Effect of titanium and chromium diffusion coatings on corrosion resistance of sintered iron

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Abstract. The authors have studied the effect of titanium and chromium diffusion coatings on corrosion resistance of sintered iron in solutions of acids and salts. The samples of 85% density were obtained from powdered iron by static pressing in press dies and sintering in vacuum. The diffusion coatings were applied in molten lead with titanium and chromium additives at the temperature of 1100°C and 2 hours exposure time. Microstructure of the samples was then explored by the optical metallography method. The content of elements in the coatings was measured using energy dispersive X-ray microanalysis. Studies of corrosion resistance of the samples in solutions of acids and salts were conducted by the gravimetric method. Corrosion resistance was also evaluated by time to the first corrosion foci emerging and the area of corrosion damage. Diffusion titanium and chromium coatings have ensured higher corrosion resistance of sintered iron in all the aggressive media studied. Chromizing is the most efficient for protecting sintered iron in solutions of sulphuric and nitric acids, as well as in media containing acetic acid and hydrogen peroxide. Meanwhile, titanizing is the most efficient for protecting sintered iron in sea water.

1. Introduction
Corrosion resistance is one of the major characteristics of machine parts; knowing it allows using the materials correctly and selecting reliable and cost-efficient coatings for them. As a rule, sintered materials feature lower corrosion resistance than the cast and rolled stocks [1]. Corrosion resistance of sintered materials decreases as the residual porosity increases. The presence of pores and porous channels leads to a larger active surface of the material, which triggers the development of corrosion processes on the external and internal surfaces simultaneously. The studies conducted [2-4] demonstrate that it is pores that are the point where corrosion emerges in sintered stainless steels in various aggressive media. The pores cause local crevice corrosion which spreads along the particle separation boundaries, which ultimately results in partial destruction of the material. According to the work [5], the speed of corrosion is by a factor of 100 higher in sintered steels than that in the massive ones.

For maintaining operability of sintered items in corrosive media, it is expedient to use protective coatings which ensure sealing open porosity of the sintered stock and feature a high strength of adhesion to the base, thus eliminating the coatings peeling from the substrate.

Such properties are found in diffusion titanium, chromium, nickel, and copper-nickel coatings applied in the medium of liquid-metal solutions [6, 7]. This method of coating application relies on the phenomenon of isothermal mass transfer of solid metals through the readily fusible "transport" melt [8, 9]. The coating technology consists in the following: isothermal holding of items in the medium of
low-melting metal is conducted, and the metal or alloy to be making up diffusion coating with the material of the items is introduced into the said medium in the form of powder, pieces, or in the compact state. The low-melting metal acting as the transport medium has to dissolve the diffusion additives while not penetrating into the bulk of the item metal. According to the iron-lead diagram [10, 11], solubility of lead in solid iron at 1530°C amounts to $2.7 \times 10^{-4} \%$ at. Meanwhile, solubility of iron in liquid lead is insignificant: it is $0.08–0.21 \%$ at within the temperature range of 1302–1495°C [11]. So, extremely low mutual solubility of the components eliminates penetration of lead into the surface of sintered iron and prevents liquid lead from dissolving the surface of the parts. This allows using lead as the "transport" melt for applying diffusion coatings on iron.

The studies conducted have shown that this method allows obtaining uniform titanium and chromium coatings on sintered iron which seal off its open porosity [6, 12, 13].

With regard to this, the objective of this paper was to study the effect of titanium and chromium diffusion coatings on corrosion resistance of sintered iron in solutions of acids and salts.

2. Materials and methods

The samples have been manufactured of powdered iron PZhV2.160.26. The blanks in the form of bushings having 16 mm OD, 8 mm ID, and 14 mm high were obtained by static pressing in press dies. The samples were then sintered in vacuum at the temperature of 1100°C. Density of the sintered samples was 85%. Part of the samples were subjected to diffusion titanizing and chromizing. The diffusion coatings were applied in molten lead with titanium and chromium additives at the temperature of 1100°C and 2 hours exposure time. Microstructure of the coated samples was investigated using the MMR-4 metallographic microscope. For making microstructure apparent, the samples were etched with 3% solution of nitric acid in the ethyl alcohol. The content of elements in the coatings was studied by the method of energy dispersive X-ray microanalysis (EDXMA) using SEM JEOL JSM-7500F.

