Surface modification of low carbon steel to improve corrosion resistance

S Pakhomova
Bauman Moscow State Technical University, 5 Second Baumanskaya Street, Moscow, 105005, Russian Federation

E-mail: mgtu2013@yandex.ru

Abstract. Issues of improving the operational properties of low-carbon steels by coating are considered. It is shown that aluminum and chromium coatings increase the corrosion resistance of precision alloys without deterioration of their magnetic properties. It has been established that chromium coatings are more promising.

Introduction

Unalloyed electrical steels have the same chemical composition as technically pure iron - they contain the same amount of carbon and impurities [1, 2]. Electrical steels are used as low-frequency soft-magnetic materials with high saturation magnetic induction for the manufacture of a wide range of magnetic conductors: low-voltage relays, switches, and the like [3, 4]. Electrical steels are supplied with guaranteed magnetic characteristics: the value of the coercive force \(H_c\) and magnetic saturation induction \(B\). The most used steel grades are 20895, 20864 and 20848, which have \(H_c\) respectively 95, 64 and 48 \(A/m\), and \(B — 2.05 T\) (GOST 3836–83). A significant disadvantage of this class of steels is their low corrosion resistance in atmospheric corrosion conditions. To increase the corrosion resistance, chemical heat treatment of steels is necessary, forming single-component or multi-component coatings that are resistant to the environment without deterioration of the soft-magnetic properties [5-8]. There are different types of chemical-thermal treatment, such as carburization and nitriding. However, it is known that after carburization, parts have low corrosion resistance [9, 10], and after nitriding — low operating temperatures.

Low electrical resistivity (less than 0.1 \(\mu\Omega m\cdot m\)) of these steels leads to an increase in heat losses when the frequency of remagnetization increases, while the loss of hysteresis depends on the magnitude of the coercive force [11]. Therefore, different types and modes of coating formation should not be accompanied by an increase in the coercive force of electrical steels, which leads to an increase in hysteresis losses.

It is known that one of the ways to increase the corrosion resistance of steels of this class is the diffusion saturation of their surface with aluminum or chromium [12, 13]. Previous studies have shown that one of the most modern and effective is the circulation method of alitizing and chrome-plating [14, 15]. Carrying out the surface deformation hardening after chemical-thermal treatment can not increase the corrosion resistance, since it will lead to an increase in stress in the surface layer [16, 17].

Improvement of the circulation method required further studies of the influence of technological factors of the process, both on the corrosion resistance of coatings and on the magnetic properties of electrical steels [18].
In this work, the purpose of applying the diffusion coatings was to provide corrosion resistance in a humid industrial air atmosphere while maintaining the magnetic properties of electrical steels of grades 20864 and 20895 (Table 1).

Table 1. Chemical composition of both steels 20864 and 20895

| No | C      | Si | Mn | S      | P      | Cu |
|----|--------|----|----|--------|--------|----|
| 1  | <0.035 | <0.3| <0.3| <0.03  | <0.02  | <0.3|

They were used to create single-component alitized or chrome-plated coatings using the circulation method. The initial microstructure of both steels where shown on Fig. 1.

![Fig. 1. The initial microstructure of steels 20864 (a) and 20895 (b)](image)

Research methods
The influence of technological factors, such as process temperature, duration of the process and the composition of the saturating medium on the coating thickness $\Delta h$, the coercive force $H_c$ and the corrosion resistance of steels, has been studied.

To preserve the soft-magnetic properties of the coating structure over the entire thickness should be single-phase. For an alitized coating, this structure is preserved if the concentration of aluminum in the steel is not more than 7% (wt.). It is obvious that the concentration of aluminum in the alitized layer is higher. Therefore, it was necessary to evaluate the effect of annealing (before or after alitizing) on the possibility of improving the soft-magnetic properties.

For chrome-plating coatings, there are no such restrictions, since the solubility of chromium in steel is unlimited. In this case, the chromium content for high corrosion resistance in humid air should be at least 12.5...13.0% (wt.).

The alitizing process was carried out by the circulation method at a temperature of 950 °C, the exposure during the diffusion saturation process was two or four hours; cooling was carried out at a certain controlled speed of 40 or 100 °C/h. For comparison, the process of alitizing combined with annealing in different sequences.

