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DETERMINING FEATURES OF APPLICATION OF FUNCTIONAL ELECTROCHEMICAL COATINGS IN TECHNOLOGIES OF SURFACE TREATMENT

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Проаналізовано підходи щодо застосування електрохімічних покривів в технологіях поверхневої обробки. Показано, що спрямоване модифікування поверхні дозволяє розширити функціональні властивості оброблюваного матеріалу, зокрема підвищити показники міцності, зносостійкості, корозійної тривкості, каталітичної активності.

Запропоновано спосіб поверхневої обробки нелегованих сталей та чавунів шляхом формування тонкоплівкових покривів тернарними сплавами заліза та кобальту з молібденом і вольфрамом. Показано, що введення тугоплавких металів до 37 ат. % в поверхневий шар призводить до зміни фазової структури покриття. Виявлено, що це забезпечує підвищення зносостійкості на 40 %, мікротвердості у 2,5–3,5 рази, а також зменшення коефіцієнту тертя в 3–4 рази порівняно з матеріалом підкладки. Сформовані матеріали можуть бути використані для зміцнення і захисту поверхонь в різних галузях промисловості.

Для модифікування поверхні поршневих силумінів запропоновано використовувати метод плазмово-електролітичного оксидування із формуванням керамікоподібних покривів. Показано, що в гальваностатичному режимі із лужних розчинів електролітів, що містять солі мангану та кобальту, можливо одержувати рівномірні щільні з високою адгезією до основного металу оксидні покриви, доповані каталітичними компонентами, вміст яких варіюється в межах 25–35 ат. %. Показано, що морфологія та фазова структура поверхневих шарів змінюється із інкорпорацією металів-допантів. Сформовані покриви мають високий ступінь розвинення поверхні, що є передумовою підвищення їх функціональних властивостей. Запропонований підхід використано для модифікування поверхні поршня КамАЗ-740. Встановлено, що використання керамікоподібних покривів поршня двигуна приводить до зниження годинної витрати палива та кількості токсичних речовин з відпрацьованими газами, що робить їх перспективними для використання у внутрішньоциліндровому каталізі

Ключові слова: поверхнева обробка, електрохімічний покрив, функціональні властивості, ремонтне виробництво

1. Introduction

Formation of functional coatings combining corrosion resistance, hardness, wear resistance and catalytic activity is a crucial problem in the creation of new materials, the use of which largely led to progress in many fields of modern technology. In particular, surface engineering combines methods of directed changes of physicochemical properties of the surface layers of structural materials by modification, deformation, application of protective layers, films and coatings in various ways. This allows forming surface layers with desired properties directly on the treated material and obtaining characteristics that exceed those of the base metal [1, 2].

Essential interest in a surface modification is due to the fact that characteristics of the surface layers in combination with the properties of the base metal determine properties of products in general. This approach is also attractive from an

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economic point of view in comparison with known methods of changing the volume characteristics of structural materials and finished products.

Surface treatment of machine parts and mechanisms is widely used to improve the functional properties of materials. Such technologies are highly efficient and resource-saving. They are used in production and repair.

The market of military and defense technologies puts forward very high requirements to structural materials used to manufacture models of weapons and equipment in general, their individual parts, components and assemblies. This is due, above all, to harsh operating conditions, intense use, need for rapid recovery of lost functions. Thus, surface modification technologies, in which a coating with well-defined properties is formed on the treated surface are demanded. The scope of coatings of various functional purposes is very wide: corrosion protection, increase of strength, conductivity, heat and wear resistance, and so forth.

Surface treatment methods can solve the issues of corrosion protection, increase of wear resistance, improvement of quality of machine parts, minimization of environmental pollution, as well as many other problems [3–5], and can be divided into several groups. These include modification, application of films and coatings, combined methods, surface microtopography management.

The low consumption of the coating material and the increased surface characteristics of parts ensure prospects for using special-purpose coatings and introducing them into manufacturing and repair practices [6, 7]. However, these technologies are not widespread yet due to the significant cost and technological complexity.

Therefore, the search for economically and technologically available methods of surface modification of parts, components and assemblies is a relevant practical task, the solution of which will increase their operational properties and expand the scope of application.

2. Literature review and problem statement

Treatment technologies with the application of thin-film coatings, in particular electrochemical, are quite common in the US defense industry. Manufacturing enterprises of military and civil equipment use electroplating with individual metals (nickel, chromium, cadmium, silver, copper, tin), anodizing of aluminum and its alloys, chemical precipitation. The system of standards of the US Department of Defense (MIL-SPEC) clearly regulates requirements to the formation and properties (characteristics) of the obtained thin-film materials [8].

An example of using such coatings is the US Army Smart Coatings ™ Materiel program [9]. Research is focused on the development of various coatings for military equipment. The developed coatings have unique properties. They are highly resistant to corrosion and sensitive to changes in environmental conditions. The resulting systems are able to change color. This is a signal to the logistics staff about the need for repair or complete replacement of parts. Electrochemical coatings obtained by electroplating or anodizing are also used.

