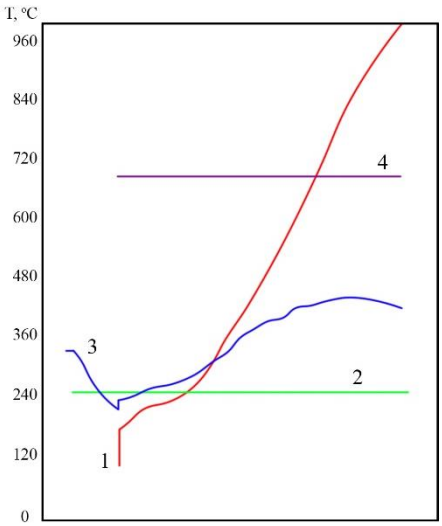

Fig. 4 – Curves of changes: heating line (1), mass (2), rate of mass change (4) and changes in heat content (3) obtained during the oxidation of chromosilicate coatingfor one hour

X-ray structural studies (Fig. 5) showed that the appearance of a thin chromium oxide film (Cr_2O_3) was recorded on the surface of the oxidized coating. The formation of silicon oxide SiO_2 is observed at a depth of 10 – 15 microns at the border of the carbide zone and the solid solution of chromium and silicon in α-iron. The latter acts as a barrier layer that inhibits the penetration of oxygen into the depth of the coating and prevents the formation of iron-based oxides, which have a low protective effect. Our results are consistent with the authors' data in [10], where the impregnation of silicon oxide in the depth of the iron-chromium-silicon alloy layer significantly increases its heat resistance. The authors discussed and confirmed the formation of barrier layers during the application of coatings to improve their functional characteristics [10, 11].

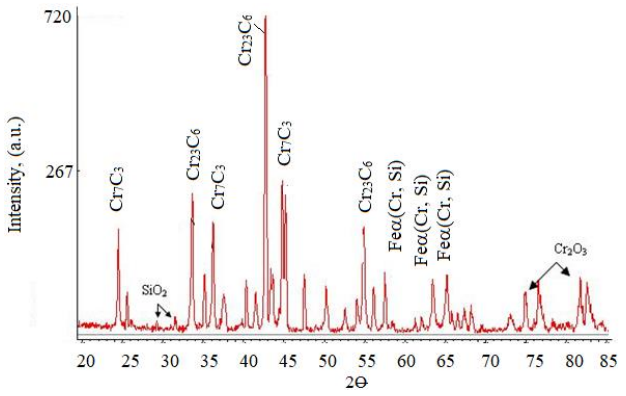

Fig. 5 – The diffractogram of steel 20 after chromosiliconizing and subsequent oxidation at a temperature of 1000 °C. $CuK_{\alpha 1}$ radiation, $\lambda = 0.1541841$ nm

Massometric studies carried out for six hours showed that the obtained chromosilicid coatings on steel 20 increased its heat resistance at 700 °C with exposure for 6 hours by 60.0 times (Fig. 6).

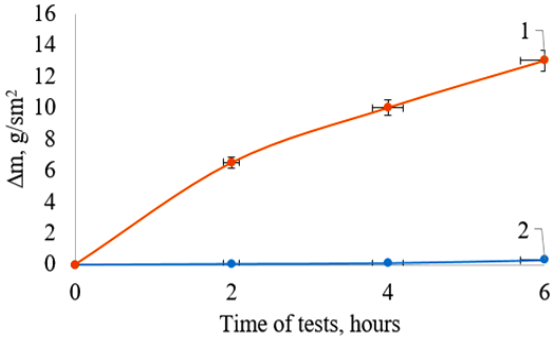

Fig. 6 – Kinetic curves of oxidation of steel 20 (1) and steel 20 with a diffusion chromosilicid coating (2) at a temperature of 700 °C

The effect of chromosilicide coatings on the corrosion of steel 20 in industrially important aqueous aggressive environments was studied. The corrosion resistance of steel with diffusion coatings, like that of steel 20, increases in the following direction: 15 % aqueous solution of H_2SO_4 → 15 % aqueous solution of HCl → 15 % aqueous solution of H_3PO_4 → 10 % aqueous solution of CH_3COOH → 3 % aqueous solution of NaCl → technical water. But unlike steel 20, chromosilicid coatings show more excellent corrosion resistance in 10 % HNO_3 than in 15 % H_2SO_4 and HCl solutions.

The established different corrosion resistance of steel and steel with coatings in the test environments is caused by the influence of several factors on the corrosion process: various types of depolarization of corrosion processes (hydrogen - in solutions of reducing acids, oxygen - in a solution of 3 % NaCl and technical water, hydrogen-oxygen - in solution of 10% CH_3COOH, mainly oxidizing - in HNO_3 solutions) and different effects of solution anions (activating - ions SO_4^{2-}, Cl^-, passivating - ions NO^{3-}, PO_4^{2-}) on anodic dissolution of metals.

