Low-temperature deposition process for black phosphate-selenide coatings

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Oxide coatings are widely used as protective and decorative coatings on ferrous metals under non-harsh operating conditions. For protective and decorative oxidation, a chemical oxidation method is widely used using concentrated alkaline solutions (600–800 g/l NaOH) operating at very high temperatures (130–150 °C). The obvious disadvantages of the process are the high energy consumption, difficult working conditions, the aggressiveness of the solutions used and low protective ability of the coatings due to their high porosity. In addition, it is known that to harden the surfaces of machine parts in order to increase wear resistance, they are thermally laser treated. The surface hardening is the more effective, the higher the absorption coefficient of the treated surface. For laser heat treatment, high-temperature (95–98 °C) processes of applying black phosphate coatings with a high absorption coefficient (0.8–0.9) are used. The disadvantages of these processes are also the instability of solutions and the irreproducibility of the results.

This work is about to the study of the process of formation of phosphate-selenide coatings on steel in order to replace high-temperature solutions of black oxidation and phosphating.

A low-temperature process has been developed for the deposition of black selenide-containing phosphate coatings on steel, corresponding to a point of 10 on a ten-point color scale, in a solution containing: 4–8 g/l Na_2SeO_3; 1–4 g/l $CuSO_4 \cdot 5H_2O$; 0.5–5 g/l NaH_2PO_4 and 0.25–2.5 g/l Na_2HPO_4 ($[NaH_2PO_4]/[Na_2HPO_4]$ molar ratio is 2); 5 min at pH = 2–3, t = 18–25 °C.

Oiling the coatings in I-20A industrial oil for 2 min leads to an increase in the protective ability of the coatings according to Akimov from 1 to 25 min.

Corrosion tests of coatings in a salt spray chamber in accordance with ASTM B117 have shown that oiled phosphate-selenide coatings have the greatest protective ability: the first spots of red corrosion appear after 20 hours of testing, while oxidized, oiled samples begin to corrode after 18 hours. After 100 hours of testing, the area of the oxidized sample affected by corrosion is 90 %, and the oiled phosphated sample is 50.

Key words: Protective ability; conversion coatings; black coatings; low temperature blackening of steel; selenide-containing phosphate coatings; passivation of steel.
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Introduction

Oxide coatings, which can be obtained by thermal, thermochemical, chemical and electrochemical methods, are widely used as protective and decorative coatings on ferrous metals under non-harsh operating conditions. Each of them finds its own, the most appropriate area of application. For protective and decorative oxidation, the most widely used chemical oxidation method with the use of alkaline solutions containing 600–800 g/l NaOH, which makes it possible to obtain black or dark blue coatings up to 3 μm thick at temperatures of 130–150 °C. The obvious disadvantages of the alkaline oxidation process are high energy consumption, difficult working conditions and aggressiveness of the solutions used. In addition, coatings formed in alkaline solutions are highly porous and therefore can be used as protective coatings only in light climatic conditions [1, 2]. A more environmentally friendly and energy efficient alternative to protective and decorative black oxide coatings could be black phosphate coatings formed in low-temperature solutions. The relevance of the development of a low-temperature process for the deposition of black coatings is also due to the following fact. It is known that to harden the surfaces of machine parts, the durability of which is determined by their wear resistance, they are thermally laser treated. In this case, surface hardening is the more effective, the higher the absorption coefficient of the treated surface. Processes for applying black phosphate coatings with a high absorption coefficient (0.8–0.9) are being developed especially for laser heat treatment. Known black phosphating processes are also high-temperature (95–98 °C). They have not found wide practical application due to such disadvantages as the instability of solutions and the irreproducibility of the results [3, 4].

This study is devoted to the development of a low-temperature black coating deposition process, which is an alternative to the high-temperature black oxidation and steel phosphating processes.

Materials and methods

When preparing phosphating solutions, reagents of “pure” and “chemically pure” qualifications and distilled water were used. As samples for the deposition of phosphate coatings, we used plates of cold-rolled steel 1008, which is widely used in the automotive industry and other industries.