Recently, considerable attention in the development of renovation, hardening and protection of surfaces of parts has been paid to the processes of formation of multicomponent electrolytic coatings based on iron triad metals alloyed with additional components. The combination of valuable properties of alloying components makes it possible to obtain coatings with enhanced corrosion resistance, microhardness, wear resistance on low-alloy steel and cast iron parts [10, 11]. However, the number of such works is extremely limited, and the results are contradictory.

In [12], Ni–Fe–Mo alloy coatings were obtained from a sulfate-citrate electrolyte on copper substrates. The current efficiency was 10 %. The coatings with varying thickness from 0.6 to 2.1 μm contain 25–40 wt. % Mo. The resulting alloys have a crystal structure and exhibit magnetic properties.

In a series of works on electroplating of multicomponent alloys of molybdenum and tungsten with metals of iron subgroup [13–17], the researchers propose a complex citrate electrolyte, pH 7.0–7.3 [13], to form Ni–Fe–Mo–W coatings. The process is carried out using a rotating disk electrode at a temperature from 25 to 60 °C at a current density of 25–75 mA/cm^2 [14]. The current efficiency of the alloy does not exceed 10 % [15]. According to the authors, co-precipitation of the components in the alloy occurs competitively [16]. Analysis of surface morphology of the obtained coatings based on SEM images suggests that they are uneven, with a large number of irregular structures and cracks [17].

The coatings with a ternary Ni–Fe–Mo alloy of crystal structure with magnetic properties were obtained on copper substrates in the sulfate-citrate electrolyte [18]. The authors draw attention to the change in molybdenum content in the coatings from 25 wt. % to 40 wt. % with a thickness of 0.6 to 2.1 μm, respectively.

Of practical interest are the results of the authors' studies [19] on the electrochemical synthesis of Fe–Co–W alloys with enhanced physicomechanical and anticorrosive properties. The researchers note an increase in the microhardness of the coating up to 1,154 units (according to Vickers) with the treatment temperature increase, and at T 600 °C, the microhardness of the Fe–Co–W coating exceeds that of electrolytic chromium.

The authors [20, 21] proposed binary Fe–Mo (W) and Fe–Cr alloy coatings with the content of alloying components at the level of 3–7 %. For coating formation, sulfate electrolytes of iron (II) with the addition of salts of alloying components are used. The resulting coatings are characterized by improved mechanical properties and can be used, in particular, for hardening and restoration of valves and track-rod ends, as well as in repair.

As for the parts made of valve metals and alloys on their basis, in particular aluminum, an effective method to form special-purpose coatings on them is plasma electrolytic oxidation (PEO) [22]. A feature of PEO compared to conventional anodizing is surface oxidation in aqueous electrolyte solutions at high voltage under the action of short-term electric discharges. In such high-energy regimes, due to electrochemical and thermochemical reactions, a highly developed oxide matrix of the base metal with incorporated compounds or remelts of electrolyte components is formed [23]. The PEO technology can be considered as an effective method for processing parts of internal combustion engines (ICE) and cylinder-piston group of ICE of aluminum alloys (silumins). The advantages of this electrochemical method of coating formation are the simplicity of processing equipment, non-toxicity of working solutions, absence of preliminary preparation of parts, possibility of effective treatment of complex-shaped and large-sized products.

In the 1950s, the Mahle company (Germany) applied coating of aluminum pistons with solid chromium. To increase adhesion, soft galvanized iron was applied at the pretreatment stage, followed by forming a layer of electrolytic chromium. The coating received the commercial name Chromal. The main drawback of this coating was the possibility of stratification under operating conditions. The next commercial product used in BMW, Ferrari, Citroen, Porsche and VW Group engines was the Nikasil cermet coating developed by Mahle in the 1960s and 1970s. The nickel-silicon carbide (Ni–SiC) coating was formed by electroplating with the deposition of a metal nickel layer, followed by saturating the resulting matrix with silicon carbide. The formed coatings have high strength and oil absorption, however, due to the complex and environmentally hazardous process this technology did not become widespread [24].

The next generation of piston coatings is based on saturation of surface layers of cast aluminum alloys with silicon [25]. At the same time, for the manufacture of components, silumins with different silicon contents are used, subjecting them to various treatments (chemical and etching, electrochemical treatment). As a result, a ceramic coating with high heat resistance, strength, wear resistance and corrosion resistance is formed on the workpiece surface. Examples of such coatings are Lokasil and Alusil (Kolbenschmidt), Silumal (Mahle) or variations thereof. These technologies are used by the leading car manufacturers, in particular, Mercedes-Benz, Honda, Porsche, Rolls-Royce Group, General Electric, BMW, Volvo, Jaguar [26]. At the same time, in open sources there is no information on the composition and technology of these coatings due to a trade secret. This indicates the relevance and prospects of research on the formation of ceramic-like coatings on piston alloys.

