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XVI International Conference

Problems of Corrosion and Corrosion Protection of Materials (Corrosion-2022)

(the 490th event of the European Federation of Corrosion)

ABSTRACT BOOK

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XVI International Conference "Problems of Corrosion and Corrosion Protection of Materials" (Corrosion-2022) was held at Karpenko Physico-Mechanical Institute of NAS of Ukraine on November 15-17, 2022. This Book of Abstract contains the results of studies devoted to fundamental aspects of corrosion and modeling; corrosion-mechanical destruction of materials; corrosion-resistant materials and coatings; inhibitors and anti-corrosion pigments; testing methods and corrosion monitoring; corrosion protection of industrial equipment; corrosion of alternative energy equipment.

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- fundamental aspects of corrosion and modeling;
- corrosion-mechanical destruction of materials;
- corrosion-resistant materials and coatings;
- inhibitors and anti-corrosion pigments;
- testing methods and corrosion monitoring;
- corrosion protection of industrial equipment;
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Ми шукаємо технічних партнерів. Наша компанія надає лабораторні приміщення, а також фінансування. Якщо ви зацікавлені, надішліть свою інформацію та опис проекту на адресу: E-mail: 65503201@qq.com WhatsApp/Viber: +380984669338 Fundamental aspects of corrosion and modeling

PECULIARITIES OF HYDROGEN INDUCED DAMAGING OF FERRITE-PEARLITE STEEL UNDER OPERATION

Zvirko O.¹, Chmelko V.², Yadzhak N.³, Glatzel U.³ ¹Karpenko Physico-Mechanical Institute of the NAS of Ukraine ²Institute of Applied Mechanics and Mechatronics, Slovak University of Technology ³University of Bayreuth, Germany olha.zvirko@gmail.com

Hydrogen, which currently plays an important role as a decarbonized energy carrier, can be transported environmentally friendly over long distances by pipelines. The usage of existing gas transmission networks is very promising for this purpose. However, the issues associated with the fact that a significant part of pipelines is operated near the end of their design life and pipeline steels could degrade under long-term operation should be considered in assessing the possibility of usage of the existing gas networks for safe hydrogen transportation [1-3]. In-service degradation of operated pipeline steels can cause enhancement of their susceptibility to hydrogen embrittlement and hydrogen assisted cracking. The degradation degree of steel properties should be taken into account in the evaluation of residual lifetime of pipelines [4].

The present paper is focused on the assessment of the susceptibility of pipeline steels in different states to hydrogen embrittlement and hydrogen assisted cracking. The low-carbon and low-alloyed pipeline steels in the as-delivered state and after long-term operation were investigated. The susceptibility of steels to hydrogen embrittlement and hydrogen assisted cracking was studied by tension of cylindrical specimens in air after their hydrogen precharging electrolytically and in a corrosive environment under cathodic polarisation, respectively. It was found that the operated pipeline steels were characterised by higher sensitivity to hydrogen embrittlement and hydrogen assisted cracking compared to asdelivered ones. In addition, a noticeable anisotropy of resistance of pipeline steels to hydrogen embrittlement was observed depending on the plane of fracture propagation relative to the rolling direction of the pipe, and on the degree of their operational degradation. The pronounced anisotropy of hydrogen embrittlement susceptibility of operated pipeline steels can influence the safe exploitation of natural gas pipelines at the transportation of hydrogen or its mixture with natural gas.

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EFFECT OF TEMPERATURE ON RESISTANCE TO PITTING CORROSION IN DUPLEX STAINLESS STEEL 2205 WELDS

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Potentiodynamic polarization was applied to AISI 2205 duplex stainless steel joints in natural seawater at different temperature to study the electrochemical behaviour of the joints and their resistance to localised corrosion. The Gas metal arc welding method was used for the manufacture of the joints with and without the simultaneous application of an external magnetic field of low intensity. The improvement of the resistance to pitting corrosion in natural seawater of the welds by the application of the external magnetic field was evaluated as a function of the electrolyte temperature. The joints welded under an external magnetic field of 3 mT presented a similar resistance to pitting corrosion than the based metal samples, whereas joints welded without magnetic field (0 mT) presented the poorest resistance to pitting corrosion. The joints welded under the external 3 mT magnetic field resisted pitting corrosion in natural seawater up to the temperature of 45° C, the base metal up to 65° C and the welded samples without magnetic field showed unstable behaviour in the layer passive from the temperature of 25° C. The 3 mT applied magnetic field during the Gas metal arc welding of the AISI 2205 duplex stainless steel improved the resistance to pitting corrosion due to the increasing of austenite-phase regeneration during the thermal cycle and the limitation of ferrite-phase gran growth. It also limited the precipitation of Cr-rich secondary phases with the consequent reduction of Cr-depleted zones, which favoured the formation of the stable and resistant passive film.

Based on the polarization curves, the joint welded with 0 mT was the piece with the most unstable behaviour in the passive layer 25° C and its rupture was at 45° C thus showing that temperature is a very important factor in the pitting corrosion in the duplex stainless steels when in contact with an electrolyte containing NaCl.

The breakdown of the passive layer, both in welding with and without magnetic field, was formed mainly in the heat affected zone, due to the microstructural discontinuity that causes the change in the δ/γ phase relationship and the formation of detrimental secondary phases. The weld metal zone (AE 2209) presented pitting on few occasions, thus showing that the microstructural composition of this zone after the welding process is favourable in the electrochemical properties of the duplex stainless steel.

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CORROSION-MECHANICAL BEHAVIOR OF Q125 CARBON STEEL IN CO₂ / H₂S ENVIRONMENT

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Corrosion and mechanical behavior of API carbon steel Q125 in model brine water (MBW), saturated by CO_2 and H_2S at the different pressure and temperature has been investigated. Corrosion rate of steel in MBW, saturated by CO_2 , increases over time. It indicates, that carbonate films do not protect the steel from corrosion. Corrosion processes are accelerated at the temperature of 60°C under CO_2 pressure 6 MPa and corrosion changes from uniform to ulcerative.

Short-term tests showed, that the corrosion rate of steel in MBW+CO₂+H₂S is proportional to the concentration of H₂S in solution and is determined by the cathode process velocity. The mechanism of corrosion does not depend on the concentration of hydrogen sulfide in solution. Long-term studies in MBW+CO₂+H₂S showed, that the corrosion rate of steel Q125 decreases ~ 2 times compared with one in MBW+CO₂ under normal conditions and 10... 15 times at t = 60°C and pressure 6 MPa. The surface films are formed on the steel surface in MBW+CO₂+H₂S and consist of a mixture of maquinavit, troilite and impurities of oxides and hydroxides of iron. The sulfide film is more compact, than carbonate film, and the corrosion rate is reduced. However, due to the porosity, the protective properties of sulfides are not effective enough.





Slow tension tests of Q125 steel at a constant deformation rate were performed in air and in the environment of MBW with different ratios of carbon dioxide and hydrogen sulfide. In the MPW saturated with carbon dioxide, the strength of Q125 steel change slightly, and the relative narrowing 4.4 times less than in air. The fraction of the brittle component increases in fractures, but cracks do not form. Therefore, due to the higher strength of Q125 steel, it is advisable to use it for casing pipes in fields where only carbon dioxide is present.

The strength of steel increases by 13...30%, and the plasticity decreases by 8...11 times in the MBW+CO₂+H₂S, due to steel hydrogenation. There are multiple cracks in fractures after the tension tests. Therefore, it is impractical to use Q125 steel for casing pipes in the presence of hydrogen sulfide in the MBW.

ASSESSMENT OF SUSCEPTIBILITY OF CASING STEELS WITH DIFFERENT MICROSTRUCTURE TO HYDROGEN EMBRITTLEMENT AND BRITTLE FRACTURE

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Pipe steels with ferritic-pearlitic microstructure are widely used in oil and gas production and transportation industry. The recent design of steels is focused on the ferriticbainitic microstructure in order to achieve higher strength. These pipes are usually operated under influence both corrosive and hydrogenating environments and mechanical loading. Long-term impact of these factors on pipe steels leads to a significant decrease in their corrosion resistance and mechanical properties [1-4]. Pipe steels produced by different manufactures, which met the requirements to strength and plasticity, can have different microstructure [5-7], since there is no requirement for microstructure in the standards.

The present research is focused on assessment of susceptibility to hydrogen embrittlement and brittle fracture of two different types of casing pipe steels. It is very important research issue defining their serviceability for oil and gas wells. The medium carbon steel with fine grain bainitic microstructure and medium-high carbon steel with coarse microstructure of ferrite-pearlite were tested. The results showed that the medium carbon steel with higher strength and with more dispersed microstructure was less susceptible to hydrogen embrittlement under preliminary electrolytic hydrogenation than the medium-high carbon steel with lower strength and with coarse-grained microstructure. To estimate the embrittlement of steels, the method of FEM load simulation of the specimens with crack was used. The constitutive relations of true stress-strain of the tested steels were defined. Stress and strain dependences in the crack tip were calculated. It was found that the medium-high carbon steel was characterized by lower plasticity on the stage of the neck formation of specimen and lower fracture toughness than the another one. The obtained results demonstrating the limitations of a usage of casing pipes made of the medium-high carbon steel with coarse-grained ferrite/pearlite microstructure in corrosive and hydrogenating environments were discussed.

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ELECTROCHEMICAL APPROACHES FOR THE STUDY OF TRIBOCORROSION PROCESSES

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Tribocorrosion encompasses the synergistic effects between mechanical, chemical and electrochemical processes due to the frictional interaction of surfaces, due to which the loss of metal mass cannot be determined by a simple summation of mechanical wear and corrosion, determined separately [1]. In many cases, during tribocorrosion, transformations of the surface layers of metals can occur as result of which it is difficult to determine the influence of individual factors and to change the mechanisms of friction. The use of electrochemical approaches in the study of corrosion-mechanical wear makes it possible to study the processes or regularities occurring in the friction zone.

A new method for estimating the rate of formation and destruction of secondary structures under conditions of tribocorrosion and forecasting the mechanisms of destruction of metals is scientifically substantiated [2]. In particular, for the AA2024 alloy, it was established that there is a certain relationship between the repassivation curve after guillotining and the tribotechnical characteristics of the AA2024 alloy in the environment of acid rain, for which friction mechanisms can be established using electrochemical characteristics. Comparison of potentials on the repassivation curve and tribocorrosion potentials E_{tr} (potential tribocorrosion) makes it possible to assess the condition of the friction surface and the behavior of secondary structures. If E_{tr} approaches the E_{rs} (renewed surface), this indicates the removal of films under the influence of friction, which can lead to adhesion of the surfaces. On the contrary, the increase in the difference between E_{tr} and E_{rs} , and the shift of E_{tr} towards the corrosion potential (E_{cor} – potencial corrosion) indicates the presence of secondary structures that prevent seizing and reduce the intensity of wear - destruction occurs with the advantage of the oxidizing mechanism.

A technique for determining the intensity of destruction during frictional contact in a corrosive-active medium of passivated metals based on changes in polarization currents is proposed [3]. The technique consists in determining the polarization current (i_{pol}) at the polarization potential equal to the corrosion potential ($E_{pol}=E_{cor}$) and analyzing the nature of its change under tribocorrosion conditions. In the absence of frictional interaction, its value is equal to zero, and the appearance of the current is caused only by the work of deformation galvanocouples: the deformed friction track (anode) - the undeformed surface (cathode), which does not participate in friction.

