ANNOTATION

dissertation for the degree of Doctor of Philosophy (PhD) in the specialty - 6D074000 « Nanomaterials and nanotechnology»

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Dissertation topic: «Nanocomposition coatings formation processes and physical and chemical properties»

The purpose of the dissertation research - study of the patterns of microstructure formation of chromium-based composite coatings modified with nanosized particles (C, SiO_2), heterogeneous binary Fe-W (Mo), Ti-Co (Mn) and triple Fe-Co-W systems obtained by the electrolytic method, as well as the study of their physico-chemical and mechanical properties.

Research objectives.

Conduct studies on the effect of the concentration of nanosized carbon and silicon dioxide, deposition modes, current efficiency and deposition rate of Cr-C-SiO_2 nanostructured electrolytic coatings, as well as Fe-W (Mo), Ti-Co (Mn) and Fe nanostructured composite systems -Co-W.

To establish the effect of the degree of dispersion and the concentration ratio of the components of the second phase on the formation of the structure and properties of Cr-C-SiO_2 of CEC, to develop optimal electrolyte compositions and a fundamentally new, easily implemented technology for controlling the nano-CEC microstructure.

To study the influence of deposition modes (continuous, pulsed) and current density on the formation of the microstructure of binary Fe-W (Mo), Ti-Co (Mn) and ternary Fe-Co-W composite systems and to develop a phenomenological model to describe the formation of the microstructure of nanocomposite coatings.

Conduct systematic comprehensive studies of the functional properties of Cr-C-SiO_2 composite electrolytic coatings, as well as Fe-W (Mo), Ti-Co (Mn) and Fe-Co-W nanocrystalline systems in laboratory and industrial conditions.

Research method

The composition of the microstructure of nano-CECs was studied by optical metallography, spectrometric and X-ray diffraction analysis, scanning electron and atomic force microscopy. To study the corrosion properties, gravimetric and potentiodynamic methods were used, as well as a method for measuring electrical resistance. Physico-mechanical properties were studied by methods of measuring microhardness and adhesion and using tribological tests. Mathematical modeling of the formation of electrolytic coatings and prediction of functional properties were carried out on the basis of the laws of electrochemistry in electrometallurgy.

The main provisions of the protection:

1. The morphology of the synthesized chromium electrolytic coatings is determined by both the temperature and current density and the ratio of the concentrations of nanodispersed carbon and silicon dioxide powders in the

electrolyte suspension, which is manifested in the formation of a spongy structure at a deposition temperature of 293-303 K, globular at 313-323 K and smooth poreless at 333-343 K.

2. The continuity, deposition rate, and current efficiency of Cr-SiO2-C nanostructured coatings can be purposefully controlled by lowering the electrodeposition current density from 7 to 3 kA / m^2, and the formation of layers on the cathode surface is satisfactorily interpreted within the framework of the Faraday-Onsager model.

3. In coatings consisting of binary Fe-W (Co), Ti-Co (Mn) and triple Fe-Co-Wo composite systems, it is possible to control crystal sizes by increasing the current density in combination with a pulsed electrodeposition mode and, thus, purposefully form nanocrystalline and amorphous-crystalline structure.

4. Corrosion-electrochemical characteristics of coatings from binary Fe-W (Co), Ti-Co (Mn) and triple Fe-Co-W nanostructure systems depend on the content of the refractory component and deposition modes, and the increase in chemical resistance in an acidic medium is due to surfaces of acid tungsten oxides.

Description of the main results of the study.

1. A technique has been developed for the deposition of nanostructured composite coatings based on chromium by the electrolytic method using carbon as a reinforcing phase in the form of lamp black with a particle size of 11–100 nm and silicon dioxide (5–50 nm) with a controlled thickness, composition, and structure. It is shown that the quantitative content of the nanodispersed phase in the chromium matrix can be controlled by changing the temperature and current density. The morphology of the synthesized chromium electrolytic coatings can be purposefully formed both by varying the deposition modes and by changing the ratio of the concentration of nanodispersed powders of carbon and silicon dioxide in the electrolyte, which manifests itself in the formation of a spongy structure at a deposition temperature of 293–303 K, globular at 313–323 K, and smooth, pore-free at 333-343 K.