The possibilities of implementing this process on the example of parts of the ICE piston group are given in [27–32]. In [27], the results of studies on the use of the PEO technology for hardening the working surfaces of the ICE cylinder block are provided. The technological possibility of implementing the PEO of large-sized castings of silumins to obtain a high-quality oxide layer is shown. The authors [28] show the possibility and prospects for using the PEO technology for repairing and restoring the geometry of the working surfaces of silumin engine parts. In [29], the results of experimental studies on surface hardening of the ASP80 piston of AK12 alloy by the PEO method in an alkaline-silicate electrolyte are given. During bench tests, it was found that the wear rate of the coated piston decreases 2.5 times. The authors [30] found a decrease in road and transport fuel consumption by 5–7 % when using PEO coatings on ICE pistons compared to conventional engine pistons. In [31, 32], an increase in ICE efficiency when using pistons with a heat-insulating aluminum oxide coating obtained by electric and percussion plasma treatment of standard engine pistons is experimentally confirmed.

The analysis allows concluding that the method of forming electrochemical coatings depends on the type of treated material and functional properties of coatings on process parameters of deposition.

However, the vast majority of the methods cannot provide an optimal combination of qualitative composition of the formed coatings and necessary properties for the targeted application of the materials obtained. First of all, this refers to thin-film iron alloy coatings for hardening and restoring worn steel and cast iron surfaces, as well as formation of catalytically active coatings on the parts of the ICE piston group for use in in-cylinder catalysis.

At the same time, there are some positive results relating to surface modification of structural materials.

It is found that for the formation of multicomponent iron alloy coatings on steels and cast irons, it is advisable to use complex citrate electrolytes with the addition of salts of refractory metals [33]. The formation of ternary coatings is possible under constant current, as well as by pulse electrolysis [34]. The coprecipitation of components in the alloy occurs competitively. The inclusion of refractory components increases the functional properties of the coatings obtained [35].

Ceramic-like coatings on valve metals possess mainly catalytic properties. Doping of oxide layers by manganese [36], zirconium [37] and iron triad metals [38] is possible. For the PEO treatment of aluminum alloys, it is advisable to use alkaline electrolytes with ligand additives for surface homogenization [39]. The systems obtained are promising in environmental catalysis technologies [40].

The analysis of the results made it possible to substantiate the choice of optimal electrolyte compositions and electrolysis modes for the preparation of ternary electroplating and oxide coatings with a high content of dopants.

3. The aim and objectives of the study

The aim of the work is to substantiate the method of surface treatment of structural materials (steel, cast iron, silumin) with the formation of electrochemical coatings with enhanced functional properties on the basis of the existing approaches of surface treatment of common structural materials. This will allow choosing the optimal parameters of the technological process of forming functional coatings with varied content of doping components and expanding their scope.

To achieve the aim, the following objectives were set:

– to develop methods of electrochemical treatment of the most common structural materials (steel, cast iron, silumins) with the formation of coatings doped with additional components;

– to explore the properties of the formed systems.

4. Method of coating production, study of composition and properties

4. 1. Method of production

Electrochemical coatings were applied on substrates of steel 3 (St 3) (GOST 380, ISO E235-C), SCh 18 gray cast iron (GOST 1412) and AK12M2MgN aluminum alloy (GOST 1583, ISO 185) used for manufacturing ICE pistons.

The composition of the working solutions for coating is given in Table 1.

Ternary coatings were formed at a cathodic current density of 6.5 A/dm^2 in the galvanostatic mode and during unipolar pulse current polarization. The ratio of the pulse and pause time was 10/20 ms. Rectangular plates made of 12Kh18N10T stainless steel were used as anodes; the ratio of the cathode and anode areas was 1:10.

Oxide coatings on silumin were formed by the PEO method in the constant current mode at an anodic current density of 5 A/dm^2.

Table 1

Composition of electrolytes and modes of coating formation

Coating	Substrate (base metal)	Electrolyte No.	Electrolyte composition	Concentration of components, mole/dm^3
Fe–Mo–W	St 3, SCh 18	No.1	$Fe_2(SO_4)_3$ Na_2MoO_4 Na_2WO_4 $Na_3C_6H_5O_7$ Na_2SO_4 H_3BO_3	0.1 0.08 0.06 0.3 0.1 0.1
Fe–Co–Mo		No.2	$Fe_2(SO_4)_3$ $CoSO_4$ Na_2MoO_4 $Na_3C_6H_5O_7$ Na_2SO_4 H_3BO_3	0.1 0.15 0.1 0.4 0.1 0.1
Fe–Co–W		No.3	$Fe_2(SO_4)_3$ $CoSO_4$ Na_2WO_4 $Na_3C_6H_5O_7$ Na_2SO_4 H_3BO_3	0.075 0.2 0.08 0.4 0.1 0.1
$Al_2O_3{\cdot}CoO_x$	AK12M2MgN	No.4	$CoSO_4$ $K_4P_2O_7$	0.1 0.4
$Al_2O_3{\cdot}MnO_y$		No.5	$KMnO_4$ KOH	0.005 0.05

The temperature of the working solutions was maintained within 20–25 °C.