It was established that cathodic polarization, depending on the value, has an ambiguous effect on the destruction of the AA2024 alloy due to tribocorrosion: with polarization within the limits of the corrosion potentials and the freshly renewed surface, corrosion and corrosion-mechanical wear are inhibited, with a shift of the potential in a more negative direction - tribocorrosion processes are intensified due to near-surface alkalinization of the medium due to hydrogen depolarization.

It was established that, in contrast to classical tribology, during tribocorrosion processes, the coefficient of friction decreases due to intensification of wear, as a result of changes in surface properties under the influence of hydrogen and corrosion factors and the formation of secondary structures.

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INFLUENCE OF A CORROSIVE ENVIRONMENT AND HYDROGENATION ON METAL CREEP

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Corrosion cracking, high-temperature hydrogenation and creep are characteristic of the equipment elements of thermal and nuclear power plants that operate at high mechanical loads and temperatures and interact with chloride-containing and hydrogen-containing working environments. The substantiation of the performance of such structural elements in relation to creep is significantly complicated by the dependence of the creep rate of structural materials on many factors - temperature, mechanical stresses and working environments.

In the report, a calculation model was built to determine the durability of structural elements at high temperature creep of metal materials under the action of long-term loads and the corrosive effect of chloride-containing and hydrogen-containing environments. The energy approach previously developed by the authors is taken as a basis [1].

The creep rate was obtained to take into account the influence of chloride and hydrogen media on metal creep:

$$\frac{\partial \varepsilon_{ij}^{cr}}{\partial t} = A \sigma_{eq}^m 10^{n\sigma + m_1 \chi} \left(1 + \alpha_H C(t) \right),$$

where σ_{eq} – equivalent stress; $\dot{\varepsilon}_{ij}^{cr}$ – the creep strain rate of the local volume; A, n, m_1 , α_H - constants that determine the resistance of steel to corrosion cracking at a given temperature; χ – percent of magnesium chloride in solution, C - hydrogen concentration.

The developed model was tested on the example of a study of U-like heat exchange pipes with an inner radius of r1 = 13.2 mm and an outer radius of r2 = 16 mm (Fig. 1.a) made of stainless steel 12X18H12T. It was assumed that the temperature of the metal of the heat exchange tubes corresponds to T = 550 °C, and the working medium acts on the inner surface of the tubes.

The results of calculations of the time until the destruction of the heat exchange tubes of superheaters of steam boilers under different pressures and the influence of corrosive environments of superheaters of steam boilers are shown in Fig. 1. b.



Fig. 1. The distribution of creep deformations on a fragment of a U-shaped heat exchange pipe (a) and the change in the time to failure due to internal pressure, at the place of the greatest deformation energy in the vicinity of the pipe bend without taking into account the influence of hydrogen (solid lines), and taking into account the influence of hydrogen (dashed lines); excluding (1), in 5% (2) and in 10% MgCl2 solutions (3) (b)

The obtained results are the basis for assessing the strength and reliability of structural elements, taking into account the mutual influence of various mechanisms.

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A QUANTITATIVE MODEL FOR THE CORROSION RATE OF COLD-ROLLED, METASTABLE, STAINLESS STEEL 316L IN DEPENDENC OF THE SURFACE ROUGHNESS, MICROSTRUCTURE AND RESIDUAL-STRESS STATE

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The high-alloy steel 316L is used for numerous components due to its excellent corrosion resistance. However, the shaping of the components influences the material condition and can thus change the corrosion resistance. In this context, the corrosion rate of the steel 316L for the case of uniform surface corrosion is determined for various cold-rolled conditions by ageing tests in 0.5 M sulphuric acid. For the different cold-rolled conditions, the microstrain, the martensite fraction, and the residual-stress state are quantified by means of X-ray diffraction. The surface roughness is measured by laser scanning microscopy. A model equation is derived by means of multiple regression that allows to predict the corrosion rate as a function of the sample state.

EFFECT OF THE NATURE OF AN AGGRESSIVE MEDIUM ON THE ELECTROCHEMICAL CHARACTERISTICS OF AMORPHOUS ALLOY

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The corrosion resistance of amorphous metal alloys (AMA) depends significantly on their elemental composition. Therefore, it is important to assess their corrosion resistance in different aggressive media when using amorphous alloys based on Fe. The rate of corrosion of iron alloys in solutions depends on the electric conductivity, concentration of the solution, access of oxygen, the nature of anions and cations. The effect of the nature of anions and cations of the medium is manifested in the formation of soluble or insoluble corrosion products, which are able to form protective layers on the surface of such alloys. In alkaline solutions in particular insoluble oxides and hydroxides of iron are formed, which show good adhesion to the metal surface and protect it from corrosion. In acids such as chloric, nonconcentrated sulfate, phosphoric, acetic, the corrosion process occurs with the formation of soluble corrosion products that do not protect the metal from further dissolution.

The corrosion resistance and the electrochemical parameters of AMA $Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}$ was studied in 0.5 M aqueous solutions of NaCl, HCl, KOH and H_2SO_4 at T = (293±1) K. The shape of the current-voltage curve of the AMA electrode on the stage of oxidation of the alloy $Fe_{78,5}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$ in 0.5 M aqueous NaCl solution. With increasing potential scan rate, the magnitude of the corrosion current tends to increase, and the corrosion potential to shift to the cathode side, which indicates a slight activation of the surface (Table). Most likely, this is due to the gradual formation of loose oxide protective layers.

		0,5 M aqueous solutions									
No. of	C f	HCl		NaCl		K	OH	H_2SO_4			
cycle	Surface	-E _{con} ,	$i_{corr} \cdot 10^4$,	-Econ,	$i_{corr} \cdot 10^4$,	-E _{con} ,	$i_{corr} \cdot 10^4$,	-Econ	$i_{corr} \cdot 10^4$,		
		В	A/cm ²	В	A/cm ²	В	A/cm ²	В	A/cm ²		
1	k	0,44	2,87	0,92	1,04	1,00	0,59	0,42	0,01		
	с	0,40	3,01	0,94	0,38	0,92	1,27	0,41	0,02		
5	k	0,40	4,26	0,93	2,32	1,01	0,36	0,36	0,08		
	с	0,37	2,85	0,91	1,24	0,98	1,55	0,36	0,09		
10	k	0,38	4,46	0,97	2,86	1,04	0,73	0,36	0,03		
	с	0,40	3,01	0,97	1,80	1,01	1,71	0,36	0,02		

 Table. 1. Parameters of electrochemical oxidation of contact (k) and external (c) surfaces of

 Fe_{78,5}Ni_{1,0}Mo_{0,5}Si_{14,0}B_{6,0} in aqueous solutions of different nature

Dissolution of $Fe_{78,5}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$ in 0.5 M aqueous HCl proceeds quickly, the values of corrosion currents are 2 times higher. With increasing potential scan rate from 20 to 50 mV/s and the number of cycles, the E_{cor} values in HCl solution do not change considerably, but are shifted by 0.5 V to the anode side compared to NaCl solution (Table). Studies of the electrochemical behavior of AMA $Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}$ in 0.5 M aqueous solution of KOH showed (Table) that the density of corrosion currents with increases slightly with increasing number of potential scanning cycles of and the value of corrosion potential shifts to the cathode side. The results of electrochemical studies indicate very different oxidation kinetics of the amorphous alloy $Fe_{78,5}Ni_{1,0}Mo_{0,5}Si_{14,0}B_{6,0}$ in different aggressive media.

INFLUENCE OF STRUCTURAL STATEOF FERRITE-MARTENSITIC STEEL T91 ON ITS CORROSION RESISTANCE IN LIQUID LEAD

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The attention of the world community and scientists to the development of nuclear energy has significantly increased in recent days. The newest nuclear power plants with increased safety anticipate fast neutron reactors with using liquid metal cooling systems [1, 2]. Candidate coolants media are melts of heavy metals (Pb, Pb-Bi). The use of ferritic, ferritic-martensitic and austenitic steels is envisaged as the main structural materials for components of liquid metal cooling systems [3]. The key problem when using heavy metal melts is their high corrosion aggressiveness in relation to the structural materials of cooling systems [4, 5].

The aim of the study was to evaluate the influence of the structural state of ferritemartensitic steel T91 on its corrosion resistance in lead melt.

Rated the peculiarities of corrosion behavior intoliquid lead with oxygen concentration $C_{[O]Pb}\approx 5\cdot 10^{-7}$ wt.% at a temperature of 500°C at exposure of 500 and 1000 hours' the samples of ferritic-martensitic steel T91 with ultra-dispersive structure, which modified by hot extrusion (875°C) and intensive plastic deformation by the method of multi-cycle "deposition-extrusion" by repeated repetitive operations of deposition and extrusion on a hydraulic press (deformation treatment). The corrosion tests were performed by ampoule method in static isothermal conditions, which are characteristic of stagnant zones of heat transfer systems with liquid metal coolant system.

It was found that for samples of ferritic-martensitic steel T91, without deformation treatment, corrosion processes are intergranular character, characterized by etching of grain boundaries and penetration of liquid lead into the matrix with simultaneous dissolution of alloying elements Cr, Mn into the melt at exposure up to 500 hours. After increasing exposure from 500 to 1000 hours, was fixed the formation of an oxide film based on Cr and Si on the surface, which serves as a barrier to liquid lead. On samples of ferrite-martensitic steel T91, which subjected to deformation treatment, the formation of a non-continuous oxide film was fixed at exposures up to 500 hours. At an exposure of 1000 hours, a continuous oxide film based on Cr and Si is formed, which protects the surface from the negative effects of liquid lead.

Thus, pre-deformation treatment, due to grinding of the structure, intensifies the formation of oxide films on the surface of ferritic-martensitic steel in contact with liquid lead, which blocking the penetration of liquid lead into the depth of the matrix and dissolution of alloying elements into the melt.

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BRASS DEZINCIFICATION AS A METHOD OF POROUS ELECTRODES OBTAINING <u>Kuntyi O.,</u> Zozula G., Shepida M. Lviv Polytechnic National University

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One of the effective methods of preparing porous metals is electrochemical or chemical [1, 2] dealloying. They are based on the selective dissolution of the more electronegative metal of alloy. The electrochemical one is much more effective in higher dissolution rates and controlled micro- and nanoporous structure formation. Relatively cheap commercial alloys, in particular brasses CuZn are promising for dealloying in the commercial aspect [3]. Their anodic dezincification occurs in electrolytes of different compositions with the formation of a porous surface. The work aims to determine the dependence of the porous surface morphology formed by electrochemical dealloying of CuZn under different modes of selective anodic dezincification of brass.