Applying chromosilicide coatings leads to inhibition of corrosion of steel 20 in all tested aggressive environments. The most excellent protective effect of chromosilicide coatings is found in a 10 % aqueous solution of HNO_3,

Table 1 – The content of elements in the coating of steel 20 after chromosiliconizing

Measurement point	Layer of coating	C, wt %	Si, wt %	Cr, wt %	Fe, wt %
Spectrum 1	$Cr_{23}C_6$	25.74	0.15	71.14	2.97
Spectrum 2	$Cr_{23}C_6$ Cr_7C_3	25.13	0.26	69.96	4.65
Spectrum 3	Feα (Cr,Si)	12.45	3.89	16.06	67.6
Spectrum 4	Feα (Cr,Si)	10.22	2.82	14.95	72.01

where during 24-hour corrosion tests, the corrosion inhibition coefficient γ is 30.1, and the degree of protection $Z = 96.7$ %. The obtained coatings have a much lower protective effect in solutions of 10 % CH_3COOH, 3 % NaCl, technical water, and 15 % H_3PO_4, while the values of corrosion inhibition coefficients γ are equal to 4.0 – 7.7 times, and the degree of corrosion protection $Z = 75 – 87$ %. The least protective effect of chromosilicide coatings is found in solutions of sulfuric and hydrochloric acids, which γ are 3.0 and 3.1, $Z = 67.7 – 66.6$ % during 24-hour corrosion tests. During more extended corrosion tests (144 – 576 hours), the corrosion inhibition coefficients γ in solutions of 10 % CH_3COOH, 3 % NaCl, and technical water increase and are equal to 12.0, 9.0, 8.5, respectively, and in solutions of sulfuric and hydrochloric acids are significantly reduced. The increase over time in the protective action of the research coatings under conditions of corrosion with oxygen depolarization (technical water, CH_3COOH solutions, 3 % NaCl) is due, in our opinion, to the formation of chromium and silicon oxide coatings on the surface, which show high chemical resistance in these environments. The decrease over time in the protective effect of chromosilicide coatings in solutions of reducing acids (sulfate, chloride) is associated with a low overvoltage of hydrogen release on chromium carbides, acceleration over time of the partial reaction of cathodic hydrogen release, and the formation of a galvanic vapor. It acts as an anode.

The possibility of increasing the corrosion resistance of steel 20 with chromosilicid coatings by introducing oxidizing inorganic additives (molybdates, chromates, permanganates) into aggressive solutions has been established [3, 12-14]. It is shown that the introduction of 3 g/l of sodium molybdate into 10 % solutions of phosphoric, hydrochloric, and sulfuric acids increases the corrosion resistance of chromosilicide coatings by 4.0; 6.0; 34.0 times, respectively, and provides a degree of protection against corrosion at the level of 75.0 – 96.2 %.

As a result, the use of an improved gas treatment method allows to obtain on steel 20 a diffusion coating based on chromium and silicon with high microhardness, heat resistance, and corrosion resistance, which makes it possible to recommend them for work under conditions of specific loads, the effect of elevated temperatures and the influence of aggressive environments.

4. CONCLUSIONS

1. Diffusion chromosiliconizing in a specially designed reaction chamber makes it possible to obtain on the surface of steel 20 complex protective coatings based on chromium carbides $Cr_{23}C_6$ and Cr_7C_3 and a zone of a solid solution of chromium and silicon in α-iron. The total thickness of the obtained coatings is 90 – 110 microns. The microhardness of the coating is 19.5 GPa on the surface and gradually decreases as it moves deeper into the coating to 4.0 GPa.

2. Chromosilicide coatings have high heat resistance up to a temperature of 1000 °C due to chromium and silicon oxides forming in the coating layer. It was established that the formed silicon oxide at the boundary of the carbide zone and the solid solution of chromium and silicon α-iron act as a barrier layer that ensures high heat resistance of chromo-silicide coatings.

3. Chromosilicide coatings have high corrosion resistance in acid solutions, 3 % NaCl solutions, and technical water solutions. Applying chromosilicide coatings on steel 20 increases corrosion resistance in the tested solutions by 2.5 – 30.0 times.

4. It is possible to increase the corrosion resistance of chromosilicide coatings in solutions of mineral acids by introducing inorganic oxidizing additives (sodium molybdate) into aggressive solutions.

5. Diffusion chromosilicide coatings, according to their composition, structure, and properties, can be promising for use in conditions of specific loads, high temperatures, and aggressive environments.