The surface of the samples for coating was prepared by machining, degreasing, etching and washing after each technological operation (Table 2).

Table 2

Solutions for surface preparation for coating

Sample material	Degreasing, g/dm^3	Chemical etching
St 3	NaOH – 10–15 Na_2CO_3 – 30–40 Na_3PO_4 – 20–70 Na_2SiO_3 – 3–5	mixture of H_2SO_4 and HCl (1:1)
SCh 18		
AK12M2MgN	NaOH – 8–12 Na_2HPO_4 – 20–50 Na_2SiO_3 – 25–30	5–10 % NaOH

The laboratory setup for coating formation included: a DC source, electrolytic cell with forced electrolyte agitation, working electrodes, temperature sensor. For coating in the pulse mode, a PI-50-1.1 potentiostat with a PR-8 programmer was introduced into the system. During the formation of oxide coatings, an additional electrolytic cell cooling system and instruments for monitoring the process parameters were used.

4. 2. Methods of study of coatings obtained

The surface morphology of the formed coatings was investigated using the ZEISS EVO 40XVP scanning electron microscope (SEM) (Germany). The topography of the surface layers was studied by atomic force microscopy using the NT-206 microscope, CSC-37 probe. The chemical composition of the coatings was determined using the Oxford INCA Energy 350 energy-dispersive spectrometer (United Kingdom) with the integrated SmartSEM software environment. The study of physicomechanical properties was performed using the PMT-3 microhardness meter and NEOPHOT-21 metallographic microscope.

Phase analysis was performed on the DRON-2 x-ray diffractometer in monochromatic Co-Kα radiation (λ==1.7902 Å). Phase determination was performed by comparing the interplanar distances and relative intensities of the experimental curve with the data from the PCPD-FWIN electronic filing.

The catalytic activity of oxide coatings was tested during bench tests in the process of combustion and catalytic conversion of toxic substances in the ICE cylinder.

5. Results of coating formation on common structural materials

5. 1. Electrochemical treatment of non-alloy steel and gray cast iron

Fe–Mo–W coatings formed on St. 3 and SCh 18 have no cracks and are uniform over the entire sample area. The surface of the alloys consists of agglomerates of spherical grains (Fig. 1, *a*), which can be explained by the inclusion of tungsten in the coating. The total content of refractory components in the surface layers is 35–37 at. % (in terms of metal).

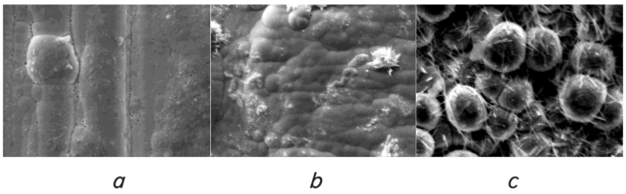


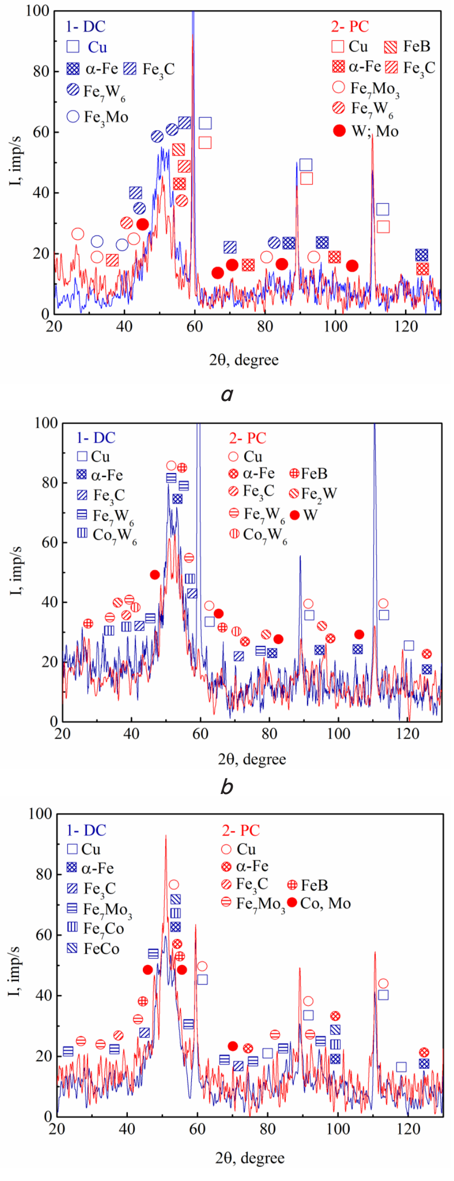
Fig. 1. SEM images of multicomponent iron and cobalt alloy coatings with refractory components: *a* — Fe—Mo—W, *b* — Fe—Co—W, *c* — Fe—Co—Mo. Magnification ×2000

The formation of Fe–Co–W alloy coatings results in competitive deposition of iron with cobalt and tungsten. In these electrolysis modes, it is possible to obtain coatings with low porosity, uniform distribution of elements on the surface, content of W up to 6–12 at. % and cobalt to 32–47 at. % The surface morphology of Fe-Co-W coatings is microglobular and is formed by agglomerates of spherical grains with a size of up to 1 μm (Fig. 1, *b*).