Electrochemical dealloying of brass Cu62Zn38 in 0.1 M HCl at E = 0.1 V occurs with selective dezincification. It results in the porous surface formation that undergoes the following stages: 1) the dissolution of Zn from the CuZn surface mainly along the grain boundaries with the formation of submicron crevices between them (Fig. 1a); 2) formation of nanopores on the surface of the grain (Fig. 1b). The content of copper on the porous surface after the first stage of dealloying is 94% at., after the second – 99% at. The value of anodic current is significant and increases with increasing anodic potential during the active process of dezincification according to reaction (1). However, as the copper-enriched porous surface forms, reaction (1). This leads to the simultaneous course of reactions (1, 2), that is, the leveling of the selective anodic dissolution of brass. However, the diffusion factor in the pores slows down the process of removal of formed Cu²⁺-ions. This causes galvanic replacement according to reaction (3), which contributes to the enrichment of the pore surface with copper.

$$\begin{array}{c} \Sigma n \to \Sigma n + 2e \\ Cu \to Cu^{2+} + 2e \end{array} \tag{1}$$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \tag{3}$$

It was established that the main parameters of the controlled formation of a porous surface are E and the duration of dezincification



Fig. SEM images of Cu-porous surfaces obtained by anodic dezincification of Cu62Zn38 in 0.2 M HCl solutions for a duration of 10 (*a*) and 30 min (*b*) at E = 0.1 V, t = 20 °C

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CORROSION RESISTANCE OF CARBON STEEL WITH SURFACE NANOCRYSTALLINE LAYER <u>Maksymiv O.,</u> Kyryliv V., Zvirko O. Karpenko Physico-Mechanical Institute of the NAS of Ukraine okyryliv@yahoo.com

Extreme operating conditions in the form of combined action of mechanical loading, corrosion and wear demand the highest performance of the materials used in many industries. The surface mechanical attrition treatment techniques are used to improve the performance of the materials [1, 2]. One of the most effective methods of protection of the material surface and significantly improvement of the overall properties is the generation of nanocrystalline structures on the material surface [2–6].

The main objective of the study was to assess corrosion resistance of the pearlite carbon steel with surface nanocrystalline structure generated by mechanical-pulse treatment using different technological environments and alloying elements. In this technique highspeed friction is used for severe plastic deformation of the surface layer of the steel specimens. Mechanical-pulse treatment combines grain refinement to the nano scale, quenching and alloying of the surface metal layer. Technological environments with different polymer additives and powders of alloying elements were supplied to the friction contact zone under the treatment. Polymer additives are undergone destruction due to high pressure and temperature in the friction contact zone. The fragmentation of the surface layer's structure to the nano scale with its simultaneous saturation by components and alloving elements took place during mechanical-pulse treatment. It has been shown that adding nickel, boron and nitrogen-containing substances into technological environment during mechanical-pulse treatment of the pearlitic carbon steels leads to alloying the surface metal layer with these elements and, consequently, to increasing their resistance to corrosion. Such treatment can offset the negative influence of intensive plastic deformation on corrosion resistance of carbon steels.

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RESISTANCE TO PITTING OF AISI 304 STEEL IN MODEL CIRCULATING WATERS Narivs'kyi O.¹, Snizhnoi G.², Pulina T.², Snizhnoi V.³, Belikov S.² ¹LCC "Ukrspetsmash" ²Zaporozhzhia Polytechnic National University ³Zaporizhzhia National University amz309@ukr.net

Corrosion-resistant steels of the austenitic class are used in the production of heat exchange equipment. Heat exchangers can undergo pitting when interacting with circulating water that contains chlorides. Critical pitting temperature (CPT) is an important parameter of corrosion resistance. CPT depends on the chemical composition of the steel, production technology and heat treatment [1]. It is proposed to use specific magnetic susceptibility as an integral parameter that characterizes the state of steel χ_0 [2]. Five heats AISI 304 steel were studied. CPT was determined in model circulating waters with pH (4...8) and chloride concentration 350...650 mg/l. Titanium and aluminum oxides (Fig. 1), as well as titanium vanadium nitrides, were detected.



Fig. 1. Titanium oxide (a) and aluminum oxide (b) in AISI 304 steel

The dependence of the CPT of AISI 304 steel on the pH of model circulating waters (Fig. 2 a) has an extremum at pH7. The dependence of the CPT on the specific magnetic susceptibility has a linear character (Fig. 2 b), which allows predicting corrosion resistance.



a: 1, 3 - heat 3; 2, 4 - heat 4; 1, 2 - C_{Cl} =350 mg/l; 3, 4 - C_{Cl} =600 mg/l
b: 1 - heat 1, 2 - heat 2, 3 - heat 3, 4 - heat 4, 5 - heat 5
Fig. 2. Dependence of CPT of AISI 304 steel on the pH of model circulating waters (a) and specific magnetic susceptibility χ_o (b)

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INFLUENCE OF THE TIME FACTOR ON CORROSION-MECHANICAL PROPERTIES OF Al-Mg-Si-Cu ALLOY WELDED JOINT <u>Nyrkova L.</u>, Goncharenko L., Osadchuk S., Labur T. Paton Electric Welding Institute of the NAS of Ukraine Inyrkova@gmail.com

In continuation of previous research [1, 2] the influence of time factor (duration of exposure to the corrosive environment) on mechanical properties of Al–Cu–Mg–Cu alloy welded joint after quenching and artificial aging was studied. It was established that corrosion resistance of welded joints was practically equal to corrosion resistance of base metal after 14 days of exposing in 3 % NaCl solution – 0.59 mm/year (Fig.1, a). Lowering of ultimate strength of base metal and welded joints after corrosion-mechanical investigation in 3 % NaCl solution for 14 days by \sim 4 % and \sim 14 % (Fig.1, b), respectively, was experimentally confirmed.



Fig. 1. Change of corrosion rate (*a*), ultimate strength (*b*) of base metal (1) and welded joints (2) after quenching and artificial aging during exposure to corrosive environment 3 % NaCl and fractographs of fracture surfaces of welded joints (*c*)

Lowering of the level of mechanical properties is confirmed by the relief of specimen fracture, the pattern of which changes from the ductile for welded joints in as-welded condition to a mixed one – ductile with signs of embrittlement of intercrystalline boundaries after soaking in a corrosive environment (Fig.1, c). Brittle fracture starts developing from the specimen surface, where individual structure regions damaged by corrosion, are formed, and moves in-depth of the specimen with greater time of exposure to the environment.

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HYDROGEN PERMEABILITY OF STRUCTURAL STEEL IN CORROSIVE ENVIRONMENTS WITH H₂S AND CO₂

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 H_2S and CO_2 in the working environment couse hydrogenation of metal structures, which deteriorates the operational characteristics of the equipment, espesially, in the oil and gas production and processing industries. The most dangerous types of corrosion damage are embrittlement and corrosion cracking. The rate of such destruction depends on the penetration and accumulation of hydrogen in product defects. In this work, the effect of cathodic polarization on the hydrogen permeability of structural steel in an aqueous solution containing H_2S and CO_2 was investigated [1].

Hydrogen permeability was determined by the Devanathan–Stakhurskyi electrochemical method. An electrochemical cell contains of two separate chambers, in which auxiliary electrodes and reference electrodes are located. The working electrode was made of steel 20 (a circle with an exposed area of 15,7 cm² and 0,04 cm thick). The anodic part of the cell was filled with a 0,2 M solution of KOH + 0,1 N Na₂MoO₄, and the cathodic part was filled with a 5% aqueous solution of NaCl + 0,5% CH₃COOH, which was bubbled with H₂S and CO₂ in the ratio of partial pressures of 1 to 3. IRS-PRO potentiostat was used for cathodic polarization of steel at 1 A/dm² using. The anodic current at/without steel polarization was measured.

The flow of hydrogen penetration (J_{as}) was calculated according to the formula [2]: $J_{as} = \frac{I_{as}}{FA} = \frac{D_{eff}C_{or}}{L}$, where: J_{as} is the flow of hydrogen penetration in the stationary mode, mol/(cm²·s); I_{as} is the current in the stationary mode of hydrogen penetration, A; A – sample area, cm²; F is the Faraday constant, C/mol; D_{eff} – coefficient of hydrogen effective diffusion, cm²/s; C_{or} is the concentration of hydrogen on the surface, mol/cm³; L is the thickness of the sample, cm. The effective hydrogen diffusion coefficient was determined from the time dependences of the hydrogen penetration flow. It characterizes the movement of hydrogen in the metal with defects according to the formula: $D_{eff} = \frac{L^2}{\epsilon t_{lag}}$, where t_{lag} is the time required to reach the condition $\frac{I(t)}{I_{as}} = 0,63$, s.

The time dependences of the flow of hydrogen penetration and the hydrogen concentration on the surface are practically the same both with and without cathodic polarization of steel. In particular, under the condition of hydrogen transport without polarization, the penetration flow (J_{as}) is equal to 7.9 $\cdot 10^{-10}$ mol/(cm²·s), and the hydrogen concentration C_{or} in the surface layer on the inlet side of the membrane is $11.3 \cdot 10^{-6}$ mol/cm³. Under cathodic polarization, these indicators decrease by only ~10%.

Therefore, the polarization of the inlet side of the steel membrane in the chlorideacetate solution in the simultaneous presence of H_2S and CO_2 in the ratio of partial pressures 1:3 does not significantly affect the process of hydrogen penetration, which is associated with a slight change in the number of adsorbed hydrogen sulfide molecules in the surface layer.

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CORROSION RESISTANCE OF 17G1SU STEEL IN A NACE ENVIRONMENT SATURATED WITH CARBON DIOXIDE AND HYDROGEN SULFIDE

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Low-alloy steel 17 Γ 1CV, which is used in the oil and gas industry, was studied. The combined effect of hydrogen sulfide and carbon dioxide on 17 Γ 1CV steel in the chloride-acetate solution saturated with carbon dioxide and hydrogen sulfide in the ratio 0:1, 1:0, 3:1, 30:1 is shown. On the basis of corrosion-electrochemical studies of 17 Γ 1CV steel samples, it was established that the corrosion potential ranges from -575...-625 mV. The current density is within 0,09...0,11 mA/cm² (fig.) and does not have a clear dependence on the concentration on H₂S and CO₂ in the gas mixture and, accordingly, in the solution. The Tafel coefficients of the cathodic reaction average 0.11 V per decade, indicating that the main cathodic process under such conditions is hydrogen depolarization. The Tafel coefficients of the anodic reaction are within 0.083...0.096 V. Corrosion proceeds under cathodic control.



Fig. Polarization curves of $17\Gamma 1CY$ steel in the chloride-acetate solution at different ratios of H_2S and CO_2 ; $1 - CO_2$; 2 - 1:30; 3 - 1:3; $4 - H_2S$

Gravimetric studies have established that with an increase in the concentration of hydrogen sulfide in the chloride-acetate solution, the rate of corrosion and the density of current will increase with the growth of hydrogen sulfide in the environment. Corrosion currents determined by the mass index of corrosion (tabl.) are approximately seven times greater than corrosion currents determined from polarization curves, which indicates an increase in the rate of corrosion in the process of steel exposure in a corrosive environment.

H ₂ S:CO ₂	t, h	$K_m(g/(m^2 \cdot h))$	l,mm/year	i, mA/cm ²				
CO ₂		0.7229	0.8057	0,0555				
1:30	722	0,41	0,4569	0,0429				
1:3		1,6627	1,8531	0,1409				
NACE		2,0955	2,3354	0,6569				

Tab	le. C	orrosion rate	of 17T1CY	' steel	in a ch	loride	e acetate	solution	n saturated	wit	hΗ	S,	and	CO	h.
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ELECTROCHEMICAL IMPEDANCE OF ZrOx/Zr-Nb SYSTEM

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Zirconium alloys are used for the manufacture of elements of the core of thermal neutron reactors: fuel cladding, components of fuel assemblies and channel pipes. In domestic VVER-1000 reactors, the E110 alloy is used as the fuel rod cladding material. Fuel rod claddings are subjected to constant mechanical, thermal and radiation loads. Maintaining the integrity and strength of the shell is the main factor in the safe operation of a nuclear reactor. Important and complex are the tasks associated with solving the issues of ensuring high radiation and corrosion resistance, since the development of technology for corrosion-resistant structural products will increase the competitiveness of Ukraine in international markets.

