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STRUCTURE AND PROPERTIES OF COMPOSITE IRON-BASED COATINGS OBTAINED BY THE ELECTROMECHANICAL TECHNIQUE

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The influence of the electrolyte temperature and current density on the content of inclusions of powder particles in composite coatings obtained by the electrochemical technique has been investigated. It has been found that the wear resistance of iron coatings with inclusions of powder particles of aluminum, kaolin, and calcium silicate increases from 5 to 10 times compared to coating without inclusions of disperse particles, and the friction coefficient therewith decreases from 0.097 to 0.026. It has been shown that the mechanical properties of iron obtained by the method of electrochemical deposition depend on their fine structure. The regimes of deposition of iron-based coatings have been optimized.

Introduction. Among the first investigators of electrochemical deposition of composite coatings are É. M. Natanson and Z. R. Ulberg, scientists from the Institute of Colloid Chemistry and Water Chemistry of the NAS of Ukraine, who made a great contribution to the further development of this scientific trend. For instance, in [1] it was shown that composite coatings have wide fields of application practically in all branches of national economy — from providing biological protection of nuclear reactors and space vehicles to the making of high-efficiency stable catalysts of chemical processes. At the present time the development of new coatings for increasing the wear resistance of the surfaces of machine elements operating under conditions of abrasive wear is one of the most important problems of advanced material science [2–4]. Here composite coatings based on iron–ceramics systems obtained by the electrochemical technique and having higher strength, hardness, and corrosion resistance can be used. However, in many cases electrochemical deposition of coatings on an industrial scale is hindered by the insufficiency of information on the conditions of obtaining them and their properties. At the same time the results of some investigations of the influence of electrolysis conditions on the properties of composite coatings are practically noncomparable. This in turn impedes the development of technologies of applying such coatings. Therefore, complex studies of the influence of electrolysis conditions on the properties and structure of iron–ceramics composite coatings (CC) obtained by electrochemical deposition [5–7] are urgent, and such studies have been made in the present work.

Methods of Investigations. The high efficiency of chloride iron plating electrolytes that permits iron plating at high current densities has made it possible to use, for obtaining a CC, an electrolyte of the following composition (g/l): iron chloride $FeCl_2$ — 200–300; sodium chloride NaCl — 90–100; hydrochloric acid HCl — 2–3 (the microscattering power is equal to –43). Sodium chloride was introduced to decrease the evaporation of the electrolyte, retard its oxidation, and increase the electrical conduction [8]. The presence of a small quantity of hydrochloric acid in the iron plating electrolyte retards the oxidation reaction of iron (II) [6]. The electrolyte was prepared from chemically and analytically pure reagents. As a dispersed phase, we used available powders of aluminum oxide of brand M5N (GOST 3647-80), kaolin (GOST 21286-82), and calcium silicate having a high dispersivity of particles. The average diameter of powder particles was ~5 μm.

The morphology of the coating surfaces was investigated on a "Cam-Scan" scanning electron microscope (GB), the CC structure — by the metallographic method on an MIM-7N, an MIM-8M, and a Reichert MeF-3 (Austria) microscopes; the fine structure was investigated by the x-ray method with the use of a DRON-3 diffractometer. The mechanical properties of the CC were investigated according to GOST 11701-84 on an RT-250 tensile test machine. The microhardness was measured according to GOST 9450-76 on a Buehler Micromet-II tester (Switzerland).

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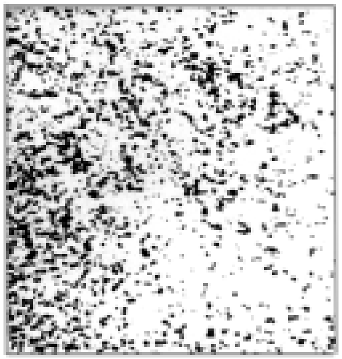


Fig. 1. Microstructure of the iron obtained by the method of electrochemical deposition without inclusions of kaolin powder particles. ×750.

Fig. 2. Microstructure of the composite coating with inclusions of kaolin powder particles. ×300.

