Investigation of Structure and Wear Resistance of Nanocomposite Coating of Chemical Nickel

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\textbf{A B S T R A C T}

The investigation results of the structure and wear resistance of composite chemical coatings on the nickel base obtained by means of mutual codeposition with nanodispersed particles of aluminum oxide and potassium polytitanate are presented. The investigations are carried out by scanning electron microscope. It is found, that composite nickel penetrates into the base metal to a depth of about 5 µm, forming diffusion layer, which provides an increased cohesive strength of the coating with base metal. Composite coating has abundance of inclusions of different size along the whole surface; which are absent in the base coating. Nanodispersed particles penetrate into the coating; accelerate the nickeling process, which provides the increase of the coating wear resistance.

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1. \textbf{INTRODUCTION}

In modern times of technology development in diverse industrial trends, the electrolytic coatings are widely used. Among them, the coatings obtained by chemical method in particular nickel deposition are of special importance. At chemical nickeling coating is deposited on an item in water solution, which main components are nickel salines, sodium hypophosphite and sodium acetate [1-5]. The process takes place in solution at the temperature of 90-95 °C without electric current.

Inasmuch as the solution for chemical nickeling always contains sodium hypophosphite, simultaneously together with nickel phosphorus is deposited on the substrate surface. Nickel phosphorous coating possesses high micro hardness, fine dispersity, good heat conductivity and heat resistance, high wear resistance and some other valuable characteristics [1,6,7]. Electroless nickel deposition unlike other
methods provides the possibility to deposit uniformly thick coatings on parts of complicated configuration without any special shade devices. Inasmuch as chemical nickeling is carried out without electrolysis to organize this process is not necessary to have specific electro technical equipment essential for galvanizing plants. Besides, bath loading factor for chemical nickeling is greater by several folds than for electrolytic ones [8,9]. For this reason, at the same production program, for chemical nickeling process organization much lesser production areas are required in comparison with galvanizing plants.

One of the development directions of chemical nickeling process is deposition of composite galvanic and chemical coatings [1,6,10-14]. The essence of this method is that together with metal from solutions nanodispersed particles, fibers and ridges of different carbides, borides, oxides, sulfides, polymer powders, etc. are deposited on the parts. Application of nanosized materials at chemical nickel coatings deposition allows considerable improvement of physical and mechanical properties of the obtained coatings [10,12-16].

Composite chemical coatings are obtained from suspensions in the form of the solution with addition of certain amount of nanosized powder. Metal (the first phase, or matrix) and powder particles (the second phase, or reinforcer) are deposited on the surface of the covered material. They are covered with matrix, forming coating structure.

In comparison with the base coatings, the peculiarity of composite coatings formation is that in the deposition process the particles of different materials intrude continuously into the coating. At chemical nickeling much higher particles quantity transfers from suspension into coating then in case of galvanic coatings at equal suspension concentration [1,4,14,15]. By the structure, composite chemical coatings also differ from galvanic ones in more uniform distribution of particles of dispersed phase in matrix [6,16]. Practically, any simple or complex subject dispersed in the solution by this method can be covered with metal. The size of the applied particles is significant. The literature [1,4,6,10,17] contains the data on metal powders and alloys with particle sizes from 0.01 to 100 μm. The application of the particles with less size is considered more effective because such particles have high sedimentation stability.

It is known, that physical and mechanical properties and wear resistance of coatings are determined with their element composition and structure. That is why the study of these parameters, which are formed in nickel chemical coating under the influence of nanodispersed particles, is of great scientific and practical interest. Thus, the goal of this work is the investigation of the nanodispersed particles influence on the chemical composition and morphology and wear resistance of nickel chemical coatings. Composite chemical coatings are residues consisting of various foreign inclusions.

The first pilot works on development of the technology of obtaining the composition coatings were done by Yu.V. Baymakov in 1925 [1,2], who found out the possibility of codeposition of electrolytic residues of ferrum with graphite impurities up to 1 %. A little later, electrolytic residues of cuprum with graphite were obtained [10,11]. However, the early studies in this direction failed to find practical application. Only in the 60s of the XX th century the method of codeposition of metals and finely dispersed solid particles found practical use for obtaining diamond tools.

