MODERN STATE OF COMPOSITE COATINGS FORMATION PROBLEM

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ABSTRACT

Engineering novel material structures has continually been pursued to further advance modern technologies. These advancements often rely on novel processing technologies. Although many processing parameters have been thoroughly examined in the field of composition coatings, the formation processes are an exception. In this work, we examine the unique microstructures of composite electrolytic coatings, obtaining from electrolytes-suspension which contains nano-size particles of SiO_2 and carbon. Metallographic researches were carried out for an establishing the reasons of essentially differences in corrosion resistance of nano- nano-composition electrolytic coatings received at various electroplating temperatures. The results of corrosion investigation show, that the best corrosion resistance has nano-composition electrolytic coatings received at 333 K temperature. This novel electro-deposition technology has the potential to open new areas of research such as obtaining materials with desired functional properties.

Keywords: coatings, composite, nanosize particles, microstructure

INTRODUCTION

One of modern material science priorities is studying of nano-structured composite electrolytic coatings (nano-CEC) protection properties. This is due to interest in fundamental problems of a multi-component systems and breadth of their application in various fields of engineering, and technology. Therefore, development of new physical processes of composite systems formation and studying mechanical features changing - one of the main problems in materials science [1-5].

The associate to grow shortage of material resources development metallurgy in the world on XXI century it was directed for effectively to use metals and economical alloying , as well as partly taken on ferrous basis – alloys of steel and cast-iron. The requirement to construction to materials, to the objects doing of machine, use to give qualities on a metallurgy it is founded for use thermally, chemical-thermally technology and settled on makes by sources energy for surface of object. It was result such the influence is structurally change first conscience object and this is identified variety process or equal to the becloud surface [6-12]. The level of the research potential, as a whole level to civilization – this is defines claiming new material. Necessity especially it was reached on high degree in last decade of XX century and in began of XXI century. The main by question now a day is corrosion metal and to fight to wear out. It especially much there is on objects, machine, in aggressive encirclement: water sea, increased, sour, makes what different salts, in productions coal and ore etc. In last year conducted home and foreign research works, for taking high strong and producing gambol instrument, nano structural strong alloys, production nano structural hard thermo and high strong pillowcase against corrosion is a future perspective ideas [13-19].

The research progress and development levels increase necessity making new materials. Composite electrolytic pillowcases plays main role in decisions of this problem. Composite electrolytic pillowcases- that in which consists matrixes of the metal and in which there is dispersion phase. If dispersion particles is will less 100 nm, then they fall into row is nano materials and particles dispersion definitively to change characteristic of the matrix of the metal. So notion composite electrolytic pillowcase adjusts in separate group, but main nano composite electrolytic pillowcase and main exploratory work elaborates their characteristic and structures. The characteristic CM not always requires full volume concentration and objects, only in determined stage to becloud it is enough. The method nano composite electrolytic pillowcase (nano-CEP) give possibility together mix dispersion particles and metal-electrolytic [20-23].

In our the country method of study determination micro hardness of alloys from 1940 years known. Method determination micro hardness metal by means of equipment PMT-3 thought up famous scientist M.M.Hrushcev and E.S.Berkovich [24-27]. Basically equipment PMT-3 is intended for determination micro hardness material microscopic measurement. Presently in enterprise this method uses in different technological operation to conversion of the processes of the particles and influence on them chemical, mechanical layer, as well as for determination micro hardness special different particles thickness below 0.1 mm.

MATERIALS AND METHODS

The purpose of our researches is developing $Cr\text{-}SiO_2$ nano-structured composition coatings obtaining. For the deposition of nano-structured composite electrolytic coatings and we chose the versatile chrome electrolyte containing dioxide of silica. Composition of electrolytes for nano-CEC precipitation is presented in Table 1.

Table 1. Composition of $Cr\text{-}SiO_2$ electrolyte

Name or formula	Units	Quantity
Chromic anhydride CrO_3	g/l	250-300
H_2SO_4	g/l	2,5-3,0
Dioxide of silica SiO_2	g/l	20-25
Modes of obtaining:		
Electrodepositing temperature T	K	303-343
Current density	A/m^2	3-7

Due to the fact chrome has most hardness, durability and anticorrosive stability in many hostile environments, they were chosen as matrix metal of CEC. Chrome can quickly passivated with formation of a strong and reliable film, and so chrome has become the basic and integral component of all sorts of rustproof and heat-resistant steels. Before testing samples were preliminary degreased, washed out by the distilled water until completely wetting. Then samples were dried up, packed into a filtering paper, kept in exiccator with dehumidifier within 1 hour and weighed on analytical scales accurate within 0,0001 g. Results are processed in accordance with GOST 9.506-87, p. 2.6, accuracy indicator – E is defined in accordance with GOST 9.502-82.