The number of disperse particles in the CC was determined by chemical dissolution of the matrix metal in nitric acid (1:1). Insoluble particles were separated by means of a fine-pore glass Shott filter. The porosity was determined according to GOST 18898-89. The investigations of the wear resistance under the conditions of sliding friction were carried out on an SMTs-2 machine in $M8G_2$ motor oil (GOST 8381-78) with the addition of finely-disperse (the mean diameter of particles was 5 μm) quartz dust in the amount of 0.18% according to the "roller–block" scheme. The counterbody was a roller made of steel 45 (GOST 1050-88) hardened to 60 HRC, whose surface roughness was $R_a \leq 0.32$ μm. Weighing was carried out on a VLR-200M analytical balance with an accuracy of up to $5 \cdot 10^{-8}$ kg. To intensify the process of electrochemical deposition, the electrolyte is stirred at a rate from 0.01 to 0.10 m/sec, as a result of which in the near-electrode layer the loss of metal ions discharged on the cathode is made up faster. As was shown in [2, 6], an increase in the stirring rate permits increasing the current density in the process of electrolysis. The solid disperse particles present in the electrolyte being stirred mechanically clear the cathode from hydrogen bubbles and passive films and thus facilitate the conditions for iron deposition. At the same time they promote removal of iron hydroxide sols from the cathode zone and loosening of the cathode hydroxide film, as a result of which the content of inclusion of hydroxide in the sediment decreases and the layer structure of iron coatings is disturbed. Therefore, ceramic-metal coatings are more dense and plastic than pure electrolytic iron [2, 6]. They have no lamination, and the fracturing of sediments markedly decreases with increasing content of the ceramic phase. The absence of pitting and dendrites makes it possible to build up coatings of considerable thickness. The electrolyte is also a medium sustaining the particles dispersed in it in the suspended state and providing their delivery to the cathode surface. Consequently, depending on the size, density, and concentration of particles, the rate of motion of the electrolyte should be different.

Results and Discussion. X-ray phase analysis has revealed that all the CCs obtained represent α-iron with inclusions of powder particles of aluminum oxide, kaolin, and calcium silicate. The period of the crystal cubic volume-centered lattice was 0.2866 ± 0.0002 nm.

The structure of the composite coatings has undergone a noticeable change [9, 10]. For instance, the structure of the iron obtained by the method of electrochemical deposition without inclusions of powder particles is highly dispersed, laminated, with dark spots in the form of streaks and a network of cracks emanating from the base (Fig. 1). In the composite coating with inclusions of aluminum oxide, kaolin, and calcium silicate particles, the structure is also highly dispersed and there is a lamination which decreases with increasing content of powder particles and practically disappears at 1.5–5.0 mass % (Fig. 2). The investigation of the CC surface morphology (Fig. 3) has made it possible to reveal that the iron matrix with inclusions of disperse particles is fine-grained due to the fact that the electrochemical deposition of iron occurs at a considerable overvoltage reaching 10^{-1} V. The linear grain size is 10^{-7} m.

We have investigated the influence of the electrolyte temperature and the current density on the content of inclusions of powder particles in the CC (Fig. 4). It has been established that at an electrolyte temperature of 40^{o}C the content of particles in the coating increases from 4.9–5.1 mass % (I = 20 A/dm^2) to 7.7 mass % (I = 70 A/dm^2),

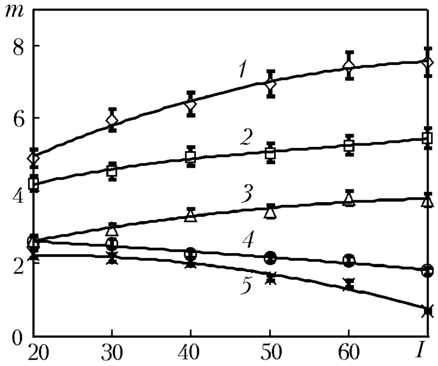


Fig. 3. Surface morphology of the coating with inclusions of kaolin particles. ×1200.

Fig. 4. Content in the CC of inclusions of kaolin particles versus the cathode current density at various temperatures of the electrolyte: 1) T = 40°C; 2) 50; 3) 60; 4) 70; 5) 80. m, mass %; I, A/dm^2.