Competitive coprecipitation of Co with Mo during Fe–Co–Mo alloy formation is indicated by the enrichment of the coatings with cobalt on account of molybdenum with increasing concentration of electrolyte components. Molybdenum content in the coatings obtained can reach 15–31 at. % at a Co concentration of 26–48 at. %. The morphology of Fe–Co–Mo coatings changes from fine-crystalline to globular with increasing cathodic current density (Fig. 1, *c*). The coatings are characterized by macroheterogeneity, as evidenced by the significant difference in the content of components on the peaks and in the valleys. Transition to pulse current allows obtaining a more uniform distribution of the alloying components in the surface layers of the coatings.

The formed coatings exhibit increased corrosion resistance in the media of different acidity, which is explained by the chemical composition of the resulting surface layers. In acidic and neutral media, oxides of refractory metals (molybdenum and tungsten) are formed on the surface. This increases the propensity of the modified surface to passivation and resistance to pitting. Inhibition of corrosion damage in an alkaline medium occurs due to the formation of insoluble iron hydroxides on the alloy surface, which complicates the access of the depolarizer (oxygen). This is confirmed by the results of experimental studies of these properties [41]. It is determined that, according to the deep corrosion indicators, the proposed ternary coatings are classified as "stable" in an acidic medium and "very stable" in neutral and alkaline media.

Fe–Co–Mo and Fe–Co–W ternary coatings contain hardening phases of compounds of refractory metals (Fig. 2).



a

b

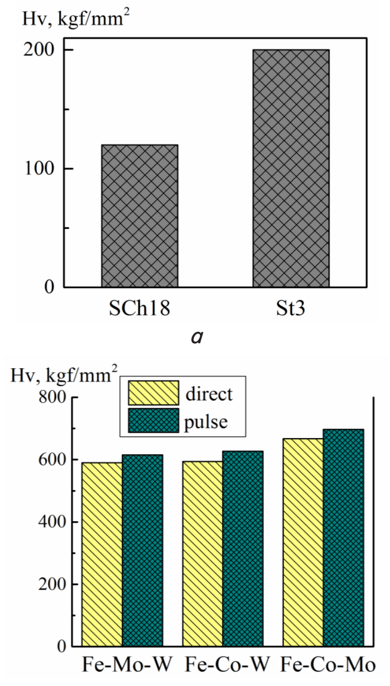
c

Fig. 2. Diffraction patterns of alloys obtained by stationary (1) and pulse (2) currents: *a* — Fe—Mo—W, *b* — Fe—Co—W, *c* — Fe—Co—Mo. DC — direct current, PC — pulse current

Based on the phase composition, such systems can be considered as composite. They should exhibit increased surface strength and hardness.

The resulting Fe–Mo–W, Fe–Co–W and Fe–Co–Mo alloy coatings have good adhesion to the base material (substrate) and retain it under mechanical loads. The strength of adhesion of the coatings to the base metal was determined by polishing with wheels made of coarse calico, felt and other materials using chromium oxide-based pastes with organic impurities at an angle of 90°, as well as during heating to 100–200 °C for at least 1 hour and subsequent air cooling according to GOST 9.302-88 (ISO 1463-82, ISO 2064-80, ISO 2106-82) [35, 41].

In terms of microhardness, the ternary coatings 2.5–3.5 times exceed the substrate material (St 3, SCh18) (Fig. 3).



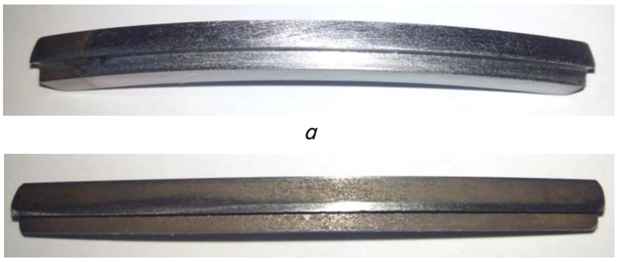
a

b

Fig. 3. Microhardness: *a* — base metal (substrate); *b* — ternary coatings obtained by direct and pulse current

Fe–Co–W and Fe–Co–Mo alloys also exhibit magnetic properties due to the presence of cobalt [42].

Fe–Mo–W coatings were used to restore a worn cast-iron shoe (Fig. 4) with subsequent testing of antifriction properties (friction coefficient) of the surface obtained.



