

RESEARCH OF CORROSION RESISTANCE OF CHROME BASED NANO-COMPOSITION ELECTROLYTIC COATINGS

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ABSTRACT

Corrosion resistance nano-composition electrolytic coatings (nano-CEC) of Cr-SiO₂ are represented in this article. Nano-CEC was used to protect against corrosion of construction steel 17Г1С. It has been established the optimum temperature of receive for best corrosion resistance is formed. Nano-sized particles of SiO₂ in chromium matrix were shown by atom-force microscopy.

Keywords: atom-force microscopy, nano-sized particles, nano-composition electrolytic coatings (nano-CEC), corrosion resistance

INTRODUCTION

Special interest to composites and coatings has emerged last decades in connection with sharp growth of requirements to operational properties of the materials working in the conditions of corrosive medium, friction and deterioration. In this connection development of effective and economic methods of nano-CEC reception, studying of processes of electroplating, also research of influence of microstructure of electrolytic coatings on its properties is the actual problems of modern materials science.

Corrosion is the most widespread cause of failures of pipelines and oil-producing equipment [1-7]. The basic constructional material of petrochemical branch is the steel 17Г1С. Therefore we have set a problem to develop an effective protection method against corrosion destruction by electroplating chrome- silicon dioxide nano - composite electrolytic coatings (nano-CEC).

EXPERIMENTS

The present work's purpose is reveal optimum modes for nano-CEC working in oil production conditions.

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.

Silicon dioxide (particles sizes 5-10 nanometers) and shungite of Kazakhstan "Koksuskij" deposit have been chosen as a second phase (disperse component). Shungite is poly-substance, which consists of carbon and various metals oxides. So chrome – shungite of CEC substantially represents a composition including not one, but many disperse phases, data about which are resulted in table 1.

Table 1. Chemical composition of Koksuskij deposit's shungite according TU-7000 KR 3873 5112-003-2002

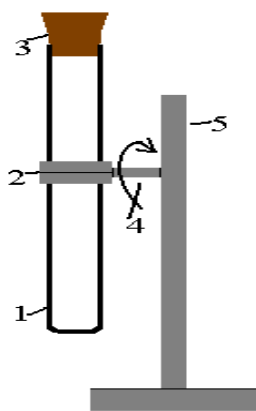
Chemical formula	Average chemical composition, %	Chemical formula	Average chemical composition, %
C	4,0-15,0	K ₂ O	2,0-0,4
Al ₂ O ₃	15,0	CaO	0,2-30,0
Na ₂ O	0,2-0,6	Fe ₂ O ₃	3,5-4,0
SiO ₂	29,0-70,0	MgO	0,7-3,7
TiO ₂	0,3-0,9	microelements	

As we can see in this table shungite represents suite of various chemical compounds, most of which are chemical compounds with oxygen and only one component - carbon is presented in the form of a chemical element.

We think use of shungite as CEC second phase is expedient due to following reasons:

- a. shungite - the natural material is not deficit and inexpensive;
- b. its chemical composition well suits as the second phase for CEC reception because of it mainly consists of oxides - proof in chromium plating electrolyte, and single element - carbon specifying shungite is also proof in chromium plating electrolyte.

In this work natural shungite were been prepared in the form of concentrate for obtaining nano-CEC. Shungite were sifted through the sieve with 5 microns-sized cells by ultrasonic disperser. The received powder was filled into sedimentation column (fig. 1), roiled and settled within 2 hours. Then the liquid was siphon selected from middle part, evaporated and shungite concentrate was received.



1: The case of sedimentation columns; 2: A holder; 3: A plug; 4: A rotation axis; 5: supports stand.

Figure 1. The scheme of sedimentation columns

It is followed from figure 2 that the shungite concentrate received at different modes has the various dispersion and microstructure - rather rough (a) and thin (b). Detailed researches show, that the first (a) in the structure always contains the second (b) in full volume whereas last one is allocated from the first (a) by additional only time consumption. Apparently, more fine-dispersed concentrate consists of light and dark particles with mainly spherical form and the sizes less than 100 nanometers, moreover light particles are much larger than the dark.