The use of coatings on the surface of fuel elements can improve the corrosion characteristics of products. In single-layer thin coatings, pores and other surface defects permeate the coating. It is known that the formation of pores and defects in multilayer coatings is reduced. On the other hand, thick coatings are capable of minimizing the number of defects, while the deposition method determines the formation structure of the coating.

The paper presents the results of a study on zirconium alloy grade E110 of oxide coatings obtained by high-temperature oxidation and microarc oxidation. High-temperature oxidation was carried out in a steam flow at a temperature of 700°C and a pressure of 0.1 MPa, the thickness of the oxide film was controlled by the treatment time. Microarc oxidation has been used to produce thick, matt oxide layers whose characteristics are affected by electrolyte concentration and current density. To study the structure of the synthesized oxide coatings, the method of impedance spectroscopy was used, based on the calculated parameters of the equation for the "electrolyte/oxide/metal" system:

$$Z = r - \frac{1}{\omega C_0} \cdot \frac{1}{1 + \left(\frac{1}{\omega C_0 R_y} + tg\delta_0\right)^2} \cdot \left(\frac{1}{\omega C_0 R_y} + tg\delta_0 + j\right),$$

Analysis of the data obtained allows us to draw the following conclusions: with an increase in the thickness of the chemically synthesized oxide film, the charge transfer resistance increases, and, starting from a thickness of 0.9 μ m, the coating demonstrates high protective properties; the dielectric loss tangent drops sharply when the thickness changes from 0.33 to 0.9 μ m, which indicates a change in the defectiveness of the oxide structure, moreover, a further increase in thickness does not affect this parameter; a similar correlation is demonstrated by the value of the capacitance of the electrical double layer. The influence of the microarc oxidation mode on the coating structure is ambiguous. With an increase in the electrolyte concentration at the beginning, the resistance increases sharply, and a further increase in the side reaction of the dissolution of the formed oxide by the components of the solution. With an increase in the current density, the defectiveness of the coatings decreases, this can be associated with an increase in the number of microdischarges that form in their place.

THE INFLUENCE OF HYDROGEN SULFIDE CONCENTRATION ON THE CORROSION AND HYDROGENATION OF STEEL 07Cr18Ni6

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The corrosion and hydrogenation of austenitic-martensitic steel 07Cr18Ni6 in standard aqueous NACE solution (mass%): 5% NaCl + 0.5% CH3COOH (pH = 2.7) with a concentration of hydrogen sulfide: 0; 25; 100; 500; 1000; 1500; 2000; 2800 mg/dm3 were studied.

Steel 07Cr16Ni6 in chloride-acetate solutions corrodes in the electrochemically active state regardless of the hydrogen sulfide concentrations. The presence of hydrogen sulfide in the solution does not change the nature of the cathode processes, but it accelerates them by 7... 9 times. Increase of hydrogen sulfide concentrations accelerates the anodic processes by 20... 35 times and changes its mechanism - the Tafel coefficient doubles. Unstable passivation was detected in solution with hydrogen sulfide concentrations less 100 mg/dm³, which turns into pitting at higher potentials.

The corrosion rate of steel 07X16H6 in solution with hydrogen sulfide concentrations 100...1500 mg/dm³ decreases by ~ 3...5 times during 720 hours and is equal to 0.4... 0.5 g/(m²·h). Sulfide films are formed on the surface, which include iron and nickel sulfidesand reduce the speed of corrosion processes. Corrosion products consist of one compact layer at hydrogen sulfide concentrationsless than 100 mg/dm³. Two layers were detected at H₂S concentration shigher than 500mg/dm³, the upper of which loses continuity due to cracking.

Steel 07Cr16Ni6 absorbs ~4.2, ~8.0 and ~17.5 ppm of hydrogen during corrosion in chloride-acetate solution at concentrations $C_{H2S} = 100$, 500, and 1500 mg/dm³ for 720 h. It is mostly diffusion-active hydrogen ($C_{200}= 62...70\%$), contained in traps with low activation energy. Defects in the corrosion layer canbe a "reservoir" for hydrogen trapping.

AN ELECTROCHEMICAL IMPEDANCE STUDY OF AMORPHOUS METAL **ALLOYS BASED ON COBALT IN 3% NaCl**

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Electrochemical impedance spectroscopy (EIS) is a powerful method for studying the surface of materials, in particular, amorphous metal alloys (AMA) [1]. Impedance spectroscopy provides quantitative and time-dependent information about electrode processes and complex interfaces, provides an understanding of boundary phase processes, which leads to a better understanding of the electrocatalytic behavior of amorphous electrodes [2], their corrosion resistance, and the properties of AMA semiconductor passivating films.

The oxide protective layers of the Co₇₂Fe₅Si₁₁B₁₂ alloy were investigated using the EIS method before and after corrosion in a 3% NaCl solution. Fig. 1 presents the Nequist curves taken in a 3% NaCl aqueous solution for the Co₇₂Fe₅Si₁₁B₁₂ amorphous alloy before and after corrosion. From fig. 1a it can be seen that the oxide layers are the most stable at a potential of -920 ... -780 mV. It is observed that the charge transfer resistance Z across the NaCl solution / oxide layer is $\approx 4 \cdot 10^3 \Omega$. The apparent resistance Z'' is $\approx 5 \cdot 6 \cdot 10^3 \Omega$, which indicates good insulating properties of the oxide film.

Fig. 1b shows the impedance dependences of the Co₇₂Fe₅Si₁₁B₁₂ alloy in 3% NaCl after cyclic scanning of the potential in the range -1200 ... -200 mV. Such a load on the metal electrode leads to a certain decrease in the resistance of the oxide film and Z" come to $3 \cdot 10^3 \Omega$. The protective effect of the films formed at potentials of -1200, -1100, -600, -550, -290 mV is significantly lower. The film is less dense, more porous and defective at the above potentials, as indicated by a decrease in the charge transfer resistance through the limit of NaCl solution / oxide layer.

A high resistance value in the range of corrosion potentials indicates the stability of the surface layers. After corrosion, it is observed a 2-fold decrease in apparent resistance. The lowest value of the resistances is observed at E = -1200 mV and E = -290 mV, which correspond to the processes of hydrogen and oxygen release, respectively.



Fig. 1. Nequist curves of Co₇₂Fe₅Si₁₁B₁₂ in 3% NaCl at different potentials before (a) and after corrosion (b)

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Corrosion-mechanical destruction of materials

EFFECT OF GRINDING-INDUCED RESIDUAL STRESSES ON SCC INITIATION IN AM 316L STEEL

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The surface quality and geometrical tolerances of as-selective laser melted (SLM) parts have been extensively addressed as one of the main concerns limiting the direct use of as-SLM parts in industrial applications. Generally, for increasing the surface quality and dimensional and/or geometrical tolerances, secondary techniques such as shot peening, selective laser remelting or more precise machining methods such as grinding are employed. Moreover, SLM process parameters, including hatch spacing, layer thickness, laser scan speed, and laser power are considered to have a significant influence on the microstructure of manufactured parts and cellular-columnar grain size. Electrochemical behaviour and stress corrosion cracking (SCC) susceptibility of SLM 316L austenitic stainless steel were investigated under the combined effect of microstructural changes due to the variation of energy input during the SLM process and the individual effect of surface residual stresses (RS) induced by machining in various magnitudes in 3.5 % sodium chloride aqueous solution. The mechanism of SCC initiation and the effect of surface residual stresses and complex microstructural characteristics of the SLM method on electrochemical response was explained. Results revealed that average columnar subgrain size and pore surface area strongly affect the electrochemical and SCC behaviour. Moreover, there was a strong correlation between RS magnitude and SCC occurrence highlighting lower threshold tensile stress needed for SCC occurrence compared to wrought counterparts. Moreover, the existence of a threshold pore size was detected to be considered as an active site for pit nucleation. Moreover, experimental observations revealed that selective corrosion attack occurred at subgrains leaving subgrain boundaries intact and the SCC mechanism was hypothesized as the synergistic effect of exceptional selective corrosion attack at subgrains and mechanical rupture of subgrain boundaries.

A SEARCH FOR ELECTROCHEMICAL SIMILITUDE IN SCC TESTING

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Crack tip electrochemical conditions are explored utilizing a reactive transport Finite Element Method model for a stainless steel 304 alloy exposed to 3 M NaCl. Under full immersion conditions, a steady state pH of 3 and metal chloride concentration of 1.4 M were calculated. It was determined that an increase in cathode length and a decrease in water layer thickness increases total cathodic current per thickness, metal chloride concentrations, and decreases crack tip pH. The presented results and discussion call into question whether electrochemical similitude is achieved between different specimens, crack lengths, and between laboratory specimen and field relevant samples.

MECHANICAL AND CORROSION PERFORMANCE OF COMPOSITE REBARS SUBJECTED TO A CORROSIVE CONDITION

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When structural or environmental conditions prevent steel reinforcing, composite bars offer an intriguing replacement for steel bars. Koch [1] lately brought attention to the fact that 3-4% of any country's GDP is invested on corrosion-related costs. Glass fiber reinforced polymer (GFRP) parts have been proposed as a potential substitution for steel alternatives as a means of preventing corrosion. Excellent corrosion resistance, low density, absence of electrical conductivity, relatively low cost, and the option to choose resins and reinforcements for particular needs are other crucial benefits [2]. The kind of fibers, the matrix, and the proportion of fibers in the composite matrix all affect the physical and mechanical characteristics of composite bars. Composite bars are lightweight, up to six times as light as steel bars, which makes it easier to strengthen concrete and lowers shipping costs [2].



Fig. 1. The Pultrusion Process. Specified systems: (a) fiber impregnation system; (b) heated pultrusion die area; (c) a control unit; (c) pneumatic puller unit and cutting-off system [3]

As seen in figure 1 above, the pultrusion method is typically used to make composite bars. This study will focus on the influence of corrosive environment on the structural integrity of rebars taking into account its mechanical and corrosion performance.

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DETERMINATION OF CRITERIA FOR CHARACTERISING CRACK-LIKE DEFECTS BASED ON THE RECEIVED IMAGES AND THEIR FURTHER PROCESSING

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The problem of safe operation of a large variety of equipments has became extremely relevant for industry. When the planned service life of the used equipment is exhausted and, in practice, a large number of damages of various natures could appear, as a consequence of the operation or were already present due to its specific manufacture. In connection with this problem, for ensuring a safer operation of the equipment, quantitative and qualitative approaches are required to assess the detection of crack-like defects, i.e., in fact, there is a need of methods for fast analysis, based on a combination of information about the condition of the researched objects, with processing of the surficial state of the object obtained by one or another solution, it is possible to analyze the existing defect that occurs in a certain structural element. In this regard, the purpose of this work is aimed at determination of criterial characteristics of transferring the received state data of the object under study to its model representation using further methods of fracture mechanics.