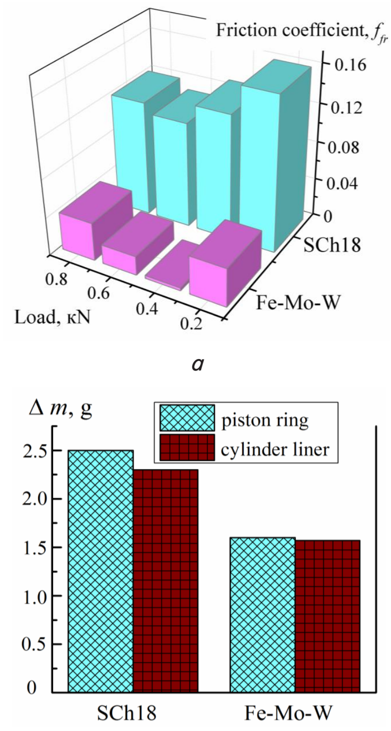
a

b

Fig. 4. SCh18 cast-iron shoe with Fe—Mo—W coating (*a*) and uncoated shoe (*b*)

The tribotechnical properties of the coating obtained were estimated by the friction coefficient f_{fr}, as well as wear resistance indices in comparison with uncoated SCh 18 samples (Fig. 5).

Studies on the 2070 SMT-1 serial machine with a step load of conjugated samples from 0.2 kN to 0.8 kN according to the "disk-shoe" scheme proved that the friction coefficient for the restored surface is 3–4 times lower than for the SCh18 base metal where Δm is the mass change of the samples during tests.



a

b

Fig. 5. Comparative characteristics of gray iron and Fe–Mo–W coating when testing the "piston ring – cylinder liner" coupling samples: *a* – friction coefficient, *b* – wear resistance

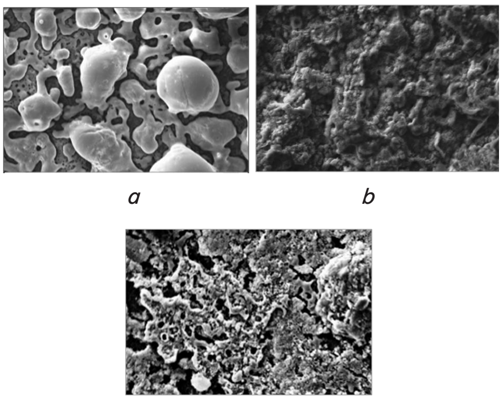
Thus, electrolytic coatings of iron and cobalt alloys with refractory metals in terms of physicomechanical and operational properties can be recommended for the effective restoration and hardening of worn surfaces of non-alloy steel and cast iron in operation and repair technologies.

5. 2. Plasma electrolytic treatment of AK12M2MgN piston alloy

By oxidizing the AK12M2MgN silumin (AL25) in alkaline solutions of electrolytes 4 and 5 (Table 1), uniform oxide coatings containing cobalt or manganese were obtained on the piston alloy samples. By successive oxidation in these electrolytes, a mixed layer of manganese and cobalt oxides can be obtained.

The surface morphology of the mixed oxide coatings varies with the incorporation of dopant metals in the aluminum oxide matrix. The inclusion of cobalt occurs in the form of spherical island structures of blue-violet color. In the process of oxidizing, such mosaic structures uniformly cover the entire surface of the sample. Cobalt content in the surface oxide layers reaches 24 at. % (Fig. 6, *a*).

PEO of silumin in a manganese-containing alkaline electrolyte ensures the formation of a uniform brown-black oxide layer with a manganese content of up to 35 at. %. The coating surface is microglobular. A significant number of conglomerates formed by small spheroids are visualized on it (Fig. 6, *b*). Two-stage oxidizing with the formation of a layer of mixed cobalt and manganese oxides allows obtaining a fine porous coating. The total content of dopant in the surface layers reaches 25–30 at. % (Fig. 6, *c*).

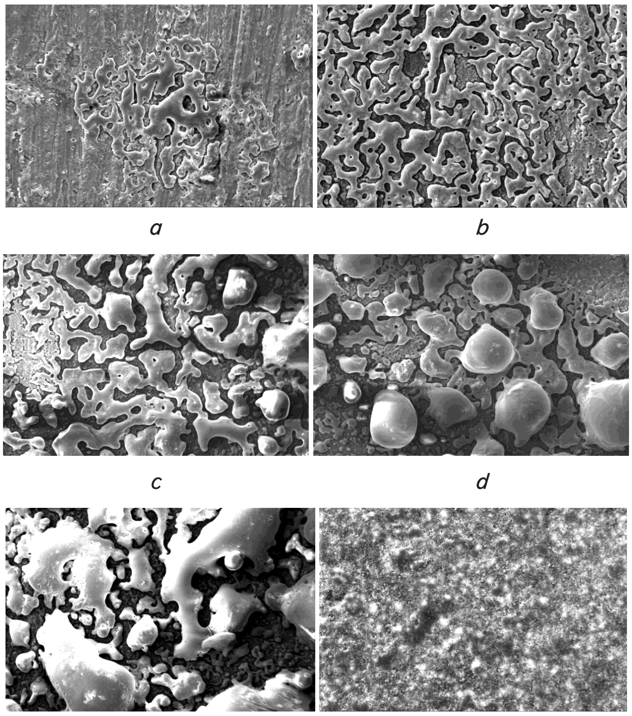


a *b*

c

Fig. 6. SEM image of oxide coatings on AK12M2MgN: *a* – Al|$Al_2O_3 \cdot CoO_x$, *b* – Al|$Al_2O_3 \cdot MnO_y$, *c* – Al|$Al_2O_3 \cdot CoO_x$, MnO_y. Magnification ×1000