RESULTS AND DISCUSSION

As is known, during mutual contact of solids, the formation of films of secondary structures occurs in surface layers in the course of friction. At present, these films are formed by the introduction of various admixtures into lubricants, special chemical heat treatment in solid, liquid, or gaseous media, as well as by electrolysis of aqueous solutions of metal salts. Our aim is to develop a method of creation of surface films by precipitation of electrolytic composite coatings. To realize this idea, we applied electrolytic composite coatings, based on chromium with disperse particles of sulfur and silicon dioxide, on specimens made of St3 steel. We achieved the formation of a modifying layer in the course of friction by tests of electrolytic composite coatings on a friction machine coupled with a counterbody made of hardened ShKh15 steel. We carried out tests without lubricants. Under such severe conditions, chemical reactions occur in the near-surface layers of bodies rubbing each other, in which not only components of electrolytic composite coatings but elements of the surroundings take part. We subjected a modified film formed during this procedure to metallographic optic and electronic examinations and to electron diffraction investigations.

The results of metallographic examinations demonstrate that, at the initial state of electrolytic composite coatings, disperse particles of silicon dioxide and sulfur are distributed quasi-uniformly in the coating volume. Therefore, we have reasons to assume that disperse particles will come uniformly from the coating volume into the contact zone in the course of tests of electrolytic composite coatings.

It is worth noting that disperse particles mostly enter the contact zone not at once but in parts as they gradually leave the metal matrix and are robbed and spread over the contact surface. In this case, all possible physicochemical processes occur simultaneously, which results in the formation of a modifying layer, i.e., a secondary structure representing a metastable phase, on which the main actions are localized in the course of friction and wear. Just this phase was the object of our investigation.

Electron diffraction investigations show that almost half of the lines in the diffractograms cannot be identified with those from any known equilibrium compound of chromium, sulfur, silicon, and oxygen. This testifies to the fact that a considerable amount of phases appearing during friction and wear are nonequilibrium, nonstoichiometric, and very complex by their composition. These phases reflect all the specific character and complexity of physicochemical processes occurring in the near-contact friction surface.

It should also be noted that a broad range of complex chemical compounds with nonstoichiometric composition is not characteristic of the actual function of the modifying layer in the course of friction and wear since it is thermodynamically unstable and passes into a more stable state as soon as friction terminates.

Diffractograms taken from the surface film of various specimens and from different sections of the same specimen differ substantially from one another: the diffraction maxima consist of individual reflections, or have the shape of distinct rings, or are vague, or include a diffusive halo. In some cases, the diffusive halo is uniform, but sometimes it is formed by several maxima. These results demonstrate the formation of a thin-film layer of secondary structures in the course of friction, their states being in the range from a fine-crystalline to amorphous one. The appearance of halos with several maxima proves that the secondary structure is transformed into a textured ultra disperse or amorphous structure. In other words, the modifying layer shows evident signs ofstructural adaptability, since the subsurface layer of a electrolytic composite coating has no such structure.

The structural adaptability of the modifying layer is most clearly expressed in diffractograms taken from the same specimen at various stages of the friction path. Its length is about 500 m. After every stage of the friction path, we investigated diffractograms of all Nnds of specimens. We have established that, at the first stage of tests, the process of friction and wear only begins at sections of the contact surface, and the diffractograms consist of individual reflections. At the second stage, the process is further developing, and the diffractograms consist of continuous distinct or vague circles. After the third stage of tests, the number of diffractograms with individual reflections gradually diminishes, the number of diffractograms with distinct circles also decreases, and the number of diffractograms with vague rings and halos grows. After the fourth stage of tests, all the diffractograms consist of halos with maxima. This stage corresponds to minimum wear and maximum structural adaptability of the modifying layer.

By comparing modifying layers obtained upon the introduction of admixtures into oils with similar layers appearing on the surface of electrolytic composite coatings, we should mention the following obvious advantages of the latter.

Disperse particles, introduced into oil as an admixture, can enter the contact zone only together with oil. But, for electrolytic composite coatings, they are automatically fed from within the coating as a result of wear or deformation of the matrix under the action of external loads. The less the coupled parts fit each other (or the greater the load), the greater is the amount of an admixture coming into the contact friction zone.