REFERENCES

1. I.P. Buryk, D.V. Velykodnyi, L.V. Odnodvorets, I.E. Protsenko, E.P. Tkach, *Tech. Phys.* **56** No 2, 232 (2011).
2. L.V. Odnodvorets, I.Yu. Protsenko, O.P. Tkach, Yu.M. Shabelnyk, N.I. Shumakova, *J. Nano- Electron. Phys.* **9** No 2, 02021 (2017).
3. I. Pohrebova, K. Yantsevych, *Visnyk KhNTU* **85** No 2, 71 (2023).
4. V.G. Hignjak, G.Y. Calashnicov, N.A. Harchenko, T.P. Hovorun, O.V. Hignjak, V.Y. Dolgikh, O.O. Holyshevskiy, *J. Nano- Electron. Phys.* **7**, No 4, 04033 (2015).
5. A.D. Pogrebnjak, V.M. Beresnev, O.V. Bondar, B.O. Postolnyi, K. Zaleski, E. Coy, S. Jurga, M.O. Lisovenko, P. Konarski, L. Rebouta, J.P. Araujo, *Mater. Design* **153** No 9(5), 47 (2018).
6. B. Sereda, I. Kruglyak, D. Sereda, I. Palehova. *Perspektyvni Tekhnolohiyi ta Prylady* **21**, 6 (2022).
7. V.I. Sihova, V.H. Khyzhnyak, N.A. Kurylo. *Visnyk Sum-DU: Tekhnichni nauky*, **2**, 73 (2007).
8. V.F. Loskutov, M.M. Bobina, T.V. Loskutova, I.S. Pohrebova, K.V. Yantsevych, *Sposib nanesennia dyfuziinykh pokryttiv*. [*The method of applying diffusion coatings*]. deklaratsiinyi patent Ukrainy na vynakhid 50165A. opubl. 15.10.2002, Biul. No 10.
9. N.A. Kharchenko, A.I. Degula, V.G. Hignjak, T.P. Hovorun, I.Y. Smokovych, *J. Nano- Electron. Phys.* **12** No 3, 03038 (2020).
10. Yu.G. Gogotsi, R.A. Andrievski, *Materials Science of Car-*

bides, Nitrides and Borides (Springer Science & Business Media: 2012).
11. M.A. Deyab, S.S. Abd El-Rehim. *Electrochimica Acta* **53** No 4, 1754 (2007).
12. V.G. Hignjak, T.V. Loskutova, T.Y. Kalashnikov, O.I. Mykolaychuk, *J. Superhard Mater.* **40** No 3, 170 (2018).
13. I.S. Pogrebova, T.M. Pilipenko, *Mater. Today: Proc.* **6** No 2, 191 (2019).
14. M.C. Saremi, Dehghanian, Sabet M. Mohammadi, *Corros. Sci.* **48** No 6, 1404 (2006).

Структура і захисні властивості комплексних хромосиліцидних дифузійних покриттів на сталі 20

І. Погребова[1], К. Янцевич[2], Т. Лоскутова[1], Н. Харченко[3], Т. Говорун[3]

[1] *Національний технічний університет України «КПІ ім. І. Сікорського», Берестейський проспект, 37, 03056 Київ, Україна*
[2] *Інститут електрозварювання ім. Є.О. Патона НАН України, вул. Казимира Малевича 11, 03150 Київ, Україна*
[3] *Сумський державний університет, вул. Римського-Корсакова, 2, 40007 Суми, Україна*

В роботі наведені результати досліджень структури, хімічного складу, мікротвердості, жаро та корозійної стійкості багатокомпонентних покриттів, отриманих при дифузійному хромосиліціюванні сталі 20. Покриття наносили у спеціально розробленій реакційній камері при температурі 1050 °С впродовж 6 годин на поверхню вуглецевої сталі 20 в замкненому реакційному просторі при пониженому тиску активної газової фази, для формування якої використовували раціональні кількості кремнію та хрому, а також чотирихлористий вуглець, як активатор. Встановлено, що отримані покриття складаються з карбідів хрому $Cr_{23}C_6$, Cr_7C_3, легованих кремнієм, і зони твердого розчину хрому і кремнію в α-залізі. Максимальна кількість кремнію спостерігається у внутрішній зоні покриття (2.82 – 3.89 мас. %) на глибині 15 – 50 мкм. Загальна товщина покриття становить 110 мкм, мікротвердість поверхневих шарів – 19.5 ГПа. Поверхневі шари покриттів, на основі хрому та кремнію, призводять до утворення захисних плівок Cr_2O_3, $A1_2O_3$, що забезпечує їх високу жаростійкість в атмосфері повітря та корозійну стійкість в окислювальних кислотах. Встановлена можливість підвищення корозійної стійкості сталі 20 з хромосиліцидними покриттями шляхом введення в агресивні розчини неорганічних окислювачів.

Ключові слова: Дифузійні покриття, Мікротвердість, Хромосиліціювання.