TABLE 1. Influence of the Content of Dispersed Phase Particles in Iron-Based Composite Coatings on the Size of Coherent Scattering Regions, Lattice Microdistortions, and the Dislocation Density

m, mass %	Aluminum oxide			Kaolin			Calcium silicate		
	λ, nm	$\Delta a/a$, 10^{-3}	ρ, 10^{10} cm^{-2}	λ, nm	$\Delta a/a$, 10^{-3}	ρ, cm^{-2}	λ, nm	$\Delta a/a$, 10^{-3}	ρ, 10^{10} cm^{-2}
0	17	1.8	6	17	1.8	6	17	1.8	6
1.5	5.2	2.7	21.7	5.3	2.6	21	5.5	2.3	18
3	5.1	2.8	21.8	5.6	2.4	19	5.4	2.5	20
4.3	5	2.9	22	6.5	2	16	6	2.1	17
6—7.7	59	1.8	2	59	1.8	2	59	1.8	2

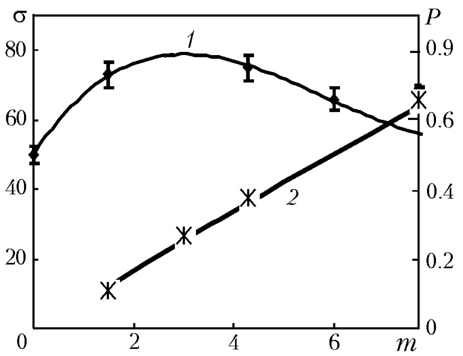
TABLE 2. Optimum Electrolysis Conditions for the Deposition of Composite Coatings Exhibiting the Highest Strength, Microhardness, and Wear Resistance

Dispersed phase	T, °C	I, A/dm^2	C, g/l	m, mass %
Aluminum oxide	50	30	100	4.3
Kaolin	80	50	100	1.5
Calcium silicate	60	30	100	3.0

and at 80°C it decreases from 2.1–2.3 mass % (I = 20 A/dm^2) to 0.6–0.8 (I = 70 A/dm^2), i.e., as the electrolyte temperature increases from 40 to 80°C, the content of powder particles (of aluminum oxide, kaolin, and calcium silicate) in the CC decreases, while the content of particles of small fractions increases. As we see it, this is due to the decrease in the electrolyte viscosity from 1.3 to 1.1 MPa·sec and, consequently, to the increase in the sedimentation rate of particles of large fractions.

The porosity of the CCs obtained by the electrochemical technique has been investigated [11]. It has been established that as the content of particles in the coating increases from 1.5 to 7.7 mass %, the porosity increases for the CCs containing, as a dispersed phase, powders of aluminum oxide (0.12–0.65%), kaolin (0.12–0.66%), and calcium silicate (0.12–0.66%).

The influence of the content of the dispersed phase on the ultimate tensile strength of the coatings has been investigated (Fig. 5). The inclusion of dispersed phase particles in the composite coating in small amounts (up to 1.5–4.3 mass %) leads to a hardenings of the matrix metal to 70–75 MPa, which is 15–30 MPa higher than in the iron obtained by the method of electrochemical deposition without inclusions of powder particles. And the microhardness



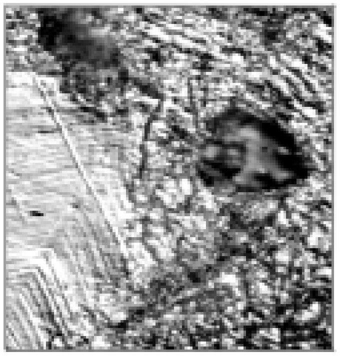


Fig. 5. Ultimate tensile strength (1) and porosity (2) of the composite coating depending on the content in it of kaolin particles. σ, MPa; P, %; m, mass %.