For verification, the proposed methodology was previously tested on samples of duplex steel 2205, which allowed to extract the necessary data for further analysis from the available images.

In a previous work, a comparison was carried out between the original Sobel differential operator and several proposed normalized versions of the Sobel operator. The assessment was conducted at a pixelwise level between the phases identified by each variation of the algorithm when compared to those manually determined. In this work, the edge recognition for further delimiting areas is automatized by using a Sobel operator for identifying edges, which is normalized by different proposed Gaussian filters (on intensity, rugosity, or both). After that, a threshold is used to discretize the edges. Different neighboring pixel configurations, sensitive to edge intensity, are proposed for thinning and cleaning the discretized edges, and hence, grain boundaries with a one-pixel thickness are obtained.

A pixel-wise comparison was also possible between the phases other author's obtained by using EBSD and the proposed methodology using the same images and a 90.23% likelihood was found with a standard deviation of 2.2%. Another comparison was conducted between the reported percentage of austenite content found by other authors, using different methods, and the proposed methodology conducted on their one images. The average discrepancy was found to be 6.3% with a standard deviation of 3.67%.

The automatization process presented, and their results are suitable for further finite element analysis and peridynamics computations, where defined phases and interphases are necessary for meshing, modeling dislocations movement as well as intrusions and extrusions formed at the between grain phase boundaries.

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DEGRADATION OF FATIGUE AND CORROSION FATIGUE STRENGTH OF STRUCTURAL STEELS UNDER LONG-TERM OPERATION

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Degradation of steels operated under the action of mechanical loading and aggressive hydrogenating environments is a crucial problem for structural integrity [1]. From the mechanical properties, the characteristics of brittle fracture resistance, namely, impact strength and fracture toughness, as well as the characteristics of plasticity are highly sensitive to the in-service degradation of steels. However, in the case of cyclic loading of structures the tendency of in-service changes of the fatigue characteristics can be unambiguous [2].

The features of assessing the in-service degradation of structural steels operated under cyclic loading are analysed. The two-stage process of steel degradation consisted in the dominance of cyclic hardening at first with the subsequent intensive development of dissipated micro-damages in a metal is considered. The influence of operational cyclic loading on the basic mechanical properties and fatigue and corrosion fatigue characteristics of steels is distinguished. In the first case, these are the characteristics of resistance to brittle fracture, in particular, impact strength and fracture toughness, in the second one – fatigue resistance, determined using smooth specimens and pre-cracked specimens. The influence of corrosive environments on the degradation intensity of steels operated under cyclic loading is also discussed. The non-monotonic character of operational degradation of the certain mechanical characteristics divides an in-service lifetime of structure for two stages (Fig. 1): deformation aging (stage I) and in-bulk dissipated damaging (stage II). Corrosive environment accelerates operational degradation of steels due to an intensification of dissipative damaging. The environmental effect on acceleration of fatigue crack growth rate is mainly revealed in the middle part of diagram $da/dN - \Delta K$, especially for the degraded metal.



Fig. 1. Changes in properties of structural steels (impact toughness KCV, fracture toughness K_{IC}, reduction in area RA, elongation δ , hardness HV, yield σ_{Y} and ultimate σ_{UTS} strength, fatigue limit σ_{-1} , and effective fatigue threshold $\Delta K_{th eff}$) depending on operation time.

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EFFECT OF THE SPECIAL TECHNOLOGICAL ENVIRONMENT ON FATIGUE CRACK GROWTH IN FERRITE-PEARLITE STEELS

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Deceleration methods of fatigue crack growth rates have been recently analysed for pearlitic rail steel [1]. One of them consists in the artificial formation of the crack closure effect using a special technological environment capable for penetrating into the crack cavity [2]. Crack closure is well known as one of the shielding mechanisms in fatigue crack growth retardation in steels in corrosive media due to the edge effect of corrosion products at the crack tip. However, this is peculiar to the near-threshold fatigue crack growth rates [3]. At the same time, the application of the proposed special technological environment to ferrite-pearlite carbon steel made it possible to obtain an abnormally high crack closure effect and suppress fatigue crack growth. It was confirmed by a comparison of the diagram $P - \delta$ obtained by the compliance method before (1) and after (2) using this environment. Such diagrams (load P of a specimen vs. displacement δ of two points located symmetrically on two sides from the fatigue crack) were registered during a semi-cycle of loading.



Fig. 1. Diagrams $P - \delta$ before (1) and after (2) using the special technological environment

The phenomenon of the revealed great crack closure under the application of the special technological environment can be explained by the electrochemical interaction of its active components with the steel on the newly formed surface of the fatigue crack, leading to filling up the crack cavity with corrosion products. It indicates the positive role of the corrosion process in the considered case since formed corrosion products mechanically prevent the closure of the crack surfaces in the vicinity of the crack tip during a semi-cycle of unloading.

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CORROSION RESISTANCE OF Mg AND Mg-Ca BINARY ALLOYS IN SIMULATED ORTHOPAEDIC APPLICATIONS

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Introduction. Mg alloys have comparable mechanical properties to the natural bones and are biodegradable in aqueous solutions due to hydrogen evolution and formation of nonprotective corrosion products [1,2]. Therefore, they have great potential for application as temporary implant materials. The aim of this study is to examine the corrosion behaviour of such alloys in simulated orthopaedic applications, namely under rotary movements and immersed in simulated body fluid (SBF).

Materials and methods. Oar-shaped Mg, Mg-Ca1 and Mg-Ca5 (0, 1 and 5 at.% Ca, respectively) samples were investigated in SBF for 8 h with and without mechanical torsion. Rotary movements with angle 1/35 degree were applied so that the maximum torque did not exceed the elastic stresses. The corrosion rate was examined by electrochemical studies: impedance spectroscopy measurements (EIS) and hydrogen evolution reaction (HER).

Results. The obtained impedance spectra (Fig. 1a) show that the corrosion rate of Mg is faster with rotary movements applied to the sample. Similar effect was observed for Mg-Ca1 alloy, however, the corrosion resistance of these samples was few times smaller than that observed for pure magnesium. Hydrogen evolution (Fig. 1b) was also higher for Mg-Ca1 samples, maintained, however, the linear trend. Mg-Ca5 sample dissolved in SBF after less than 8 h, it was, therefore, impossible to determine an electrochemical behaviour of this alloy.



Fig. 1. Electrochemical results of Mg and Mg-Ca1 alloy immersed in SBF for 8 h with and without torsion a) Nyquist plots, b) hydrogen evolution reaction (HER)

Conclusions. Addition of calcium and application of rotary movements speed up the hydrogen evolution and corrosion rate of magnesium alloys. Even though their good mechanical properties, the corrosion resistance of such alloys is too low to use them as medical implant. Therefore, some extra protective layers should be applied on metallic surface to slow down the dissolution process what will be subject of the further studies.

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THE INFLUENCE OF THE MANEUVERING LOAD OF THE RECTIFICATION COLUMN ON ITS RESIDUAL LIFETIME

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Fig. 1. Distillation column for ethylene production. The arrow indicates cir-cumferential cracks on the welded joint.

The article investigates corrosion-mechanical fracture (stress corrosion) of structural elements under the action of long-term maneuvering load and local electrochemical corrosion. In particular, mathematical model of the fracture, which takes place through the propagation of a corrosion-mechanical crack, have been built, and on this basis, a method for estimating the residual lifetime of structural elements have been developed. The model is based on the first law of thermodynamics, written for the elementary act of material fracture (crack jump), as well as the mechanisms of anodic dissolution and hydrogen embrittlement during electrochemical corrosion. The model was used to predict the residual lifetime of rectification column made of steel $09\Gamma 2C$ (height H = 74800 mm with diameter D = 3200 mm and wall thickness h = 22 mm) in which the support is welded to the elliptical bottom (Fig. 1). During operation, the column is exposed to wind load, which is maneuverable - constant bending pressure on the column with frequent gusts, and atmospheric corrosion. Under the action of such a maneuvering load (long-term static with concentrated dynamic loads), large deformations occur near the weld seam, as a result of which the protective paint coating on the outer surface of the column body is damaged, which contributes to the localization of electrochemical corrosion. As a result of the combined effect of

significant mechanical stresses from the above-mentioned maneuvering loads and the corrosive environment in the weld seam in the places of damage to the paint coating, surface corrosion-mechanical cracks nucleation and continue to develop. The critical development of such cracks can lead to the destruction of the column. One of these high-rise columns collapsed after 22 years of operation with the support separating from the bottom along the weld seam. On the basis of the model formulated in the paper, a calculation method for forecasting the residual lifetime of a rectification column exposed to wind load and atmospheric corrosion has been developed. The dependence of the residual lifetime of the steel $09\Gamma 2C$ column on the number of wind gusts was studied. If the column is bent an average of 45,000 times a year due to gusts of wind, then its predicted lifetime is 18 years, which roughly corresponds to the operating time (22 years) of a rectification column. Obviously, a surface crack with a depth of at least 3 mm appeared in the destroyed column. Comparing the calculated column life time forecast with the previously known one, it was established that the results of the developed model satisfy sufficient accuracy for engineering practice.

STUDY OF ELECTROCHEMICAL PROPERTIES OF LONG-TERM OPERATED GAS PIPELINE PIPES MADE OF CONTROLLABLE ROLLING STEEL

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World experience in the operation of main gas pipelines shows an increase in the number of accidents with increasing duration of operation due to mechanical aging of metal pipes [1, 2]. There is evidence [3] of deterioration of electrochemical properties. The complex of electrochemical properties of the main gas pipeline pipes made of X70 controllable rolling steel has been studied (their characteristics are given in the caption to the figures).

The structural characteristics of X70 pipe steel of different manufacturers are typical for controllable rolling steel, microalloyed vanadium and niobium. These differences in structural characteristics are due to differences in the chemical composition of steel (e.g, low carbon and silicon content) and the peculiarities of the technology of steel production by different manufacturers.



Fig. 1. Polarization curves of the base metal (a) in NS4 and changing the ratio $j_{c.p.}/j_{o_2}$ and the residual

corrosion rate (b) of X70 steel: 1 – pipe after 20 years of operation of main pipeline, steel manufacturer France, pipe manufacturer Khartsyzk pipe plant (KhPP); 2 – pipe after 20 years of operation, steel and pipe manufacturer is Japan Kawasaki; 3 – pipe after 20 years of storage, the steel producer is not established, pipes manufacturer KhPP; 4 – sample of unexploited pipe steel X70 manufactured by KhPP approximately in 2012 year

The difference in electrochemical parameters of the base metal of X70 steel pipes in different states, in particular, corrosion potential, hydrogen reduction potential, slopes of anode curves determined from polarization curves (Fig. 1, a), is detected, but due to the fact that for unused pipe and stock pipe that have not been subjected to loads, these figures are very close, it is concluded that such differences are due to differences in chemical composition rather than operating loads.

The ratio of cathodic protection current to the maximum diffusion current (Fig. 1, b), which characterizes the state of the metal under cathodic protection, for the base metal of different pipes increases with approximately the same trend, differing in numerical values from (0.42-0.69) at the minimum protective potential -0.75 V to (2.38-3.4) – at the maximum protective potential -1.05 V.