The mass of phosphate layer (m_{ph}) and the mass of stripped metal (m_{str}) were determined by the gravimetric method according to GOST 9.402-2004 (point 5) [5].

For an accelerated assessment of the protective ability of phosphate coatings, the drop method was used using a solution based on copper sulfate, sodium chloride and hydrochloric acid — Akimov`s reagent [6]. The criterion for assessing the quality of the coating was the time until the color of the control area under the drop changes from gray to red-brown.

Corrosion tests of phosphate coatings were carried out in an Ascott S120iP salt fog chamber in accordance with the international standard ASTM B117 [7], adopted in the automotive industry, and in accordance with GOST 9.401-2018 [8]. The method consists in cyclic alternation of exposure to an aggressive environment (5 % NaCl), tropical atmosphere and indoor conditions.

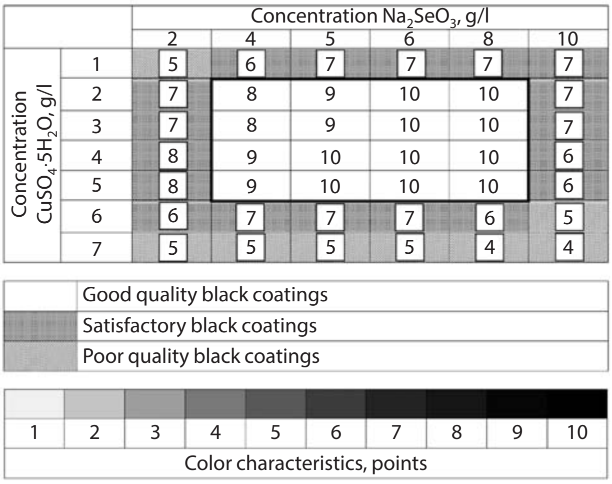
The XPS spectra were recorded using a special CLAM100 camera mounted on an Auger microscope HB100 (Vacuum Generators, GB). The pressure in the working chamber was maintained below 10^{-8} Torr. The Al anode (1486.6 eV) with a power of 200 W was used as an X-ray source. The instrument was calibrated by XPS of Au 4f7/2 metal peaks (Eb = 84.0 eV), Cu 2p3/2 (Eb = 932.5 eV). The pass energy of analyzer was set at 50 eV.

According to the results of the study were obtained survey spectra of coatings, which were decomposed into the constituent spectra of the elements after subtracting the background [9, 10].

Experimental results and their discussion

Taking into account the literature data, initially for the formation black protective and decorative coatings a solution containing sodium selenite Na_2SeO_3 and copper sulfate $CuSO_4{\cdot}5H_2O$ was prepared. The influence of the concentration of the solution components on the appearance and protective ability of the forming coatings at a solution with pH = 2.5 and a temperature of 22 °C was investigated.

The experiments carried out made it possible to determine the concentration range of the solution components, in which it is possible to obtain homogeneous continuous coatings: 4–8 g/l Na_2SeO_3 and 2–5 g/l $CuSO_4{\cdot}5H_2O$ — it is surrounded by a black frame in the diagram (**Fig. 1**).



Concentration $CuSO_4{\cdot}5H_2O$, g/l	Concentration Na_2SeO_3, g/l: 2	4	5	6	8	10
1	5	6	7	7	7	7
2	7	8	9	10	10	7
3	7	8	9	10	10	7
4	8	9	10	10	10	6
5	8	9	10	10	10	6
6	6	7	7	7	6	5
7	5	5	5	5	4	4

☐	Good quality black coatings
▩	Satisfactory black coatings
▨	Poor quality black coatings

1	2	3	4	5	6	7	8	9	10

Color characteristics, points

Fig. 1. Dependence of the appearance of coatings from concentration Na_2SeO_3 and $CuSO_4{\cdot}5H_2O$ on a ten-point color scale (pH = 2–3; t = 22 °C; τ = 5 min)

Outside these ranges, the quality of coatings is degraded. At lower concentrations of selenite ions and copper ions in solution, apparently, formed in the process of conversion of copper and iron selenides, which provide the black color of the coatings, are still insufficient. At high concentrations of selenite ions in the solution, most likely, the etching of the base increases, which leads to a decrease in the compactness of the coatings, and at high concentrations of copper ions in the solution, apparently, the quality of the coating is negatively affected by its contact release on the steel base.