Creation of the composite coatings was dictated by the need to improve the physical and mechanical and performance properties of the conventional galvanic coatings. Numerous research works in this sphere revealed that, the dispersed filler inclusion into the chemical coatings on the nickel ground in many cases results in substantial increase of its micro-hardness and wear resistance [1-6,12-14,16-17].

The composite coatings micro-hardness can reach the values that 1.5–2 times higher in comparison with the base nickel coating. Micro-hardness value is determined, in the first place, with the dispersed phase nature. For example, thus, the usage of silicium carbid increases micro-hardness up to 700 MPa. The mass wear of the nickel coating with silicium carbid impurities is 3-4 times less and with boron carbide impurities is 4–5 times less in comparison with the coating without particles [6].
The process of electroless nickel laced with Teflon is developed [21]. It provides high wear resistance of the coating. Ptotoplast (Teflon) – is a polymeric antifriction material with the coefficient of sliding friction equal to 0.05. Very weak intermolecular forces are the cause that Teflon has minimal friction ratio among all solid materials. However, because of softness and fluidity, it is irrelevant for heavy loaded friction units and mainly it is used in tool engineering.

Consequently, it is possible to conclude that to increase micro-hardness and corrosion resistance of the chemical coating on the nickel ground it is possible to apply the powders of aluminum oxide, titanium, silicium carbide, etc. However, for wear resistance increase, it is insufficient to increase micro-hardness only, but also it is necessary to improve antifriction characteristics of the coating. For this purpose, the best thing is to apply available nanosized powders of different polymers – Teflon, polytetrafluoroethylene (Teflon varieties), potassium polytitanate.

Potassium polytitanate (K₂OₙTiO₂) is a compound presenting a lamellar crystal of the scaled form. It is synthesis intermediated product of fibrous potassium titanates and consists of the particles sized 50–80 µm [4].

2. MATERIALS AND METHODS

Now, the technologies of obtaining particles of nanometer range have appeared; in particular, method of plasma Ostwald ripening of the original material [5-7]. The method is based on evaporation of coarse powder (raw material) in plasma flow with temperature 4500-6000 °C and vapor condensation to the particles of the required size. The obtained particles are characterized with the following size – 0.01-0.1 µm (Fig 1).

The nanodispersed particles synthesis was carried out in the following way (Figs. 2 and 3). The original material from dispensing mechanism 4 with the pneumatic transport gas was fed into plasma evaporator 5, where the raw material evaporation and the dispersed particles condensation took place. The aerosol with the nanodispersed particles was cooled in the refrigerator and was sent through cyclone 7 to bin 8, where the part of the nanodispersed particles were collected. The final separation of the nanodispersed particles from the technological gas took place with the help of filter 9. Elimination of pyrophorosity of the powder was done in reactor 10. Liquid hydrocarbon was fed from reservoir 12 through dispenser mechanism 11 and covered the nanodispersed particles. The process took place in the medium of the neutral gas – argon, circulating with the help of compressor 1 through receiver 2. The gas handling according to the scheme was done by means of gas ramp 3.

To obtain composite coatings is possible to apply various nanosized materials: pure, binary, alloyed and compositional [1,9,13,18,25].

Fig. 1. Morphology of nanodispersed particles surface used to obtain nanocomposite coating.

Fig. 2. Installation for obtaining nanosized powders.
Wide array of nanosized materials applied for coatings obtained, gives the opportunity to produce them with the preset physical and mechanical properties according to the manufacture requirements. To improve one or other physical and mechanical properties of the obtained coatings is necessary to use the corresponding nanosized materials [4,5,26-28]. In this regard, for carrying out the investigations we chose the nanosized powder of aluminum oxide - for micro-hardness increase and the nanosized powder of potassium polytitanate - for antifriction properties improvement of the obtained coatings.

At the present time, the chemical coating on the nickel base is obtained from acid and alkaline solutions. The coatings obtained from acid solutions have a number of advantages: high hardness to 600 MPa and deposition velocity to 20 μm/h. Accordingly, we chose the conventional acid solution of the following composition: nickel sulphate - 30 g/l, sodium acetate - 10 g/l, hypophosphite - 15 g/l with addition of nanodispersed particles of aluminium oxide - 1 g/l, potassium polytitanate - 1 g/l. The technological process of nanocomposite coating deposition consists in the following operations: coating preparation; coating deposition; coating heat treatment; coating quality control.