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STUDY OF CORROSION AND PHYSICAL-MECHANICAL PROPERTIES OF DEGRADED STEELS OF POWER EQUIPMENT, OF THAT HAVE BEEN EXPOSED TO HYDROGEN-CONTAINING MEDIA

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During long-term operation, the properties of power equipment parts made of complex alloys are affected by technological environments containing hydrogen [1, 2].

Samples of 38Cr3MFA steel were examined:

1) in the initial state;

2) subjected to degradation processes during long-term operation in contact with technological hydrogen-containing media.

I used potentiometer an EG&INSTRUMETS Model N_{2} 36 at a potential sweep rate of 10 mV/min. Electrochemical characteristics: E_{cor} - corrosion potential, i_{cor} - corrosion current density. For electrochemical studies I used a standard trielectrode electrochemical cell with a silver chloride reference electrode, which was brought to the electrode under study with an electrolytic bridge and a Gaber-Luggin capillary, as well as with an additional platinum electrode.

Polarization curves were obtained on 11.3 mm diameter cylinders pre-pressed in fluoroplastic.

Samples of new cutting coolants (CC) based on sunflower (CCs), rapeseed (CCr) and petroleum oils (CCp) were examined.

Analysis of changes in the corrosion potential of steels in different CC, allowed to establish that it has a similar nature. The value of corrosion current density for 38KhN3MFA steel depends on the nature of CC base and grows in the following sequence: sunflower < rapeseed < oil.

For material samples cut from different degrees of degradation of the shaft sections of power equipment and different times of operation are characterized by a lower corrosion resistance by 8...17% compared to the steels in their original state.

Roughness value for samples (Rz) (after machining): (conditionally original state / subjected to degradation processes after 200 thousand hours of operation): 37.08/57.47 (dry cutting); 5.01/7.11 (with water); 6,36/8.77(CCp); 4.43/5.71 (CCs).

The corrosion-fatigue endurance for materials cut from different sections of power equipment subjected to different degrees of degradation turned out to be 20...30% lower compared to alloy samples in the state of delivery.

On the basis of results of experimental data the regression equation and values of reliability of approximation R^2 describing the change of electrochemical parameters of 38KhN3MFA steel samples after 200, 225, 250 thousand hours of operation were obtained.

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GROWTH OF FATIGUE CRACKS IN STEEL AND COMPOSITE SUCKER RODS <u>Kopey B.¹</u>, Krechkovska G.², Kopey I.¹, Bakun B.¹ ¹IFNTUNG ² Karpenko Physico-Mechanical Institute of NAS of Ukraine kopeyb@ukr.net

Comparative experimental studies of full scale steel as well as fiberglass and hybrid sucker rods were conducted on a laboratory installation [1,2]. Corrosion and fatigue tests in aggressive environments of sucker rods with technological and operational defects allowed to determine the dangerous size of these defects and on this basis to carry out rational rejection of rods. Analyzing the crack growth rate curves depending on the number of load cycles, it was concluded that the critical crack growth rate is reached when the length of its crack in a circle is 15 ... 16 mm, and the depth is 4.5 ... 5.6 mm for 22 mm rods. During the experiment, the dependence of the incubation period before the appearance of the first visible crack in the hybrid rods was found and it was shown that it increases from 0.4 to 0.85 with increasing load from 110 to 175 MPa. In steel rods, the range of resource before the crack initation is smaller and can be in the value of 0.18-0.4 with increasing of load from 100 to 150 MPa. The regularities of crack growth with increasing of fatigue life of specimen are analyzed and a graph of the dependence of crack length on the value of alternating stress for polymer sucker rods is constructed. As the value of variable load increases, a greater number of cracks (up to 13 ones) arises in the hybrid rods near the steel head than at low loads (2 ones).



Fig. 1. Dependence of crack length Lmax on the value of alternating cycle stress in fiberglass (1) and hybrid (2) sucker rods after failure

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CORROSIVE BEHAVIOR OF PIPELINE STEEL 17G1C AND 13G1C-U IN ENVIRONMENTS NS1-NS3

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The urgency of the problem. Energy transport pipelines, laid in soils of various corrosive activity, undergo destruction due to exceeding the normative resource of their operation (more than 30 years), degradation of the insulating coating, the influence of the soil electrolyte and the action of the association of microorganisms. To date, the corrosive behavior of pipeline steels 17G1C and St.13 in model environments NS1- NS3, as imitations of soil electrolyte [1].

The purpose of the work is to study the corrosive behavior of pipeline steels in model environments NS1-NS3, as imitations of soil electrolyte, in a long-term experiment.

Object and research methods. Samples of pipe steel 17G1C and St.13, measuring 10x60x1.0 mm, were exposed in the studied environments for 609 days. During the research, conditions similar to the operating conditions of main pipelines on the territory of Ukraine were modeled. 3 compositions of model media of soil electrolyte NS1–NS3 were prepared according to European composition standards, mM: 1.999 KCl, 5.999 NaHCO₃, 1.082 CaCl₂ 2H₂O, 0.430 MgSO₄ 7H₂O; 1.905 KCl, 12.868 NaHCO₃, 0.497 CaCl₂ 2H₂O, 1.031 MgSO₄ 7H₂O and 0.496 KCl, 6.654 NaHCO₃, 0.054 CaCl₂ 2H₂O, 0.361 MgSO₄ 7H₂O with initial pH values of 7.80; 8.87 and 8.74 (293K). The hydrogen index of the media (pH) was determined using a pH meter of the MI-1500 brand. The phase composition and structure of corrosion products were analyzed by X-ray analysis using a Shimadzu XRD-7000 X-ray diffractometer (CuK α radiation was used with 2 θ scanning from 10° to 60°, 2° per minute with a step of 0.02°). Processing of diffraction patterns involved Rietveld analysis (Match!/FullProf software). The rate of corrosion of metal samples was determined by the gravimetric indicator of the rate of corrosion K_{gr} . = $m - m_0/S \tau$ (mg/(dm²day), where:m – final mass of the sample, mg; m₀ – mass of the sample before corrosion, mg; S – surface area of the sample, dm²; τ – exposure time, day.

Research results and discussion. The analysis of radiographs showed that the corrosion products of pipe steel grades 17G1C and 13G1C-U are represented by various iron oxides - with the structure of lepidocrocite, goethite, magnetite and hematite. The composition of corrosion products varied depending on the mineralization of the environment. Thus, for steel 13G1C-U, the composition of corrosion products in the NS1 environment was mainly characterized by the presence of crystals with the structure of lepidocrocite and magnetite, in the NS2 environment - goethite and magnetite, in the NS3 environment - lepidocrocite, goethite, and in small amounts of hematite and magnetite. In environments NS1-NS3, corrosion products of 17G1C steel were characterized by the presence of crystals with a magnetite structure. In addition, lepidocrocite prevailed in NS1, goethite in NS2, and goethite lepidocrocite in NS3.

Steel brand	Environment	pH of the beginning.	pH of the end	Kgr.mg/dm ² day		
	NS1	7,80	8,81	20,53		
17G1S	NS2	8,87	9,64	12,59		
	NS3	8,74	9,36	16,09		
	NS1	7,80	8,62	22,33		
113G1S-U	NS2	8,87	9,72	15,91		
	NS3	8,74	9,24	17,54		

Table 1. Influence of the composition of model environments and pH

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INFLUENCE OF CORROSIVE ENVIRONMENT ON FATIGUE CRACK GROWTH IN LONG-TERM OPERATED STEEL OF A PORTAL CRANE

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Sea hoisting equipment is commonly operated under intense cyclic loading which is an important factor in its possible structural integrity loss. Degradation of mechanical properties is one of the main causes of structural strength deterioration [1]. It consists primarily in reducing the characteristics of brittle fracture resistance, in particular, impact toughness [2]. The investigations of failure cases of such structures show that their abrupt fractures are often caused by fatigue crack growth, and corrosive marine environment can additionally facilitate this process. The aspects of corrosion-fatigue fracture are considered in this paper for rolled ferrite-pearlite steel St38-b2 from a 30-year operated portal crane taking into account its operational degradation. Fatigue testing were performed on single edge notch bend specimens by cantilever bending with a frequency of 10 Hz in air and 1 Hz in 3% NaCl water solution simulating marine environment. The chosen load ratio R = 0.5 is close to real loading conditions of cranes. Steel texture resulted from the rolling process was taken into account by studying specimens cut along and across the rolling direction.



Fig. 1. Fatigue crack growth curve $da/dN - \Delta K$ for the steel St38-b2 in the as-received state (1) and after operation (2, 3) in air (1, 2) and 3% NaCl (3) under testing longitudinal (1) and transversal (2, 3) specimens

Concerning the tests in air, operational degradation manifested itself only in lower threshold values of stress intensity factor for the operated steel (Fig.1, curves 1 and 2). The acceleration of fatigue crack growth in corrosive environment is most considerable in the case of transversal specimens under higher ΔK values. The revealed positive effect of the corrosive solution at the near-threshold region of the fatigue crack growth curve is concerned with crack tip blunting and, obviously, enhancing crack closure.

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CAVITATION WEAR OF T91 FERRITIC-MARTENSITIC STEEL

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Ferritic-martensitic (F/M) steels are chosen as structural materials for Gen-IV nuclear reactors [1] due to their lower thermal expansion and higher thermal conductivity compared to austenitic steels of type 316 and 304, as well as significant corrosion resistance, high temperature strength and heat resistance and also high radiation resistance. One of the most promising material of this class is T91 steel [2], which contains approximately (in wt%) 9 Cr, 0.1 C, 0.9 Mo, 0.6 Mn, 0.3 Si, 0.19 V, 0.07Nb. In this regard, it becomes necessary to study the mechanical, erosion and corrosion properties of this material. Data on cavitation resistance, which also depends on the corrosion characteristics and hardness of the material, are not currently known for T91 steel.

In present study the microstructure, hardness and cavitation wear of F/M T91 steel in standard structural state (normalization at 1040°C during 30 minutes with air cooling and subsequent tempering at 730°C during 60 minutes) have been investigated. The dependence of the weight loss on the time of exposure to the cavitation was measured [3], and from these data, kinetic curves of destruction of the samples were plotted. The average cavitation wear rate of the material was determined in the quasilinear sections of the cavitation wear rate curves. All the data are shown on Fig. 1.



Fig. 1. Cavitation wear mass loss (a) and cavitation wear rate (b) for T91 and other reactor steels

It was revealed that the cavitation resistance of the T91 F/M steel is by an order of magnitude higher than that of another F/M steel Eurofer 97 and 6 times higher than that of the Cr18Ni10Ti austenitic steel [3]. The microhardness values of the T91 steel and the Eurofer 97 were 247.3 kg/mm² and 207.2 kg/mm², respectively. The results obtained show the high erosion strength of T91 steel compared to other reactor steels.

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FATIGUE LIFE OF BUTT-WELDED JOINTS WITH ACCUMULATED FATIGUE DAMAGE IN 3% NACL SOLUTION AFTER TREATED BY HIGH-FREQUENCY MECHANICAL PEENING

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Fatigue tests of butt-welded joints of low-alloy steel 15KHSND were carried out in 3% NaCl solution after previous long-term work-in and treated by high-frequency mechanical peening (HFMP). The blanks for butt welded joints dimensions 650x360x12 mm were made by automatic flux welding and then specimens of butt-welded joint were cut out from welded blanks. After cutting, in order to accumulate fatigue damage, a cyclic loading with a stress ratio of R = 0, maximum stress 150 MPa and a loading frequency of 5 Hz was applied to the specimens until 2 million cycles of stress changes in air had occurred. Subsequently, the specimens were treated by the HFMP and tested for fatigue in a 3% NaCl solution also at stress ratio of R = 0 with a frequency of 5 Hz until complete failure.