The protective ability according to Akimov (PAA) of coatings formed under these conditions is 15–21 sec, and the color of the formed coatings corresponds to a score of 8–10 on a ten-point black scale (Fig. 1).

Studies have shown that the permissible pH values of solutions are in the range of 2–3 units. Up to pH 2, coatings are not formed, and at pH more than 3 units, the quality of coatings deteriorates — they become discontinuous.

It should be noted that the coatings formed even in the selected area of concentrations were solid, homogeneous and deep black, but they were all smeared.

Taking into account the literature recommendations, the possibility of eliminating this defect by introducing nickel or zinc ions into the solution was investigated. It was found that the introduction of 0.8–1.6 g/l of Zn^{2+} or Ni^{2+} ions into the solution increases the protective ability of the resulting coatings from 20 to 38 sec, however, the desired effect on the compactness of the coatings is not achieved, in addition, the black color of the coatings is lost — point color decreases from 10 to 8.

The possibility of improving the quality of coatings by introducing nitrate ions into the solution has been investigated. It was found that the introduction of 6–12 g/l of sodium nitrate into the solution makes it possible to improve the compactness of the coatings and increase their protective ability, however, the color of the coatings in this case changes from black to dark gray. Despite the improvement in the quality and increase in the protective ability of the forming coatings, it was necessary to abandon the introduction of these additives because of the color of the coatings.

The possibility of achieving the required characteristics of the coating was also tested by introducing into the solution such compounds as m-NBS, hydroxylamine sulfate, and ammonium molybdate. There were no positive effects from the introduction of these substances; moreover, in all cases, the protective ability decreased and the appearance of the coatings deteriorated.

It was possible to improve the quality of the coatings without losing their black color by introducing sodium salts of phosphoric acid Na_2HPO_4, NaH_2PO_4 or Na_3PO_4 into the solution.

The influence of the concentration of phosphates on the quality and protective characteristics of the obtained coatings was investigated (**Fig. 2**). It was found that the introduction of Na_3PO_4 into the working solution practically does not affect the characteristics of the layers. The presence of NaH_2PO_4 or Na_2HPO_4 in the solution leads to an increase in the protective ability of the forming layers. The introduction of 2–3 g/l NaH_2PO_4 or 1–3 g/l Na_2HPO_4 into the solution leads to an increase in the protective ability from 20 to 40 and 33 sec, respectively.

The effect of the concentration of phosphates on the quality and protective characteristics of the coatings has been studied when they are present together in the working solution. It was found that coatings of good quality with maximum protective ability are formed when the NaH_2PO_4/Na_2HPO_4 ratio is 2/1 (**Fig. 3**).