The thickness of the alitized coating was determined by metallographic method on cross-sections after etching in a 5% alcohol solution of nitric acid.

Chrome-plating was performed by the same circulation method. The composition of the sending gas medium was characterized by the amount of chromium metal and ammonium chloride NH4Cl. The influence of the process temperature, the duration of exposure at diffusion saturation, and the composition of the sending gas medium on the thickness of the chrome coating was studied.
The thickness of the chrome-plating coating was also measured metallographically on strips etched first with a 5% solution of nitric acid to reveal the structure of the base, and then - in a special reagent (a mixture of picric and hydrochloric acids) to reveal the structure of the coating itself. In some cases, the thickness of the coating was estimated by the value of microhardness.

The influence of heat treatment on the structure and properties of single-component coatings was studied by x-ray and microstructure studies.

**Experimental results and their discussion**

Studies have shown that alitized layer has a sufficient thickness and uniform at different sites of the coating (Fig. 2a). The coating has good corrosion resistance. X-ray studies have revealed the presence of several phases in the structure that contribute to a decrease in soft-magnetic properties and an increase in the coercive force (Table 2).

![Fig. 2. The microstructure of steel 20864 after the alitizing 950°C, 4 h (a) and chrome-plating 950°C, 4 h (b)](image)

| Chemical heat treatment          | Cooling speed, °C/h | Layer thickness Δh, μm |
|---------------------------------|---------------------|------------------------|
| Type of processing              | τ, °C | τ, h |                     |
| Alitizing                       | 2    |  100 | 150                  |
| 950                             | 2    |  40  | 130                  |
| Alitizing + annealing            | 2 + 2 | 40  | 210                  |
| Annealing + alitizing           | 2 + 2 | 40  | 200                  |

Increasing the exposure time from 2 h to 4 h increases the thickness from 130 μm to 200 μm. The effect of the cooling rate on the coating thickness is negligible. The effect of annealing in the same installation without supplying a saturating mixture was studied. Annealing for 4 h, only due to the remains of saturating mixtures in the chamber created a coating with a thickness of 75 μm. Annealing before and after of alitizing effect on the properties as well as increasing the exposure time.

At the obtained thicknesses, we should expect significant concentrations of aluminum in the layer, and, consequently, the presence of Fe₃Al, FeAl or FeAl₂ type aluminides. The presence of such phases increases the coercive force, while reducing the magnetic properties. For corrosion resistance, such phases are not dangerous, since they are cathodes that accelerate the passivation of the aluminum coating. However, too large thicknesses are still undesirable, because the outer surface of the layer becomes loose and therefore less resistant to corrosion [19].
Studies of chrome coatings have shown that the microhardness of the coating is higher than that of the base. This is the result of the formation of a solid solution-chromic ferrite, since the dissolution of chromium in ferrite creates stresses in the crystal lattice.

The obtained values of layer thicknesses during chrome-plating are significantly less than during alitizing, although the chromium saturation process was performed at higher temperatures and longer exposures (Fig. 2b). At the same time, even at a thickness of 90 \( \mu \text{m} \), the outer surface of the coating was loose.

The effect of chrome plating temperature on the coating thickness is more effective than the duration of exposure (Fig. 3). The intensity of chromium saturation increases with an increase in the amount of ammonium chloride in the saturating gas medium.

![Fig. 3. Depens of thickness \( \Delta h \) from electrical steel 20864 chrome-plating technological modes: 1 — 850°C, 2 — 950°C, 3 — 1050°C, 4 and 5 — 1150°C; composition of the medium: 1 — 4 — (Cr 100 g + NH4Cl 25 g), 5 — (Cr 100 g + NH4Cl 50 g).]

The measured coating thicknesses are in good agreement with the basic laws of diffusion and kinetics of chemical reactions: exponential temperature dependence and power-time dependence [20, 21].

Based on the diffusion representations [3, 12], it becomes understandable that at the same temperatures and time parameters of diffusion saturation, the thickness of the layers in alitizing is significantly greater than in chrome-plating. It is known that the diffusion mobility of aluminum in steel is much greater than that of refractory chromium [22]. This confirms the reliability of the results obtained.