2. New electrolytes-suspensions of optimal composition have been developed, which make it possible to obtain nanostructured Cr-SiO_2-C CEC with improved physicochemical properties. It has been established that the scattering and hiding power of the developed electrolyte-suspensions is well described in terms of the Faraday-Onsager model, for which the coating continuity increases with a decrease in the electrodeposition current density from 7 to 3 kA/m SiO_2 in electrolyte 6/14 g/l. The microstructure and phase composition of Cr-SiO_2-C nanocomposite coatings have been studied by optical metallography, X-ray diffraction analysis, scanning electron and atomic force microscopy. As a result of the research, it was established that the reinforcing phase has a significant effect on the morphology of the coatings in the concentration range of the nanodispersed phase in the electrolyte-suspension of 16.0-25.0 g/l.

3. The technology for the synthesis of nanocrystalline coatings with double Fe-W(Mo) and ternary Fe-Co-W alloys, Ti-Co(Mo) oxide coatings with enhanced tribological, anticorrosion and catalytic properties was developed with a study of the influence of deposition modes (stationary, pulsed) on the size of nanocrystals. It has

been found that in nanocrystalline coatings of double Fe-W(Mo), Ti-Co(Mo) and ternary Fe-Co-Wo alloys deposited by the electrolytic method, an increase in current density affects the reduction in crystal size and the formation of an amorphous-crystalline structure. Using AFM, SEM, TEM and X-ray diffraction analysis, it was found that binary electrolytic Fe-W alloys are thin nanocrystalline compounds with a phase composition that is a solid solution of tungsten in α-Fe. X-ray patterns of Fe-Co-W ternary alloys reflect an amorphous-crystalline structure containing phases of α-Fe, intermetallic compounds Fe7W6, Co7W6.

4. Gravimetric and potentiostatic studies of the corrosion resistance of the obtained nano-CECs in a 3% NaCl solution showed that the corrosion-electrochemical characteristics of coatings from binary and ternary composite systems depend on the content of the refractory component and deposition modes, and the increase in chemical resistance in an acidic medium is due to the formation of surfaces of acidic tungsten oxides. On average, nano-CEC showed an increase in corrosion resistance from 10.2 to 85.3 times. According to the ACT “On the results of testing electrolytes for applying nano-CEP iron-cobalt-tungsten on electrical equipment components at the enterprise INTERCOM LLP, semi-industrial tests showed that coatings from double Fe-W (Co) and triple Fe-Co-W, Cr-SiO_2-C nanosystems can be effectively used to harden steel and cast iron surfaces.

Substantiation of the novelty and importance of the obtained results.

For the first time, a comprehensive study of the processes of microstructure formation and physicochemical properties, chromium-based composite coatings structured by nanoscale particles (C, SiO_2), as well as nanocrystalline coatings from double Fe-W (Co), Ti-Co (Mn) and triple Fe- Co-W systems obtained by the electrochemical method.

A new approach has been developed for controlling the size of crystals in binary Fe-W (Co), Ti-Co (Mn), and ternary composite Fe-Co-W systems based on variations in current density and formation modes of multicomponent coatings.

The mechanism of co-precipitation of iron with tungsten and iron with molybdenum into a nanostructured alloy was established for the first time and the effect of the composition of electrolytes and deposition modes on the content of components, morphology, structure, properties and efficiency of the electrodeposition process of Cr-SiO2-C, Fe-W (Co) coatings was substantiated. Ti-Co (Mn), Fe-Co-W.

Based on a quantitative analysis of experimental data on the kinetics of oxidation, as well as on the results of tests of physicomechanical properties (microhardness and tribolgia), a phenomenological model is proposed to describe the formation of the microstructure of nanocomposite coatings obtained on a substrate of steel St3, AISI304 and 17Г1С

Based on the presented theoretical and experimental studies, the composition of nanostructured composite coatings based on chromium, as well as nanocrystalline coatings from iron-tungsten and iron-cobalt alloys for corrosion protection of surfaces made of carbon steel St3 and structural AISI304 and 17Г1С steels to improve functional properties in neutral and alkaline, is proposed. environments.

Based on the research results, a new electrolyte was developed, obtained for the utility model “Electrolyte for applying nanocoatings with an iron-tungsten alloy” (patent of the Republic of Kazakhstan No. 3440 dated 11.11.2019).

Compliance with the directions of scientific development or state programs. The work was carried out in accordance with the project of grant financing of the Ministry of Education and Science of the Republic of Kazakhstan 2018-2020. AR05130069 “Development of nanotechnology for the synthesis of functional galvanic coatings for electrical components” in the priority area “Rational use of natural resources, including water resources, geology, processing, new materials and technologies, safe products and structures”. State registration number 0118РК00315.