The investigations were carried out on the samples in the form of plates with the sizes of 100x15x2 mm, made of medium carbon steel. The sample surface preparation for deposition of composite coating included degreasing and etching. Degreasing was done in the solution of the following composition: tri-sodium phosphate 30-70 g/l; sodium carbonate 20-25 g/l; sodium hydroxide 5-15 g/l; fluid glass 5-7 g/l. The solution temperature was 60-70 °C, degreasing duration - 20 min. Then the sample was washed in hot water at temperature of 70-80 °C during 1-2 min and further in flowing water at room temperature during 1-2 min. For removing different kinds of oxides: rust, slag and corrosion products from the surface etching were done in 10 % hydrochloric acid solution 50-100 g/l. The solution temperature was 15-30 °C, etching duration was 1-2 min. Then the sample was washed in flow water during 1-2 min.

The coating deposition on the sample was done on the laboratory installation. The solution temperature 90-92 °C was kept with regulator. Thermal coating treatment was done in muffle furnace at temperature of 400 °C during 1 h. Coating quality control was carried out visually. Samples with bubbles, pores and uncovered areas were rejected.

One of the most important physical and mechanical characteristics of coating is reliability of its adherence with the base metal [29,30]. In-service the coating is subjected to the influence of temperature, mechanical loadings and other external and internal forces. The most stressed area in the coating is interface region between it and the base metal of a part. One of the indicators characterizing coating adhesion properties is diffusion layer thickness [31,32].

Structure investigations were carried out on sections and outside surface of coatings without mechanical treatment, just after the process of coating deposition and after thermal treatment. Indicative particle sizes, conceptual differences between base and composite coatings determined the character of modifiers distribution in the coating matrix. For the investigations, we used scanning electron microscope «MIRA II TESCAN». This research complex is intended for obtaining the image of the object surface with high space resolution and the information on composition of the coatings upper layers. The microscope operating principle is based on the some effects usage appearing under the coating surface radiation, with thinly focused electron beam - a probe. Different signals are generated because of interaction of electrons with the sample surface.
The main among them are electron flow: reflected, secondary, Auger-electrons, absorbed, and radiations: cathodoluminescent and X-ray. To obtain the sample surface image secondary, reflected and absorbed electrons are used. The rest radiations are applied in the microscope as additional information sources. The scanning electron microscope allows operating in the range from 10 to 1000000 manifold increases.

While studying the element composition of composite nickel coating and detection in it nanodispersed particles of powders of aluminum oxides and potassium polytitanate, the emission analysis of the samples according to the reflected electrons diffraction. For this, the research complex «MIRA II TESCAN» was supplied with chemical composition microanalyzers. This provided detailed information on the coating under investigation. The element chemical coating composition investigation is based on the reflected electron diffraction method.

**Fig. 4.** Scheme of the coating wear test: 1 – roller transmitting loading to block; 2 – block; 3 – roller with coating.

Wear resistance of the obtained coatings was determined on the friction machine MH-1M according to the scheme «roller-block» (Fig. 4). Blocks were manufactured from grey cast iron C4-20 full circle length 20 mm, width 10 mm. Roller was manufactured from medium carbon steel 40 with diameter 50 and width 12 mm. The composite nickel coatings were deposited on the roller. The tests were carried out on pure industrial oil H-20. The basic test loading was 900 N, shaft speed of friction machine 300 min⁻¹. Before tests, we ran in the friction pair samples during 3 h in the basic test modes. The sample lubrication was performed by immersing the bottom roller by 1/3 of a diameter into the lubricating bath with the volume of 150 sm³. The loading on the rollers was increased from 0 to the test load value gradually by 250 N after each 3 min. Load was changed by means of the loading device, mounted on the friction machine. During the tests, each experiment was repeated 3 times. On test completing, the parts were washed in the solvent petroleum spirit «Kalosha», dried in the air during 24 h and were weighted on the analytical balance HR – 250 AZG within the accuracy of 0,1 mg.