X-ray study of the effect of heat treatment on the structure and properties of single-component coatings showed that alitized coatings in all treatment modes have multiphase structures consisting of a solid solution of aluminum in a low-temperature modification of iron and aluminides. The presence of such intermediate phases is favorable for corrosion resistance and undesirable for the soft-magnetic properties of steel.

Cold-rolled steel 20864 with traces of riveting was used for alitizing, which adversely affected the magnetic properties, which were determined on ring samples by the ballistic method (GOST 11036–75). The use of vacuum pre-annealing significantly improved the magnetic characteristics by eliminating the hardening. Since the altering was carried out practically at annealing temperatures, this made it possible to assume that the slope would be eliminated during the altering process. In order to find out whether pre-annealing can be canceled, alitizing was performed before and after annealing (see Table 2 and Table 3).
Table 3. Effect of heat treatment on the layer thickness and properties of steel 20864

| Annealing | Type of coating | Layer thickness Δh, µm | Hc, A/m |
|-----------|-----------------|------------------------|--------|
| t, °C     | COMPOSITION OF THE MEDIUM |                      |        |
| 950       | 2 – Al          | 130                    | 110    |
| 1150      | 3 NH4CL        | 90                     | 63     |
| 1000      | 5 NH4CL        | 45                     | 82     |
| 1040      | 8 Si/Al=1      | 7                      | 65     |
| 1100      | 8 Si/Al=1/2    | 20                     | 72     |

The results obtained showed that heat pre-treatment does not significantly change either the layer thickness or properties, and an increase in the annealing temperature affects the properties as well as an increase in the exposure time during the alitizing process.

The study of the coating structure after the chrome-plating showed that it is mainly single-phase due to the unlimited solubility of chromium in the low-temperature modification of iron. X-ray structural analysis showed the traces of chromium carbide and σ–phase on the outer surface of the chrome-layer. This structure is favorable for obtaining high corrosion resistance and preserving the magnetically soft properties of steel. At the same time, the thicker the dense part of the coating and more chromium in it, the higher the corrosion resistance and magnetic properties.

Compared with aluminum, the diffusive mobility of chromium is less, so to obtain larger thicknesses, the chrome plating process requires higher temperatures and exposures. Such modes create a large-crystal structure, which significantly improves the magnetic properties.

Table 4. Effect of chrome-plating modes in a chloride environment on the layer thickness and magnetic properties of steel 20895

| Chrome-plating | Layer thickness Δh, µm | Hc, A/m |
|---------------|------------------------|--------|
| t, °C         | NH4CL, g on 100 g Cr   |        |
| 850           | 3                      | 15     | 90    |
|               | 1                      | 25     | 76    |
| 950           | 3                      | 25     | 30    | 86    |
|               | 6                      | 25     | 38    | 77    |
| 1000          | 6                      | 25     | 35    | 87    |
|               | 1                      | 25     | 25    | 87    |
| 1040          | 3                      | 25     | 50    | 78    |
|               | 6                      | 25     | 75    | 78    |
| 1100          | 6                      | 25     | 120   | 72    |
|               | 9                      | 25     | 75    | 78    |
| 1150          | 6                      | 25     | 40    | 73    |
|               | 3                      | 25     | 65    | 72    |
|               | 3,5                    | 10     | –     | 60    |
|               | 3,5                    | 25     | 65    | 69    |
|               | 2,5                    | 20     | 65    | 72    |
|               | 2,5                    | 50     | 65    | 58    |
|               | 1                      | 50     | 100   | 84    |
|               | 3                      | 50     | 138   | 69    |
|               | 3,5                    | 25     | 88    | 69    |
|               | 6                      | 25     | 165   | 62    |
|               | 3                      | 50     | 165   | 62    |
The study of chrome-plating modes on the coating thickness and magnetic characteristics of steel 20895 was conducted. The first series of tests included circulation chrome-plating in the medium of solid chromium and ammonium chloride (Table 4). The composition of the mixture was studied by changing the ratio of chromium and ammonium chloride. It was found that the thickness and properties of coatings are less affected by changes in the ratio of the mixture than the exposure time and, especially, the temperature of chrome-plating.

The possibility of chrome-plating in an iodide medium containing chromium and crystalline iodine was studied. Table 5 shows the amount of iodine in grams per 100 g of chromium.