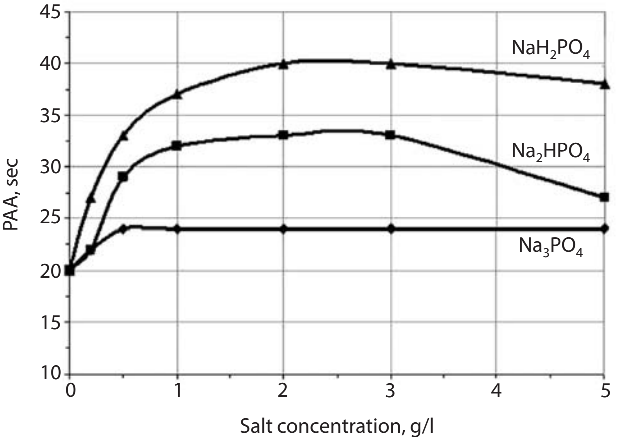


Fig. 2. Effect of phosphate concentration on the protective ability of coatings

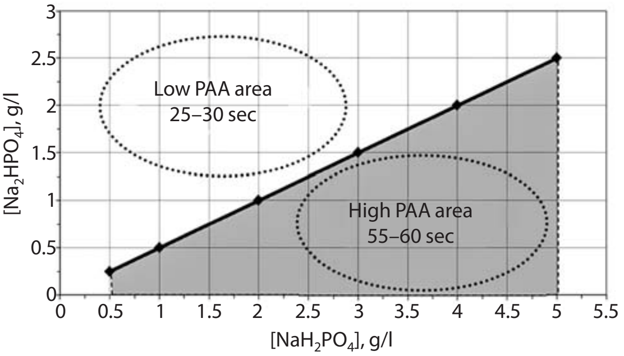


Fig. 3. Dependence of the protective ability of coatings on the ratio $[NaH_2PO_4]/[Na_2HPO_4]$

So, for example, a solution containing 0.5–5.0 g/l NaH_2PO_4 and 0.25–2.5 g/l Na_2HPO_4 ($[NaH_2PO_4]/[Na_2HPO_4] = 2$) allows you to obtain compact, smear-free coatings of deep black colors with a protective ability of 55–60 sec. Outside the limits of this range, the PAA decreases to 25–30 sec.

Thus, the developed solution containing: 4–8 g/l Na_2SeO_3; 1–4 g/l $CuSO_4 \cdot 5H_2O$; 0,5–5 g/l NaH_2PO_4 and 0,25–2,5 g/l Na_2HPO_4 ($[NaH_2PO_4]/[Na_2HPO_4] = 2$); pH = 2–3, t = 18–25°C.

It can be assumed that the process of formation of phosphate-selenide coatings in the developed solution is described by the reactions:

$$Fe + 4NaH_2PO_4 \rightarrow Fe(H_2PO_4)_2 + 2Na_2HPO_4 + H_2$$

$$2Fe(H_2PO_4)_2 + 2Na_2HPO_4 + 0.5O_2 \rightarrow 2FePO_4 + + 4NaH_2PO_4 + H_2O$$

$$3Fe + SeO_3^{2-} + 6H^+ \rightarrow 3Fe^{2+} + Se^{2-} + 3H_2O$$

$$Cu^{2+} + Se^{2-} \rightarrow CuSe$$

$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$$

$$Fe^{2+} + Se^{2-} \rightarrow FeSe$$

Taking into account the above reactions, the forming coating should, probably, along with iron phosphates, also contain copper and iron selenides: CuSe and FeSe. X-ray phase studies have shown that the composition of the coatings, indeed, includes FeSe, CuSe, $FePO_4$ (**Table**).

The criterion for the completion of the conversion coating formation process is the stabilization of the mass of the phosphate layer during the process. As can be seen from the presented kinetic curve, the formation of the coating in the developed solution is completed within 8 min (**Fig. 4**).

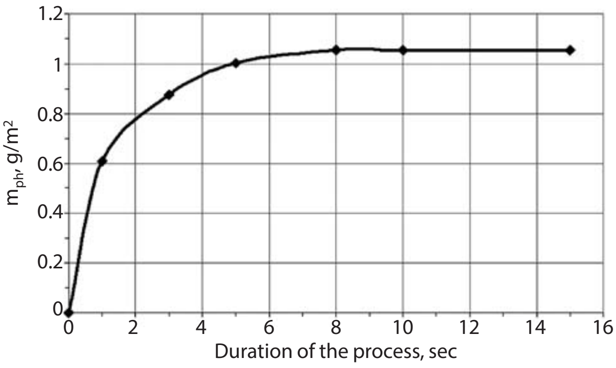


Fig. 4. Change in m_{ph} during coating

Coating composition

Component	Line Designation	Binding Energy (eV)	Literary source	Quantitative composition, at.%
FeSe	Fe 2p	710.9	[11]	33
	Se 3d	54.75		
CuSe	Cu $2p_{3/2}$	934.85	[12]	38
	Se 3d	54.75		
$FeP0_4$	Fe $2p_{3/2}$	712.80	[13]	16
	P 1s	2148.15	[14]	
	P 2s	192.52	[15]	