Fig. 6. Deformation bands in the composite coating with inclusions of kaolin powder particles. ×1200.

thereby reaches 5.5–6.3 GPa, whereas the microhardness of the iron obtained without inclusions of powder particles is 4.0–4.8 GPa. This is due to the decrease in the content of inclusions of trivalent iron compounds in the material, the creation of barriers (in the form of powder particles and pores) to the propagation of cracks in the coating, and the increase in the dislocation density in the coating metal. For instance, it has been established that in the iron without inclusions of powder particles the size of the coherent scattering regions is 17 nm, the lattice microdistortions $\Delta a/a = 1.8 \cdot 10^{-3}$, and the dislocation density is $6 \cdot 10^{10}$ cm^{-2} (Table 1). As the mass content of powder particles in the CC increases to 1.5–4.3%, the size of the coherent-scattering regions decreases to 5.0–5.4 nm, the lattice microdistortions grow to $(2.5–2.9) \cdot 10^{-3}$, and the dislocation density also increases to $(20–22) \cdot 10^{10}$ cm^{-2} (Fig. 6), with the strength and microhardness of the coating reaching maximum values. This is due to the fact that in the process of coating deposition with overgrowth of powder particles a dislocation step is formed, the ordering of crystallite growth is disturbed as a result of the screening of individual faces by nonconductive particles, and accumulation of dislocation loops around the powder particles in the slip plane occurs (also due to the spontaneous motion of dislocations), which induces additional reactive voltage, which the dislocations have to overcome in their motion (the hardening thereby is directly proportional to he number of dislocation loops).

A further increase in the mass content of powder particles in composite coatings (up to 6.0–7.7%) increases the size of the coherent scattering regions to 59 nm, decreases the lattice microdistortions to $1.8 \cdot 10^{-3}$, and decreases the dislocation density to $2 \cdot 10^{10}$ cm^{-2}. In so doing, the strength and microhardness of the CCs also decrease, since the coating porosity increases, and the interparticle spacing decreases with increasing mass percent of inclusions of powder particles, as well as the dislocation density decreases, since with increasing content of inclusions of the dispersed phase the latter increases, but upon reaching the critical value begins to decrease because of the formation of cracks in the coatings (as a result of the coalescence of the dislocations into a crack with increasing concentration of stresses near a barrier, a powder particle) and their coalescence with pores. The total current efficiency of the iron was 90%. The presence in the electrolyte of powder particles has practically no effect on this index. The application of composite coatings makes it possible to increase the wear resistance in abrasive wear by a factor of 5–10 compared to the coating without inclusions of dispersed particles and by a factor of 1.5–2.5 compared to hardened steel 45. The highest wear resistance of coatings is attained with the following content of powders: aluminum oxide 4.3 mass %, kaolin 1.5 mass %, calcium silicate 3 mass %.

The presence of pores promotes relaxation of stresses that arise and provides penetration into the coating of the lubricant and its uniform distribution between the friction surfaces, which increases the wear resistance of the CCs. In composite coatings containing 1.5–4.3 mass % of inclusions of powder particles, the friction coefficient decreases to 0.026, whereas in the iron without inclusions of powder particles it equals 0.097.

The optimization of the results of the investigations performed has shown that composite coatings with a maximum microhardness of 5.5–6.3 GPa and strength of 70–75 MPa (the highest wear resistance) are obtained under the electrolysis conditions given in Table 2.

CONCLUSIONS

1. Relationships between the electrolyte temperature, the current density, and the content of the dispersed phase in the coating have been revealed.

2. It has been shown that the wear resistance of CCs increases 5–10 times compared to the coating without inclusions of disperse particles and by a factors of 1.5–2.5 compared to hardened steel 45.

3. It has been established that the increase in the wear resistance of CCs containing 1.5–4.3 mass % of additives is due to the decrease in the content of inclusions in the coating of trivalent iron compounds (iron (III) hydroxide $Fe(OH)_3$), the creation of barriers (in the form of powder particles and pores) to the propagation of cracks in the coating, the increase in the dislocation density in the iron matrix, and the increase in the microhardness and strength due to the introduction into it of the optimum quantity of the dispersed phase.

4. Optimal regimes of deposition of iron-based composite coatings have been determined (Table 2).

NOTATION

$\Delta a/a$, microdistortions of the crystal lattice; C, concentration of the dispersed phase in the electrolyte, %; I, cathode current density, A/dm^2; m, content of inclusions of particles in the composite coating, mass %; P, porosity, %; T, temperature, ^oC; λ, size of coherent x-ray scattering regions, nm; ρ, dislocation density, cm^{-2}; σ, ultimate tensile strength, MPa.

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