Table 5. Effect of chrome-plating modes in an iodide medium on the layer thickness and magnetic characteristics of steel 20895

| Temperature, °C | Iodine, g on 100 g Cr | Layer thickness Δh, µm | Magnetic induction, Hc, A/m |
|----------------|-----------------------|-------------------------|---------------------------|
| 1100           | 3                     | 17                      | 55                        |
| 1100           | 3                     | 20                      | 58                        |
| 1150           | 3                     | 76                      | 63                        |

The process of chrome-plating in an iodide medium has shown the better magnetic properties, but chrome-plating in chlorides is a more environmentally friendly process.

Research has shown that circulation chrome-plating of electrical steels in an active chloride medium gives a uniform diffusion layer, which significantly improves both corrosion resistance and soft-magnetic properties. Thus, electrical steel 20895 in the initial state had \( H_c = 140 \, \text{A/m} \), and after chrome-plating in a mixture of 25% \( \text{NH}_4\text{Cl} \) per 100 g (for 3 h at \( t = 1150^\circ\text{C} \)) — 63 A/m.

Conclusions
1. Alitizing and chrome-plating of electrical steels is accompanied by an increase in their corrosion resistance.
2. Chrome-plating coatings with a thickness of 30...60 µm and chromium content of 50...58 % have the highest corrosion resistance.
3. Chrome-plating of electrical steels improves their soft-magnetic properties due to the refining action of chromium.
4. Alitizing increases the coercive force and reduces the magnetic properties as a result of the formation of \( \text{Fe}_3\text{Al} \) and \( \text{FeAl} \) type aluminides.

References
[1] Qin J., Yang P., Mao W., Ye F. Effect of texture and grain size on the magnetic flux density and core loss of cold-rolled high silicon steel sheets. J Magn Magn Mater, 2015, 393:537–43.
[2] Yajiang L., Juang V., Puchkov Yu.A., Gerasimov S.A. Structure and composition of the transition zone of welded joints of \( \text{Fe}_3\text{Al} \) intermetallic and low-carbon steel // Metal Science and Heat Treatment. 2008, vol. 50, No 3–4, pp 200–203. DOI: 10.1007/s11041-008-9026-3.
[3] Evangelista L.R., Lenzi E.K. Fractional diffusion equations and anomalous diffusion. Publisher: Cambridge University Press, 2018, 358 p. DOI: 10.1017/9781316534649
[4] Suslov A.G. Inzheneriya poverkhnosti detaley [Engineering of surface parts]. M.: Mashinostrojenyi, 2008, 320 p.
[5] Kablov E.N., Muboyadzhyan S.A. Erosion-resistant coatings for gas turbine engine compressor blades // Russian metallurgy (Metally). 2017, vol. 2017, No 6, pp 494–504. DOI: 10.1134/S0036029517060118
[6] Muboyadzhyan S.A., Gorlov D.S., Egorova L.P., Bulavintseva E.E. Corrosion-resistant antifretting coating for the protection of blade locking pieces in gte compressors and fans // Russian metallurgy (Metally). 2014, vol. 2014, No 9, pp 725–732. DOI: 10.1134/S0036029514090134
[7] Bakulo A.V., Yakushin B.F., Puchkov Y.A. Structure and corrosion resistance of welded joints of alloy 1151 in marine atmosphere // Metal Science and Heat Treatment. 2017, vol. 59, No 3–4, pp 218–222. DOI: 10.1007/s11041-017-0132-y.

[8] Polyanskiy V.M., Puchkov Y.A., Orlov M.R., Napriyenko S.A., Lavrov A.V. Influence of tensile stresses on the corrosion resistance of titanium alloy VT22 in aqueous solution of NaCl // Inorganic Materials: Applied Research. 2017, vol. No 1, pp 94–99. DOI: 10.1134/S2075113317010294.

[9] Pakhomova S., Fakhurdinov R., Tsinkolenko O., Zolotov B. The influence of carburization technology on performance properties of high-loaded gear wheels // IOP Conf. Series: Materials Science and Engineering. 2020, 747 (2020), pp 012126. DOI:10.1088/1757-899X/747/1/012126.