It was experimentally established that the treating of butt-welded joints with accumulated fatigue damage by HFMP technology increased their fatigue strength based on 2 million cycles of stress changes by 53% (from 141 up to 216 MPa) in a 3% NaCl solution (Fig.1). At the same time, the fatigue life of welded joints treated by HFMP increased by 10 times. The fatigue strength based on 2 million cycles in a 3% NaCl solution after treated by HFMP of butt-welded joints with accumulated fatigue damage is even 15% higher than fatigue strength of as-welded joints in air, 216 and 187 MPa, respectively.



Fig. 1. *S-N* curves of butt-welded joints of 15KhSND steel: (1) as-welded in air; (2) as-welded joints in a 3% NaCl solution after preloading to 2 million cycles; (3) treated by HFMP welded joints in a 3% NaCl solution after preloading to 2 million cycles in air.

Thus, experimental results affirm that HFMI treatment may be a useful tool for buttwelded joints of structures even after long-term use in their service life.

INFLUENCE OF ELECTROLYTIC HYDROGENATION ON THE STRUCTURAL AND MECHANICAL STATE OF HEAT-RESISTANT STEEL

AND MECHANICAL STATE OF HEAT-RESISTANT STEEL <u>Tsybailo I.</u>¹, Svirska L.¹, Solovei P.^{1,2}, Krechkovska H.², Datsko B.¹, Student O.¹ ¹Karpenko Physico-Mechanical Institute of the NAS of Ukraine, ²Lviv Polytechnic National University oleksandrastudent1@gmail.com

The decrease in the serviceability of the main steam pipelines of the TPP is due to the influence of operational factors, such as temperature and pressure of steam, operating time and the number of shutdowns of the units [1]. These factors facilitate to the creep and fatigue of the metal, which contributes to the degradation of steel [2]. Taking into account effects of steel hydrogenation from the process environment are important. After all, hydrogen absorbed by the metal during operation can intensify structural transformations, accelerating the diffusion of carbon and alloying elements and the precipitation of carbides along grain boundaries. This weakens the adhesion between the grain boundaries, contributes to the delayed internal fracture of the metal at the micro structural level. Such a transformation of the steel structure weakens the adhesion between the grain boundaries, contributes to its internal delayed fracture. As a rule, the mechanical characteristics after tensile tests in air are not sufficiently sensitive to the inservice degradation of heat-resistant steels. At the same time, their sensitivity to the degradation of hydrogenated steels increases significantly, which is important, since it is impossible to exclude metal hydrogenation during operation at power facilities. Therefore, in order to increase the sensitivity to degradation of the characteristics of the operated steels of steam pipelines, it is advisable to assess their technical state after its hydrogenation.

The mechanical properties of heat-resistant steel 15Kh1M1F in the initial state and after ~ $2 \cdot 10^5$ h operation at a temperature of 545°C and a pressure of 24 MPa on the main steam pipelines were compared. With the same operating time, both pipelines differed in the number of shutdowns. The total their numbers for power units No. 1 and No. 2 was 501 and 576, respectively. The corresponding mechanical characteristics of steel, tensile tested in air after preliminary electrolytic hydrogenation of the specimens and without it, were compared. The specimens were subjected to electrolytic hydrogenation for 15 min at a current density of 50 mA/cm² in a 5% aqueous solution of H₂SO₄ (pH = 0) with the addition of 2 g/L of thiourea. Thus, the effect of internal hydrogen was modelled.

It was established that shutdowns of the units affected the strength and ductility characteristics of the operated steam pipeline steel. The properties of the steel from unit No. 2 turned out to be lower than steel from unit No. 1. However, the elongation of the steel in unit No. 2 was an exception to this rule. A higher value of δ was associated with the opening of internal defects at the stage of uniform deformation of the specimens during their tensile test. Steel degradation (especially with more shutdowns) was even more pronounced on hydrogenated steel. On specimens of axial orientation, the negative effect of degradation turned out to be somewhat weaker in the vicinity of the outer surface of the pipe and increased near its inner surface. This was explained by opening of the operational defects under the influence of hydrogenation. An increase in the elongation of specimens of tangential orientation was recorded only near the inner surface of the pipe, which is due to defects located in the diametrical section. It was believed that these defects were caused by thermal fatigue. After all, creep defects are oriented, as a rule, in the axial direction. Therefore, the opening of such defects near the inner surface of the operated steel pipe would be insignificant and could not increase δ of tangential specimens.

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Corrosion-resistant materials and coatings

CORROSION PROTECTION OF MAGNESIUM ALLOYS FOR BIOMEDICAL APPLICATIONS

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Magnesium and its alloys have been investigated as potential candidates in the field of biodegradable materials for bone implants. If the Mg corrosion rate is controlled, allowing for a slow dissolution of implants, this might eliminate the need of a second surgery for implant removal. One of the most common and effective ways to control corrosion is the use of coatings.

In this work, a brief review of several coatings developed for this purpose is presented. A particular emphasis will be given to a new composite coating, involving an inner oxide layer followed by an outer layer of organic nature, which was tested on magnesium alloys AZ31 and RZ5. The first layer is obtained by anodizing in alkaline solution, whereas the organic layer consists of a new formulation, based on polycaprolactone (PCL), with or without addition of hydroxyapatite nanoparticles. Electrochemical Impedance Spectroscopy (EIS) was used to assess the behaviour of the composite coating during immersion in Hank's solution, showing a remarkable increase in the corrosion resistance, compared to the bare material, with initial impedance values in the range of $10^9 \ \Omega.cm^2$. The polymeric layer was found to significantly reduce the degradation rate of magnesium, whereas the anodized layer does not control, by itself, the corrosion rate, although being effective in establishing bonds for polymer adhesion.

Keywords: Mg alloys; anodized film; corrosion protection; biodegradable coating.

ELECTROCHEMICAL CHARACTERIZATION OF FILMS OF SEMICONDUCTOR OXIDES

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This work presents the study of the electrochemical behaviour of CuBi2O4 (copper bismuthate) films using Scanning Electrochemical Microscopy [1]. The study was conducted using a 25 μ m diameter platinum ultramicroelectrode in a phosphates buffer solution at pH 7.0, using FcMeOH as the mediator and a platinum wire as the auxiliary electrode [2]. All electrochemical measurements were performed using an Ag/AgCl reference electrode saturated with KCl. Different solutions were evaluated by cyclic voltammetry at different concentration of the mediator (FcMeOH), the supporting electrolyte (KNO₃) and the aggressive agent (K₂SO₄). The kinetics of the reactions occurring on the surface of the copper bismuth were evaluated by approximation curves of the ultramicroelectrode towards the semiconductor oxide. An increase in the apparent electron transfer rate constant was observed in the samples when the thickness of the semiconductor films was enlarged, which can be associated with a greater photoconversion of species due to greater absorption of photons.

It was possible to observe the oxidation phenomenon in the Fe passing first from Fe^{2+} to Fe^{3+} and the following scan passing from Fe^{3+} to Fe^{2+} .

The reaction kinetics was studied, using approximation curves involving the ultramicroelectrode and the semiconductor oxide films immersed in the appropriate electrolytic solution, being able to observe the change in the reaction kinetics in the presence of light compared to the results obtained in its absence, to study the photo-electrochemical behaviour of this semiconductor. An increase in the apparent electron transfer rate constant was observed in the samples as the thickness of the semiconductor films increased, which is due to a greater photoconversion of species related to greater absorption of photons.

Finally, it was shown that Scanning Electrochemical Microscopy is a good technique to correctly study the photoelectrochemical behaviour of semiconductors. However, it is still necessary to optimize the deposition process of semiconductor films, to improve their uniformity and obtain higher current signals.

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ELECTROCHEMICAL BEHAVIOR OF VT20 TITANIUM ALLOY FABRICATED BY DIFFERENT TECHNOLOGIES

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Titanium alloys are widely used for the production of pumps, condensers, piping systems, coolers, vessels, heat exchangers, tanks and agitators, pipelines for aggressive liquids, desalination plants, filters, valves, etc. Despite the previously mentioned properties, the use of titanium and its alloys in the chemical industry is limited due to the high cost of manufacturing titanium products. To solve this problem, the direction of the manufacturing of titanium products using additive technologies (manufacturing) is actively developed in scientific and industrial laboratory centres [1, 2].

The purpose of this study was to investigate the corrosion behaviour of VT20 nearalpha titanium alloy (Ti–6Al–Mo–1.5V–2Zr) fabricated by additive manufacturing (AM) in 20 wt.% HCl. Titanium alloy specimens were fabricated by electron beam melting (EBM) and laser metal deposition (LMD). The same titanium alloy manufactured by traditional technology with initial equiaxed (TTE) and lamellar (TTL) structure was used as a control.

It investigated the correlations between corrosion resistance, microstructure and phase composition of titanium alloys fabricated by different technologies, through the use of electrochemical corrosion testing, scanning electron microscopy, X-ray diffraction and hardness testing. It was shown that the corrosion resistance of AM samples is lower than TT samples. The corrosion resistance of AM samples was attributed to the presence of more α' martensite and less β -Ti phases in the microstructure of titanium alloy than for TT samples. The electrochemical results suggest that titanium alloy fabricated by EBM has better corrosion resistance in 20% HCl solution at room temperature compared to titanium alloy fabricated by LMD.



Fig. 1. Tafel curves of titanium alloy manufactured by different technologies in 20wt.% HCl solution at a room temperature

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CORROSION RESISTANCE OF DIFFUSION CHROMOSILICIDE COATINGS OBTAINED ON STEEL 45

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The complex saturation of steel by silicon and transitive metals is known to lead to a change in their several physico-chemical properties. In a given work, an effect of the complex saturation of the carbonaceous steel by silicon and chromium on its corrosive stability in the concentrated solutions of acids at a temperature of 20^{0} C has been studied.

The applying process of the alloyed chromosilicide coatings onto the steel surface has been performed at a temperature of 1323 K for 6 h on gases methods [1]. After the process completion, the samples underwent the external examination as well as microstructure and X-ray analyses. The corrosive and electrochemical studies have been performed in the various aggressive solutions.

The coatings got under the accepted conditions of diffusive saturation have been established to represent themselves a composition of the $Cr_{23}C_6$, Cr_7C_3 and α -solid silicon and chromium solution in iron. The silicon concentration directly onto the surface of samples equals to 0,15 %, and further in the depth of the diffusion layer varies between 8,24%. The silicon concentration decreases sharply with penetrating into the diffusive layer. The reasonable thickness of coatings is 100 µm. Microhardness - 19.5 GPa.