**3. RESULTS AND DISCUSSION**

When determining diffusion layer thickness (Ni-Fe) on metallographic specimen we differentiated several control points, where we registered the chemical elements content of nickel and ferrum (Fig. 5).

**Fig. 5.** Section with control points.

The results of these substances determination in each control point are presented in Fig. 6.

From the received data, it is obvious that nickel penetrates into the base metal at depth about 5 µm, forming diffusion layer that provides coating adhesion resistance with the base metal.
The surfaces of the base and composite chemical coatings on the nickel ground are presented in Fig. 7.

As it is seen from Fig. 7, outside surfaces differ greatly. The base coating is even free of foreign matters. Composite coating has great number of foreign matters of different size along the investigated surface. At that, the process of particle introduction occurs regularly and they are «planted» at different stages of coating formation.

It is found that nanodispersed particles are distributed in the coating regularly enough.

Therewith, we investigated end face of composite coating fracture immediately before and after thermal treatment at a temperature of 400 °C during 1 h (Fig. 8). On the coating fracture there is a number of parallel layers (Fig. 8a). The presence of strongly pronounced layers can be explained with change in phosphorus concentration through residue sickness [11]. In residue sickness, the embedded particles of the nanosized phase are observed (Fig. 8b). After thermal treatment at 400 °C during 1 h layering in nickel residue disappears [24]. Figure 8b
presents that boundary between layers is weakly distinguished. This fact is verified with the investigations [11,24,25]. Thus, the nanosized phase particles, penetrating into the coating change its structure, but do not disturb habitual way of the nickel chemical deposition.

To determine the amount of aluminum and potassium polytitanate in composite coating the spectral analysis of nickeled samples was carried out. The spectrograms of base and composite coatings on nickel ground were obtained (Fig. 9), according which we calculated the element content in each of them (Table 1). The content of the elements, which are not included in the table, is no more than 0.05 %.

Fig. 9. Spectrograms of base (a) and composite (b) coatings on nickel ground.

Judging by the data obtained, the composite coating, except nickel, phosphorus and sodium, contains aluminum, potassium, titanium. It proves that nanodispersed particles penetrate into coating.

Wear test results are presented in Table 2.

As a results of the samples test on wear resistance it is found that minimal mass wear is observed in the roller with composite chemical coating on the base of nickel and is 2,2 mg, whereas sample wear with the base coating is 3,4 mg. Thus, sample mass wear with the composite coating is 1,5 times less than the wear of the samples with the nickel coating without particle additives. Wear of the block contacting with the roller with the composite coating is 4 times less than the blocks contacting with the roller with the base nickel coating. Wear resistance of the sliding joint with the composite coating is 2 times more than analogical indicator of the friction pair with the base coating. Apparently, it can be explained with the implementation of the antifriction particles of potassium polytitanate into the coating. Besides, at the testing of the samples with the composite coating we recorded the decrease of the friction moment by 1,2 times in comparison with the samples with the base coating. As a result, the

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composite coating in comparison with the base coating possesses the increased wear resistance and better antifriction characteristics at the sake of the implementation of the particles with high strength and antifriction properties.

4. CONCLUSIONS

As the result of the investigations, composite chemical nickel-phosphate coatings containing nanodispersed particles of aluminum oxide and potassium polytitanate were obtained.

It has been established that at the boundary of «composite coating – base metal» the diffusion layer with the thickness of the order of 5 µm is formed. It provides the increase of cohesive resistance of coating with the base metal. In the process of composite coatings obtaining nanodispersed particles penetrate into it. It provides more dense structure conditioned with microscopic deformation of nickel lattice round nanodispersed particles. Pores were not observed on the composite coating surface.

It is found that at the border «composite coating – base metal» the diffusion layer with the thickness of about 5 µm is deposited. It provides the increase of the coating cohesive strength with the base metal. In the process of the composite coatings deposition the nanodispersed particles penetrate into it.

The samples with the composite coating possess the wear resistance 1,5 times higher than the samples with the base coating with chemical nickel, and the total wear of the sliding joint with the composite coating is 2,2 times lower than the total wear of the analogical joint with the base coating.

The obtained results suggest that the formation of composite coatings with the preset chemical composition can be an effective tool at solution of the problems that are vital for various industry branches.

REFERENCES