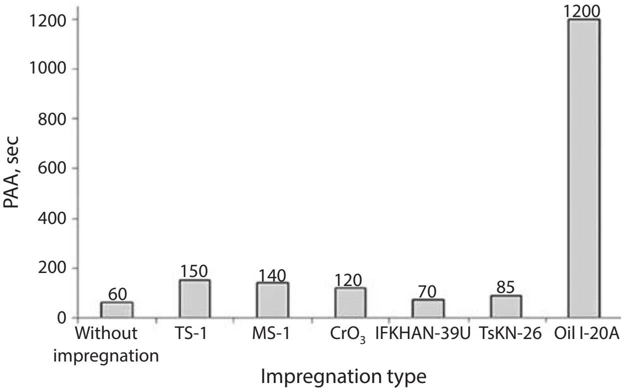


Fig. 5. Influence of the nature of the impregnating composition on the protective ability of coatings

It is known that to increase the protective ability of conversion coatings, they are finished with the purpose of additional protection in the form of organic or inorganic thin films ("top-coat") or impregnating compositions ("sealer").

IFKHAN-39U (mixture of carboxylate type corrosion inhibitors), TsKN-26 (water-soluble polymer composition based on styrene and acrylic acid), CrO_3, TS-1 (organic additive based on gallic acid compounds) and MS-1 (inorganic additive based on sodium metasilicate), as well as technical oil I-20A, were tested as impregnating compositions. The selenide-phosphate layers treated with I-20A oil have the greatest protective ability (**Fig. 5**).

It was also found that the impregnation of black phosphate-selenide coatings in industrial oil for 1 min leads to an increase in the protective ability from 1 to 20 min. With an increase in the duration of soaking in oil to 2 min, the protective ability increases to 25 min. It should be noted that the color of the coatings after oiling becomes deeper and more saturated.

Experiments have shown that the protective ability according to Akimov of oiled phosphate-selenide coatings is slightly higher than the protective ability of oiled oxide layers obtained from a standard alkaline solution of chemical oxidation: 25 min versus 21 min, respectively.

Corrosion testing of coatings in a salt spray chamber was carried out in accordance with ASTM B117. Tests have shown that oiled phosphate-selenide coatings have the greatest protective ability: the first spots of red corrosion appear after 20 hours of testing, while oxidized, oiled samples begin to corrode after 18 hours. After 100 hours of testing, the area of the oxidized sample affected by corrosion is 90 %, and the oiled phosphated sample is 50 %.

Conclusions

1. A low-temperature process has been developed for applying black phosphate-selenide coatings on steel in a solution containing: 4–8 g/l Na_2SeO_3; 1–4 g/l $CuSO_4 \cdot 5H_2O$; 0.5–5 g/l NaH_2PO_4 and 0.25–2.5 g/l Na_2HPO_4 (molar ratio $[NaH_2PO_4]/[Na_2HPO_4] = 2$); pH = 2–3, t = 18–25 °C.

2. It was found that copper and iron selenides are included in the composition of conversion phosphate-selenide coatings: 33 % FeSe, 38 % CuSe and 16 % $FePO_4$.

3. It was found that the impregnation of black phosphate-selenide coatings in industrial oil leads to an increase in the protective ability according to Akimov from 1 to 25 minutes, and the color of the coatings becomes deeper and more saturated.

4. Corrosion tests of coatings in a salt spray chamber in accordance with ASTM B117 showed that oiled phosphate-selenide coatings have the greatest protective ability: the first spots of red corrosion appear after 20 hours of testing, while oxidized oiled samples begin to corrode after 18 hours. After 100 hours of testing, the area of the oxidized sample affected by corrosion is 90 %, and the oiled phosphated sample is 50 %.

5. The developed coatings can serve as an alternative to high-temperature protective and decorative black oxide and phosphate coatings on steel.

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