[10] Pakhomova S.A., Unchikova M.V., Fakhurdinov R.S. Gear wheels surface engineering by deformation hardening and carburization // Materials Science Forum. 2016, T. 870. pp 383–391. DOI: 10.4028/www.scientific.net/MSF.870.383.

[11] Dems M., Komeza K., Szulakowski J., Kubiak W. Modeling of core loss for non-oriented electrical steel // The International Journal for Computation and Mathematics in Electrical and Electronic Engineering. 2019. T. 38, No 6, pp 1874–1884. DOI: 10.1108/COMPEL-09-2018-0339.

[12] Wei-Jen Cheng, Chaur-Jeng Wang. Study of microstructure and phase evolution of hot-dipped aluminide mild steel during high-temperature diffusion using electron backscatter diffraction // Appl. Surf. Sci. 2011, No 257, pp 4663–4668. DOI: 10.1016/j.apsusc.2010.12.118.

[13] Wei-Jen Cheng, Chaur-Jeng Wang. Growth of intermetallic layer in the aluminide mild steel during hot-dipping // Surf. Coat. Technol. 2009, No 204, pp 824–828. DOI: 10.1016/j.surfcoat.2009.09.061.

[14] Arzamasov, B.N., Simonov, V.N. Circulation method for depositing diffusion coatings // Metal Science and Heat Treatment. 2011. vol. 52, No 9–10, pp 403–407. DOI: 10.1007/s11041-010-9291-9.

[15] Simonov, V.N., Unchikova, M.V., Shkretov, Yu.P. One-stage process of chromoaluminizing of gas turbine blades by the method of circulation // Metal Science and Heat Treatment. 2009, vol. 52, No 9–10, pp 501–504. DOI: 10.1007/s11041-010-9201-1.

[16] Pakhomova S. A., Manayev O. I. Effect of Heat Shotblast Treatment Exerted on the Contact Fatigue of Carburised Heat-Resistant Steel C0.12Cr2NiWV // Inorganic Materials: Applied Research. July. 2018. T 9, No 4, pp 732–735. DOI: 10.1134/S2075113318040251.

[17] Pakhomova, S.A., Ryzhov, N.M., and Vasil’ev, V.R., Changes in the structure of martensite of iron-nickel alloys under the action of thermal shot blast treatment // Met. Sci. Heat Treat. 2001, vol. 43, No. 11–12, pp. 438–439. DOI: 10.1023/A:1014855712535.

[18] Simonov, V.N., Abramov, N.V., Shkretov, Yu.P., Lukina, V.V., Terekhin, A.M. Chromo-aluminizing of cooled blades of gas turbines by circulation method // Metal Science and Heat Treatment. 2007, vol. 49, No 7–8, pp 362–365. DOI: 10.1007/s11041-007-0066-x.

[19] Muboyadzhyan S.A., Galoyan A.G. Diffusion aluminide coatings for protecting the surface of the internal space of single-crystal turbine blades made of rhenium- and rhenium-ruthenium-containing high-temperature alloys: part 2 // Russian metallurgy (Metally). 2013 vol. 2013, No 3, pp 198–205. DOI: 10.1134/S0036029513030075.

[20] Budinovskii S.A., Muboyadzhyan S.A., Gayamov A.M., Stepanova S.V. Ion-plasma heat-resistant coatings with composite barrier layer for protecting alloy ZHS36VI from oxidation // Metal Science and Heat Treatment. 2011, vol. 53, No 1–2, pp 32–38. DOI: 10.1007/s11041-011-9336-8.

[21] Brodova I.G., Shirinkina I.G., Yablonskikh T.I., Astafev V.V., Zaikov Y.P., Kovrov V.A., Shchepanyuk Y.M., Pingin V.V., Vinogradov D.A., Golubev M.V. Structure and phase composition of protective coatings on steel produced by methods of liquid-phase calorizing // The Physics of Metals and Metallography. 2015, vol. 116, No 9, pp 879–887. DOI: 10.7868/S0015323015090041.
[22] Święcz R., Oniszczuk-Święcz D. Experimental investigation of surface layer properties of high thermal conductivity tool steel after electrical discharge machining // Metals. 2017, vol. 7. No 12, pp 550. DOI: 10.3390/met7120550.