With increasing treatment time, the morphology and composition of the formed oxide layer changes (on the example of cobalt-doped coatings) (Fig. 7, 8).



a *b*

c *d*

e *f*

Fig. 7. Morphology of $Al_2O_3 \cdot CoO_x$ oxide coatings formed on AK12M2MgN for, min: *a* – 15, *b* – 20, *c* – 30, *d* – 40, *e* – 55, *f* – 60. Magnification ×500

In [41, 43], the effect of various parameters on the morphology, composition, and properties of the modified surface of piston silumin was also considered.

The results of X-ray diffraction analysis of the modified surface of the AK12M2MgN piston silumin indicate that in the surface layers of the oxidized alloy, in addition to aluminum, there are Si and α-Al_2O_3 phases, and the formed coatings contain oxides of dopant metals (Fig. 9). The intensity of the lines on the diffraction patterns is a reflection of the quantitative composition of the systems obtained.

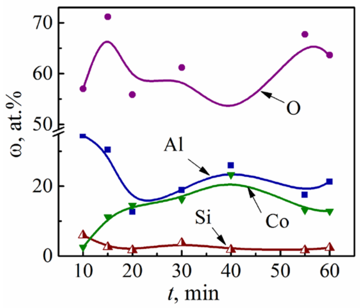
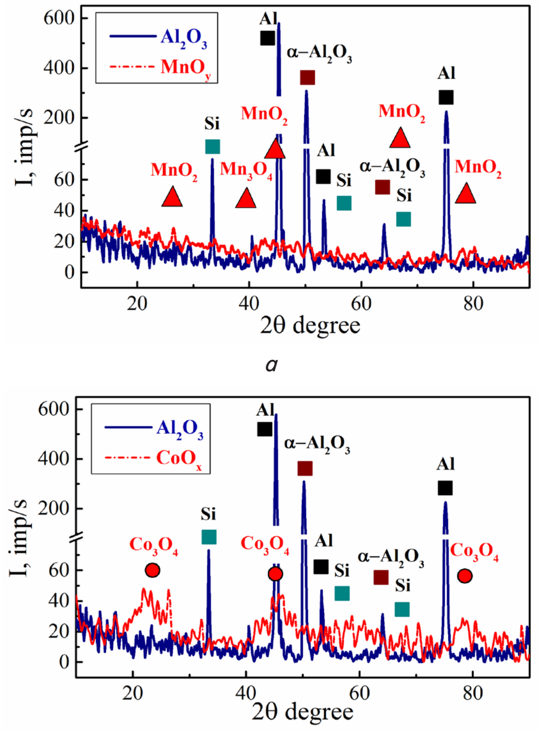


Fig. 8. Changes in the chemical composition of $Al_2O_3 \cdot CoO_x$ coatings during PEO



a

b

Fig. 9. X-ray diffraction patterns of ceramic-like coatings formed on AK12M2MgN: *a* – $Al|Al_2O_3 \cdot MnO_y$, *b* – $Al|Al_2O_3 \cdot CoO_x$

The obtained oxide coatings have a high degree of surface development in combination with a significant content of dopants in the oxide coating. This is a prerequisite for the high catalytic activity of the systems formed [44].

It should be noted that the compounds of the surface layer of the modified surface (α-Al_2O_3, manganese and cobalt oxides) are characterized by high thermal stability. And the peculiarities of the formation of PEO coatings provide a high adhesion of the oxide layer to the treated material. This allows using the resulting coatings $Al_2O_3 \cdot CoO_x$ and $Al_2O_3 \cdot MnO_y$ in the engine combustion chamber at elevated temperatures, pressures, high mechanical loads.

Testing of oxide PEO systems in a model reaction of conversion of carbon (II) oxide to CO_2 showed [44] that their activity (ignition temperature, complete conversion temperature) is similar to the platinum catalyst and exceeds aluminum oxide values.

The results correlate with data for oxide PEO systems on aluminum alloys and other valve metals [4, 43–45].

Testing of the possibility of using the developed technology for the plasma-electrolytic treatment of ICE pistons was carried out by means of PEO of the KAMAZ-740 engine piston with the formation of oxide coatings on the piston cover [46] (Fig. 10).

a *b*

Fig. 10. Coated KAMAZ-740 piston: *a* – $Al|Al_2O_3 \cdot MnO_y$, *b* – $Al|Al_2O_3 \cdot CoO_x$ [46]

The phase structure of the modified silumin surface in combination with the developed surface and significant content of oxides of catalytic components is a prerequisite for improving the functional properties of the formed coatings.