Rather large light particles in comparison with small and dark ones possess the enhanced tendency for conglomerations formation. Results of particles structure research testify that light large particles (a) mainly consist of silicon dioxide and small ones (b) mainly - carbon.

Researches of schungite concentrate fractional composition by atom-force microscopy (AFM) have shown (figure 3) that the most of particles (b) have the sizes less than 100 nanometers. The received powder was used as the composite additive for nano-CEC reception.

Nano-CEC puton steel 17Г1С samples with size (50x20x2) mm³ at various temperatures of electric precipitation, and comparison of the corrosion resistance was carried out with steel 17Г1С without coating, traditionally used in this branch. Nano-CEC were received from the chromium plating electrolytes which composition is resulted in table 2.

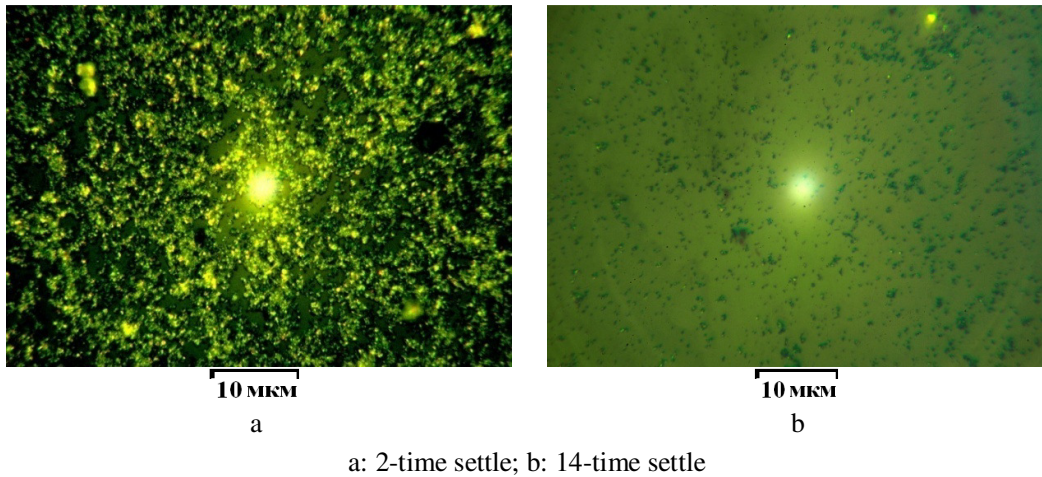


Figure 2. Optical microscope pictures of schungite concentrate received at different modes

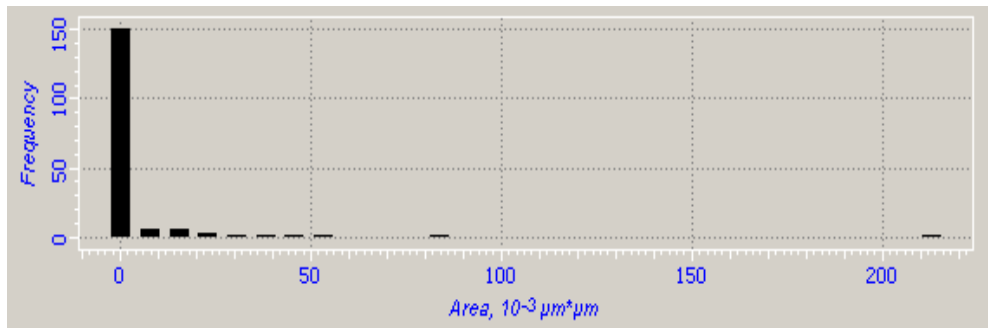


Figure 3. AFM - histogram of the particles used for chrome- schungite nano-CEC reception

Table 2. Composition of electrolytes for nano-CEC precipitation (g/l)

A ₀	A ₁	A ₂	A ₂
CrO ₃ - 200	CrO ₃ - 250	CrO ₃ -250	CrO ₃ - 250
Ni SO ₄ - 25	H ₂ SO ₄ - 2,5	SrSO ₄ - 7	H ₂ SO ₄ -2,5
CaCO ₃ - 55	schungite - 25	schungite - 25	SiO ₂ - 25
Schungite - 25			

Precipitation temperature is: 333-343 K, Density of a current: 5 kA/m² with periodic ultrasonic influence on suspension. The action period is 10 minutes.