With use of data of Table 2 and results of the chemical analysis of five melts of alloy 06XN28MDT [5] In chloride-containing solution with pH7 Zc_r coefficient value vibrated from 0.17 melt 1 to 1.04 melt 4. It was known that [10] at $Z_{(Cr,\ Ni)} \leq 1$ Cr quantity on surface of alloy is larger than in its volume. Thus, in melts 1-3; 5 of alloy 06XH28MDT Cr quantity on surface of the samples increased after endurance in chloride-containing solution with pH7 and concentration of chlorides 600 mg/1. At decrease of pH chloride-containing solution to 6 a value of Zc_r increased from 0,61 (melt 5) to 1.48 (melt 3). In this case Zc_r melts 1 didn't changed and melts 2 slightly decreased(Table 2). However, such tendency has been connected with high determination error of Cr in solution after endurance of samples. Therefore one can consider that in decrease of pH chloride-containing solution Z_{Cr} value of alloy 06XN28MDT grows. Thus, the pitting corrosion of alloy in chloride-containing solution with pH7 is more dangerous than in solution with pH6. This is agreed with data [11]. The corrosion losses of Cr, Ni of alloy 06XN28MDT and coefficients values Z_{Cr} and Z_{Ni} (Table l; 2) have been stipulated by influence of the chemical composition of all within the ranges of standard and its structural heterogeneity. It has been established by the correlation and regressive analysis of the results of the investigations that the corrosion losses of Cr from alloy 06XN28MDT on straight-line regularity grow in increase of content of Mn(2), Si(3), average number of austenite grain d_3(4) and decrease of Mo(5) in it:

Table 2. Z_{Cr} and Z_{Ni} coefficients of alloy 06XN28MDT in the studied chloride-containing commercial waters

№	1		2		3		4		5	
pH	Z_{Cr}	Z_{Ni}	Z_{Cr}	Z_{Ni}	Z_{Cr}	Z_{Ni}	Z_{Cr}	Z_{Ni}	Z_{Cr}	Z_{Ni}
6	0,17	0,54	0,17	0,83	1,48	1,95	1,28	0,69	0,61	1,74
7	0,17	1,33	0,22	1,09	0,23	0,84	1,04	0,80	0,44	0,67

$$\Delta Cr = 10^{-6} (-1044{,}43+5000Mn); \qquad r= 0{,}72 \qquad (1)$$

$$\Delta Cr = 10^{-6} (-3589{,}92+5000Si); \qquad r= 0{,}87 \qquad (2)$$

$$\Delta Cr = 10^{-6} (-262{,}52+50000d_3); \qquad r= 0{,}72 \qquad (3)$$

$$\Delta Cr = 10^{-6} (9840{,}20-3333Mo); \qquad r= -0{,}71 \qquad (4)$$

In addition, it has been established by graphical analysis that a content of C, Cr, Ni, P, volume of titanium nitrides V_H, volume of oxysulfides V_{0K}, and also average distance between titanium nitrides L_H and oxysulfides L_{0K} ambiguously influence on corrosion losses of Cr frod alloy in chloride-containing solution with pH6 and concentration of chlorides 600 mg/1.

In particular, between ΔCr and parameters of alloy the parabolic dependence, and between ΔCr and V_{0K}, LOK - hyperbolic has been established. In increase of averse distance between inclusions their sizes grow. Therefore it follows from data of Table 2 that ΔCr is decreased in increase of sizes of titanium nitrides to average value. The subsequent increase of sizes of titanium nitrides favors growth of ΔCr of alloy. Taking into account such tendency and data of Table 2. e, one can assume that titanium nitrides of average sizes cathodally protect an alloy 06XN28MDT in the investigated chloride-containing solution and thus, decrease the corrosion losses of Cr. At the border of large titanium nitrides with austenite matrix the dissolution of Cr from alloy is intensified.

CONCLUSIONS

The introduction of modified electrolytic composite coatings at a cable plant has shown that they give the possibility:

- to increase the service life of draft tires by up to 20 times as compared with commercial ones made of deficient and expensive ShKhl5 steel;

- to organize a waste-free technology due to multiple recycling of worn tires by repeated application of electrolytic composite coatings, which gives considerable savings in energy and materials and enables us to free a machine stock for industrial needs.

Since admixtures, as a rule, are polydisperse and their finest particles most easily penetrate, together with oil, into the near-contact zone. As the rubbing surfaces work in and better fit each other, less and less coarse particles enter this zone, i.e., the efficiency of action of the admixture will decrease. But this is impossible-for electrolytic composite coatings. All the particles, irrespective of their sizes, are equally fed into the near-contact layer, which guarantees high efficiency of their participation in the formation of the modifying layer.

According to the results of the corrosion tests, correlation, regressive and graphical analysis the regularities and mechanisms of the corrosion dissolution of Cr and Ni from alloy 06XN28MDT in chloride-containing commercial waters of Karachaganak deposit with pH=6; 7 and concentration of chlorides 600 mg/1 have been established, exactly:

-in chloride-containing solution with pH=6 the corrosion losses of Ni on straight-line regularity grow in increase of content C, P in alloy, average distance between titanium nitrides and decrease of Mn, and also volume of titanium nitrides. At the borders of the large oxysulfides and titanium nitrides Ni from alloy is intensively dissolved. The small oxysulfides, titanium nitrides and complex carbides at the borders of grains block dissolution of Ni, and P as a surface-active element intensifies this process;

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