When testing coatings during bench tests of a single-cylinder naturally aspirated diesel [46], hourly fuel consumption was found to decrease by 1–4 %. Higher fuel efficiency is demonstrated by the piston coated with non-stoichiometric manganese oxides. Cobalt mixed oxide systems exhibit higher catalytic activity. The piston with $Al_2O_3 \cdot CoO_x$ coating allows reducing NO_x emissions within 10 % and CO – 15–18 %, whereas for Mn-containing oxide coatings, these figures are significantly lower.

6. Discussion of the results of formation of electrochemical coatings on common structural materials

The observed differences in the surface topography of ternary coatings, all other things being equal, are also connected with the difference in the phase composition of thin-film materials. So, for example, the surface topography of Fe–Mo–W coatings is similar to Fe–Co–W. This is due to the presence of iron intermetallic compounds with refractory metals and tungsten compounds with cobalt and iron in the formed coatings. That is, an amorphization metal (molybdenum and tungsten) binds the alloy base and contributes to the formation of a relatively uniform microglobular surface. At the same time for electrochemical Fe–Co–Mo alloy coatings, sections of various morphology are visualized, namely crystalline (Fe_7Co, FeCo phases) and globular (Fe_7Mo). Therefore, a combination of catalytic, magnetic properties with increased microhardness is characteristic of the Fe–Co–Mo alloy [38].

The defining operating characteristics of electrochemical coatings are adhesion to the substrate material and microhardness. It is also known that tribotechnical characteristics of contact surfaces, and especially friction units, are directly influenced by roughness, degree of dispersion and phase composition of surface layers.

Higher antifriction properties of electrolytic coatings of iron and cobalt are explained by the inclusion of refractory metals in alloys and their amorphous structure. Besides, the morphology, topography and porosity of coatings are a number of factors of increasing antifriction properties due to the additional retention of lubricant materials in the recesses and pores of coatings.

The results of tribological tests determine the feasibility of using electrolytic coatings of multicomponent iron alloys on steels and cast irons in friction pairs, especially if the coating is applied to the contact surfaces of conjugated parts. This will ensure optimal tribotechnical characteristics of contact parts with minimal wear and antifriction interaction and increase the life of materials.

The analysis of the obtained results allows recommending multicomponent coatings of iron and cobalt alloys with molybdenum and tungsten for hardening surfaces of low-alloy steels, and, especially, gray cast irons, which will significantly improve their characteristics.

Incorporation of dopants (cobalt, manganese) into the surface layers of the coating substantially changes their morphology and causes the formation of bulk structures with a high specific surface [43]. This is confirmed by the analysis of SEM images (Fig. 6, 7) and study of the surface of coatings by the contact method [36].

The formation of ceramic-like PEO structures occurs under non-equilibrium conditions, as evidenced by the amorphous ring at the angles of 2~20° on the X-ray diffraction patterns, as well as the formation of oxides of dopant metals of various valences.

The use of ceramic-like coatings of the ICE piston leads to a decrease in the ignition temperature of the fuel mixture. Due to the thermal insulation properties of the catalytic coating layer, for all the oxide systems studied, air consumption is reduced compared to a piston with an untreated surface. Due to the peculiarities of catalytic combustion of fuel in the near-wall areas of the ICE combustion chamber, the phase of uncontrolled fuel combustion and combustion time are reduced [42].

Lowering the combustion temperature eliminates the possibility of air nitrogen participation in gas-phase reactions. These features of the combustion process and catalytic processes in the surface oxide layers of the piston reduce the amount of toxic engine gas emissions.

Thus, the PEO treatment of ICE pistons allows the formation of manganese- and cobalt-containing ceramic-like coatings with high catalytic properties. These systems can be used in technologies of in-cylinder catalysis for reducing the toxicity of emissions of engines and increasing their fuel efficiency, in particular, engines with AK12M2MgN silumin pistons.

The limitations of this study are associated with the need to study the influence of various factors on the process of surface treatment of the specified structural materials.

Prospects for further research are related to the adaptation of the proposed technology for the surface treatment of other structural materials and expansion of the range of dopants used. This will improve the efficiency of the electrochemical surface treatment method and expand the scope of mixed oxide systems.

7. Conclusions

1. The method of electrochemical treatment of non-alloy steels and cast irons with the formation of thin-film iron and cobalt coatings containing up to 37 at. % refractory components (in terms of metal) is developed. In terms of microhardness, the obtained coatings 2.5–3.5 times exceed the treated material and have higher anti-friction characteristics. The friction coefficient for the modified surface is 3–4 times lower than for the base metal. The combination of physicomechanical and operational properties makes it possible to recommend ternary iron alloys for hardening and restoring worn surfaces of non-alloy steel and cast iron.

2. The method of surface treatment of piston silumins in alkaline electrolytes by the PEO method is proposed. It is shown that in the proposed modes it is possible to form uniform, dense, ceramic-like coatings with high adhesion to the treated material. Due to the incorporation of manganese and cobalt oxides into the surface layers, the modified surface has catalytic activity. The obtained manganese-doped oxide systems demonstrate a decrease in hourly fuel consumption within 1–4 %. The ceramic-like cobalt coating reduces NO_x emissions by up to 10 % and CO emissions by up to 15–18 %.

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