RESULTS AND DISCUSSIONS

Well-known, that during composite coatings precipitation the disperse phase entered into electrolyte not always gets to a coating and is overgrown with electrodeposited metal. To confirm incorporation into a chromic matrix of silicon dioxide nano-particles entered into electrolyte we have carried out researches on an atom-force microscope (AFM) "Itetra Terma". AFM allows receiving the unique information about a surface structure, to define deformation-strength and relaxation properties on micro- and nano-dimensioned level. AFM research of the sample can carry out due to the forces arising between cantilever and nano-CEC surface. Various forces prevail depending on distance between the surface and a sonde. We carried out researches by a contactless method at cantilever-sample distances about several tens angstrom, where the main interaction is the intermolecular one named Van der Waals forces. The atom-force microscopy gives the opportunity for realization of the new approach in research of the surface, and allows expanding possibility for getting the many-sided information on morphology and surface characteristics of nano-CEC with the high spatial permission.

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.

Because of Kazakhstani oil deposits are basically on shore of Caspian sea, tests are carried out in modelling solution of «Zhanazhol» deposit's commercial water containing table salt and other compounds similar to natural corrosion environment of operation conditions (g/l): sodium chloride, 60,7; calcium chloride-17,4; sulphate of magnesium 3,3; magnesium chloride - 1,6. Tests were carried out at the stand designed by STC "KING" JSC within 10 hours at temperature 293K. Tests were carried out in dynamic conditions of liquid motion generated by peristaltic pump with speed 0,2 m/s. Whereas the commercial water obtained as a result of oil settling is high corrosive, test conditions at the stand are undoubtedly more rigid than in real conditions of petroleum production.

Data on electric precipitation temperatures and results of comparative corrosion tests of a steel 17Г1С without nano-CEC (batch 1) and with nano-CEC (batch 2-6) are resulted in table 3.

For an establishing of the causes of essential difference in corrosion resistance of nano-CEC received at different temperatures of electrolyte, we have carried out metallographic researches, which have shown, that one of the principal causes is the nano-CEC microstructure and microporosity dissimilarity. So nano-CEC received at electric precipitation temperatures 333-343 K have more homogeneous structure and practically porousless, whereas nano-CEC received from electrolyte at 318 K possess considerable porosity and microcracking.

Table 3. Results of corrosion resistance test of nano-CEC put on steel 17Г1С

<i>Batch No</i>	<i>Samples</i>	<i>Electrolyte temperature, K</i>	<i>Corrosion Rate, g/m²h</i>	<i>Corrosion accuracy indicator on, E %</i>	<i>Corrosion resistance increase, times</i>
1	Steel 17Г1С	-	0,8696	8,34	1
2	Nano-CECCr-SiO ₂	318	0,126	6,58	6,9
3	Nano-CECCr-SiO ₂	323	0,129	4,32	7,07
4	Nano-CEC Cr-SiO ₂	328	0,124	7,12	7,01
5	Nano-CECCr-SiO ₂	333	0,016	5,24	54,35
6	Nano-CECCr-SiO ₂	343	0,043	8,31	24,22
7	Nano-CECCr- schungite	318	0,128	6,3	6,5
8	Nano-CECCr- schungite	323	0,109	4,2	8,05
9	Nano-CECCr- schungite	328	0,101	5,58	9,1
10	Nano-CECCr- schungite	333	0,098	5,32	10,07
11	Nano-CECCr- schungite	343	0,095	5,12	9,09

The estimation of protective ability i.e. steels corrosion resistance increase as result of nano-CEC electroplating was executed by comparison of corrosion rate of steel 17Г1С and steel 3 without nano-CEC (batch 1) with corrosion rate of nano-CEC electroplated on these sorts of steel at different temperatures of electric precipitation (batch 2-6).

CONCLUSION

It is follows from the received results:

1. Nano-CEC received at electric precipitation temperatures 333 K possess the best protective properties (the resistance increases up to 54 times);
2. Nano-CECCr-SiO₂ received at electrolyte temperatures 318 K possess the least protective properties, but also they possess higher (approximately in 7 times) corrosion resistance in comparison with steel 17Г1С without nano-composition coatings.

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