The studies of corrosion resistance of the diffusion coated samples in solutions of acids and salts have been conducted by the gravimetric method. The samples were weighed before and after exposure to aggressive media using the Adventurer AR2140 analytical balance. Before weighing, the samples were carefully cleaned of the corrosion products according to the technique [14] and rinsed with ethyl alcohol. According to the test results, the intensity of corrosion was evaluated as the loss of mass per surface area unit within a certain time. Corrosion resistance of the coatings was also assessed according to the technique [14], by the time to emergence of the first corrosion foci and by the area of corrosion damage. Corrosion resistance of the coatings obtained was tested in the following media:

- 3% aqueous solution of NaCl;
- 20% CH$_3$COOH +20% H$_2$O$_2$ + 60% H$_2$O;
- 10% aqueous solution of H$_2$SO$_4$;
- 0.5% aqueous solution of HNO$_3$.

3. Results and discussion

3.1. Chemical composition and structure of the coatings

Microstructure of the samples with titanium and chromium coatings is shown in figure 1. On the surface of the titanium coating, there is a layer of about 10 µm thickness consisting of the TiFe intermetallic compound with the titanium content of 48 wt % [11]. Under this layer, there is a solid solution of titanium in α-iron with the 2.2–3 wt % content of titanium. At the temperature of 1100°C, diffusion of titanium in γ-iron leads to the γ→α transformation. This results in the diffusion layer forming which consists of α-phase columnar grains aligned with the diffusion flow direction. It can be seen from figure 1 that the coating is differentiated from its base by the line of phase recrystallization. The total thickness of the titanium coating amounts to 120 µm.
The chromium coating represents a solid solution of chromium in α-iron. The content of chromium is 38 wt % on the surface. With distance from the surface, it goes down to making up 12 wt % at the line of phase recrystallization. The average thickness of the chromium coating is 105 µm, but on individual areas, chromium has penetrated into the base somewhat deeper owing to diffusion along defects of the sintered iron structure.

![Figure 1. Microstructure of diffusion coatings on sintered iron, magnified at ×200: (a) titanium coating; (b) chromium coating.](image)

3.2. Corrosion resistance of the coatings. Test results
Figure 2 shows the results of corrosion tests conducted on the 15 hours basis for 85% density iron. It can be seen that chromium coatings feature the highest resistance to the solution containing 20% of CH₃COOH + 20% of H₂O₂ + 60% of H₂O. As for the titanized parts, corrosion foci of around 100–300 µm diameter and approximately the same depth have been found on them after exposure for 15 hours. Obviously, their emergence must be associated with open pores being present in titanium coating. The quantity of corrosion foci amounts to 2–3 per cm². Meanwhile, no such damage occurs if the test duration is up to 1.5 hours.

In the 3% aqueous solution of NaCl imitating sea water, the most efficient protection of sintered iron is ensured by titanium coatings. However, this is only achieved with the high quality of coating having no discontinuities. In the opposite case, the process of electrochemical corrosion develops at the points of discontinuities, and corrosion pits form on the surface of the items. On materials of various densities, resistance of the titanium coatings to 3% aqueous solution of NaCl does not differ significantly.

Diffusion chromizing improves corrosion resistance of sintered iron in 10% aqueous solution of H₂SO₄ and 0.5% solution of HNO₃. It should be noted that chromizing in liquid metal solutions ensures a higher corrosion resistance as compared to solid phase chromizing. In particular, diffusion coating on powdered iron obtained by the solid phase method can only protect the items in 0.5% solution of H₂SO₄ and 0.5 % solution of HNO₃ during time-limited work (less than 1 hour) [8]. Meanwhile, with chromium coatings obtained from liquid metal solutions, no noticeable damage is observed in case of over 6 hours of operation.
Figure 2. Effect of titanizing and chromizing on the weight loss of sintered iron. (a) in solution containing 20% of CH$_3$COOH + 20% of H$_2$O$_2$ + 60% of H$_2$O; (b) in 3% aqueous solution of NaCl; (c) in 10% aqueous solution of H$_2$SO$_4$ and 0.5% solution of HNO$_3$. 
4. Conclusion

Diffusion titanium and chromium coatings have ensured higher corrosion resistance for sintered iron in all the aggressive media under study. Chromizing is the most efficient for protecting sintered iron in solutions of sulphuric and nitric acids, as well as in media containing acetic acid and hydrogen peroxide. Meanwhile, the most efficient coating for protecting sintered iron in sea water is titanizing.

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