15 publications were published on the topic of the dissertation, in which the doctoral student was directly involved as an author and co-author:

High impact factor articles from the Thomson Reuters database or from publications in the Scopus international science database:

1. Ved’ M., Sakhnenko N., Yermolenko I., Yar-Mukhamedova G., Atchibayev R. Composition and corrosion behavior of iron-cobalt-tungsten/ Eurasian Chemico-Technological Journal. 20 (2), 2018.- P. 145-152.

Articles in publications recommended by the Committee for control in the field of education and science of the Ministry of education and science of the Republic of Kazakhstan:

1. Сахненко Н.Д., Ведь М.В., Каракуркчи А.В., Яр-Мухамедова Г.Ш., Атчибаев Р. А., /Антикоррозионные свойстваsuccнанокомпозиционных покрытий в аминовых средах/ Вестник КазНИТУ. №3 (127). 2018. - С. 588 – 593.
2. Наривский А.Э., Субботин С.А., Беликов С.Б., Яр-Мухамедова Г.Ш., Атчибаев Р. А. Влияние параметров оборотных вод, химического состава и структурной гетерогенности стали AISI304 на ее питтингостойкость / Вестник КазНИТУ. №3 (127). 2018. - С. 588 – 593.
3. Яр-Мухамедова Г.Ш., Атчибаев Р. А. Исследование морфологии и микротвердости антикоррозионных нанокомпозитных электролитических покрытий $Cr\text{-}C\text{-}SiO_2$ / Вестник КазНИТУ. №5 (141). 2020. - С. 340 – 348.
4. Патент РК № 3440. Электролит для нанесения нанопокрытий сплавом железо-вольфрам. Опубл. 11.11.2019.

Publications in abstracts collections:

1. Кызырова А., Атчибаев Р. А. Исследование коррозионной стойкости нанокомпозиционных электролитических покрытий на основе хрома/ Сборник трудов III конфренции студентов и молодых ученых «Химическая физика и наноматериалы» посвященной памяти Мансурова Б. З. Алматы, Казахстан. 2018.- С. 123 – 128.
2. Яр-Мухамедова Г. Ш., Атчибаев Р. А. Исследование нанокомпозитных электролитических покрытий $Cr\text{-}C\text{-}SiO_2$ методом низковакуумного сканирующего электронного микроскопа Phenom ProX / Международная научная конференция студентов и молодых учёных «Фараби әлемі». Алматы, Казахстан. 2020- С. 189- 193.

In foreign international conferences:

1. Yar-Mukhamedova, G., Ved, M., Karakurkchi, A., Sakhnenko, N., Atchibayev R/Research on the improvement of mixed titania and Co (Mn) oxide nano-composite coatings/ IOP Conference Series: Materials Science and Engineering, Vol. 369, № 1. K 2018, 012019.
2. Яр-Мухамедова Г.Ш., Мукашев К. М., Мурадов А. Д., Атчибаев Р. А., / Модифицированный электролит для получения нанокомпозиционных покрытий с улучшенными антикоррозионными свойствами / Intern. Conf. «Advanced technologies in research and education». Severodonetsk, Ukraine. 2018.- Pp. 24-25.
3. Ved', M., Sakhnenko, N., Yermolenko, I., Yar-Mukhamedova, G. Atchibayev R. Nano composition Ti-Co(Mn) coatings investigation / 18th International Sc. GeoConf. SGEM 2018. Vol. 19 (6.1). 2018.- Pp.307-315.
4. Atchibayev R., Mukashev K., Muradov A., Kyzyrova A., Aitbayev Z. Anti – corrosion properties of nanocomposite coatings in amine environments/18th International Sc. GeoConf. SGEM 2018. Vol. 19 (6.1). 2018.- Pp.39-47.
5. Яр-Мухамедова Г.Ш., Мукашев К. М., Мурадов А. Д., Атчибаев Р. А. Разработка рекомендаций по применению коррозионностойких нано-КЭП для защиты насосов воды ТЭЦ / International conference «Problems of corrosion protection of materials». Lvov, Ukraine. 2018. - P. 249-252.
6. Temirgaliyeva E., Belisarova F., Kalmurzayeva V., Yar-Mukhamedov Y., Atchibayev R. Effect of deposition temperature on corrosion resistance of nano-CEC / 19th International Sc. GeoConf. SGEM 2019. Vol. 19 (6.1). 2019.- Pp.167-173.
7. Yar-Mukhamedov Y., Atchibayev R. Baisholanova K., Myrzakul S. Computer simulation of composition coatings with set properties / 19th International Sc. GeoConf. SGEM 2019. Vol. 19 (6.1). 2019.- Pp. 125-130.