The results of studies we performed showed that applying of the chromo-silicide coatings permits one to decrease a corrosion rate of the steel 45 in the 5% and 30% solutions of sulphuric acid 2.2 and 2.7 times, respectively. In the solutions of 5, 10 and 20% of nitric acid, this rate decreases 10, 45 and 700 times, respectively. The complex saturation of carbonaceous steel by the above elements gives rise to an inhibition in the cathodic reaction rate of the corrosive processes: hydrogen liberation in H_2SO_4 , reduction of anions in HNO₃ solutions.

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CORROSION RESISTANCE OF PSEUDO-ALLOY COATINGS OF THE COPPER-IRON SYSTEM PRODUCED BY THE METHOD OF ELECTRIC ARC SPRAYING

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Today, the problem of providing corrosion resistance of parts and structures is relevant for different industries. In the manufacture of engineering products and metal structures of engineering constructions, the use of expensive corrosion-resistant materials is most often economically unprofitable. In this regard, the development of inexpensive and simple technological solutions for creation of highly efficient functional protective layers and coatings is an urgent task.

Among the contemporary technologies of thermal spraying of corrosion-resistant coatings, the most widespread method is electric arc wire spraying. The advantages of this method are predetermined by economical efficiency of the process, high effectiveness, use of simple equipment and non-scarce materials.

For corrosion protection, electric arc coatings of aluminium, zinc and pseudo-alloy zinc-aluminium coatings are the most widely used. Pseudo-alloy Zn-Al coatings are used to protect pipelines, tanks and agrochemical equipment against corrosion. However, these coatings have insufficient stability during operation in extreme conditions (at boundary and dry friction, high temperatures, significant mechanical and thermal stresses and effect of aggressive environments) due to their low strength and hardness. Therefore, pseudo-alloy coatings of Cu-Al, Fe-Al and Fe-Cu-Al systems are actively studied.

In the work, the composition, structure and corrosion resistance of electric arc pseudoalloy coatings of copper-iron system deposited on the steel base were investigated.

Pseudo-alloy coatings of the copper-iron system were produced by the method of combined electric arc spraying of copper and iron wires. For spraying, wires of M1 copper and Sv08A steel of a solid cross-section with a diameter of 2 mm were used. Spraying was performed by the electric arc spraying EM-14M device.

Electrochemical tests were performed in the P - 5827M potentiostat at a scanning rate of 20 mV/s. Studies were performed in 3% NaCl solution on steel with the coating at a temperature of 18-20 °C.

Metallographic examinations have shown that the produced coatings tightly adhere to the steel base, cracks and defects at the coating-base boundary are absent. Microhardness of the coating amounted to 2130 ± 700 MPa. X-ray diffraction phase analysis showed that the coating consists of the original components of copper, iron, as well as their oxides Cu₂O and FeO.

The carried out examinations have shown that the corrosion resistance of Cu-Fe coating in 3% NaCl solution corresponds to the resistance of stainless 40Kh13 steel and exceeds the resistance of St3 steel by 14 times.

Based on electrochemical tests, it was found that electric arc pseudo-alloy coatings of Cu-Fe system are able to provide a galvanic protection of the steel base in a medium containing sodium chloride, and can be used to increase the resistance of parts subjected to wear and corrosion.

CORROSION RESISTANCE OF STAINLESS STEEL AISI 310S IN LEAD MELT AT THE TEMPERATURE 450 °C

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The corrosion resistance of heat resistant AISI 310s steel in lead melt with limited oxygen access after 240, 480, 720 and 1440 h exposure at 450 °C were investigated. As a corrosion tests result, it is established that the dynamics of changes in the corrosion rate of AISI 310s steel is shows the tendency the decrease in the value of the index from 0.474 mm/year to 0.045 mm/year with an increase in test duration from 240 h to 1440 h, respectively. A likely cause of this character of the corrosion rate change of steel AISI 310s is the formation of protective oxide films on the surface of the samples. According to the results of scanning and optical microscopy, a change in the duration of testing is shown (Fig. 1).



Fig. 1. Microsection photo of the AISI 310s steel surface after 240 h (a), 720 h (b) and 1440 h (c) of testing at 450 °C in lead melt with the measurement results

It has been established that with an increase in the duration of testing up to 720 h, a homogeneous, dense and continuous structure of a corrosion products layer, consisting of O, Si, Ca, Cr, Mn, Fe, Ni and Pb, formed after 240 h of testing, into a two-layer structure with a clear separation of layers, differing in composition, to adjacent directly to the base metal (O, Cr, Fe, Ni and Pb) and in contact with the lead melt (O, Cr, Fe and Pb). In addition, coagulation of carbides on the base metal and their precipitation along the grain boundaries and along the rolling lines after 720 h of testing were established. It is found that the Vickers microhardness of the base metal is 1630 ± 50 MPa, 1650 ± 50 MPa, 1855 ± 45 MPa and 1730 ± 60 MPa, in the initial state and after 240, 720 and 1440 h of testing in lead melt, respectively. While the microhardness of the corrosion products is 3710 ± 425 MPa and 3020 ± 615 MPa after 240 and 720 h of testing in lead melt, respectively.

ELECTROCHEMICAL CORROSION OF ALUMINIUM-MATRIX COMPOSITES OBTAINED BY HOT FORGING

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In the process of operation, many types of industrial equipment undergo electrochemical oxidation, which can be simulated with a 3% NaCl solution. Therefore, the development of new materials is an urgent task, especially in connection with the progressive need for corrosion-resistant materials [1]. The corrosion behavior of aluminum and its alloys depends on the operating conditions, namely the nature of the components of the aggressive environment, their concentration, temperature, etc [2]. The purpose of the work is to study the processes of cathodic and anodic oxidation in 3% NaCl of aluminium-matrix composites obtained by hot forging. The polarization curves were obtained by the electrochemical method of polarization anodic and cathodic curves in the potentiostatic mode with a potential deployment speed of 0.5 mV/sec on a PI 50-1 potentiostat at a temperature of 24°C.



Fig. 1. Anodic and cathodic polarization curves in a 3%-NaCl solution of alumino-matrix composites of different compositions

The electrochemical behavior of the studied materials is presented in fig. 1. The polarization curves show the cathodic recovery process (N \ge 1-3) and the anodic process (N \ge 4, 5) of sample oxidation that occur on the surface of the studied composites. The intensity of the cathodic process for the 85Al-15(40Al-54Ti-6C) wt.% composite (N \ge 1), which determines the corrosion rate, is slightly lower than the similar intensity for composites (N \ge 2, 3). The course of polarization curves for Al-15(20Al-64Ti-16C) wt.% materials shows that the recovery process of composites (N \ge 4, 5) occurs in a wide range of potentials E = - 0.75 V to E = -0.05, which is further accompanied by anodic oxidation process, which is controlled by the formation of an oxide film in the region of potentials, as a result of which, starting from the stationary potential E = 0 V to E = 0.5.

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MICROSTRUCTURE AND CORROSION RESISTANCE OF Ni-B MATRIX COMPOSITE COATINGS WITH BORON AS A DISPERSION PHASE PRODUCED BY ELECTROLESS PLATING

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Over the past few years, a trend in surface engineering related to nickel-based coatings produced by electroless plating can be observed. Materials of this type are of great interest to the world of science and industry [1-5].

The results of studies of composite coatings with nickel-boron matrix and boron particles as a dispersion phase were presented. The composite coatings were produced by electroless plating method on a steel substrate with different variants of dispersion phase content in bath, namely 0.1; 0.5; 1.0, 1.5 g/dm³. A nickel-boron coating without a dispersion phase was also deposited for comparison.

The topography and surface morphology were investigated by means of scanning electron microscopy (SEM). Characterization of the structure of the produced coatings was performed using X-ray diffraction analysis. The electrochemical potentiodynamic method was used for the corrosion tests of the Ni-B and Ni-B/B coatings.

Presence of the boron particles in the Ni-B matrix affects the structure, morphology and properties of the deposited coatings. The microhardness of composite coatings is higher that Ni-B alloy coating. An incorporation of boron particles increases the corrosion resistance of the composite coating compared to coatings without dispersion phase. With the addition of B particles in the range of 0.1 to 1.0 g/dm³, a shift in the corrosion potential toward positive values (from -380 mV for Ni-B coating to -321 mV for Ni-B/B (1.0 g/dm³) coating) was detected. A gradual reduction in the value of the corrosion current was also obtained, which for the Ni-B coating was 2.2 μ A/cm² while for Ni-B/B (1.0 g/dm³) 0,85 μ A/cm².



Fig. 1. SEM images of boron powder and produced coatings

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INFLUENCE OF SURFACTANT ELEMENTS ON GRAIN BOUNDARY STRUCTURE AND RESISTANCE AGAINST INTERCRGRANULAR CORROSION OF AUSTENITE Cr-Ni AND Cr-Ni-Mo STEELS

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The aim of the work is to establish the maximum allowable contents of surfactants carbon, boron, nitrogen, which provide high resistance to intergranular corrosion (IGC) of austenitic Cr-Ni and Cr-Ni-Mo steels in highly oxidizing and weakly oxidizing media.

Research materials: austenitic steels 03Cr18Ni11 (304L), 03Cr17Ni14Mo3 (316L), 02Cr25Ni22NMo2 (TP310MoLN/KES U2/) with content of 0.01...0.03% C, 0.003 and 0.03% B and 0.04...0.3% N, after hardening from 1000...1200° C, after double hardening and tempering at 650° C, 1 hour.

Research methods: light and electron microscopy; tests for resistance against IGC in media: strong oxidizing – boiling 65% HNO₃ and weakly oxidizing – boiling 35% H₂SO₄ with the addition of CuSO₄ and pure copper, according to the methods of DU and AMU, GOST 6032 (C and B according to ASTM A 262), respectively, and electrochemical methods.

Research results. It was found that to ensure high resistance to IGC when tested in boiling 65% HNO₃ (corrosion rate ≤ 0.5 mm/year), the carbon content in steel 03Cr18Ni11 should be less than 0.025%, and in steel 03Cr17Ni14Mo3 – less than 0.015%. This is due to reduced solubility and increased effective carbon content with increasing nickel content in steel, as well as lower corrosion resistance of molybdenum and its carbides in 65% HNO₃. In addition, a significant impact on the test results at the IGC of sample preparation technology has been established. When tested in boiling 35% H₂SO₄, the maximum allowable carbon content in both test steels is 0.03%.

It was found that nitrogen in the amount of up to 0.20% does not adversely affect the resistance to IGC steel 03Cr18Ni11 with a content of up to 0.025% C. Increasing nitrogen to 0.3% increases the corrosion rate of this steel to 1.4 mm/year. With a simultaneous increase in the carbon content to 0.03%, the corrosion rate of steel increases to 1.9 mm/year, i.e. there is a negative synergy effect. High resistance against IGC steel 03Cr17Ni14Mo3 with 0.3% N is provided at a content of 0.010% C, which is also confirmed by electrochemical studies [1, 2].

More high-alloy steel 02Cr25Ni22NMo2 showed high resistance to IGC when tested by both methods, even at contents up to 0.035% C and 0.3% N; the corrosion rate of its samples in boiling 65% HNO₃ did not exceed 0.2 mm/year.

A significant negative effect of 0.003 and 0.03% B on the resistance against IGC steels 03Cr18Ni11 and 03Cr17Ni14Mo3, subjected to hardening from 1150-1200° C, when tested in boiling 65% HNO₃ (corrosion rate of samples reached 6-8 mm/year) [2, 3]. When tested in 35% H₂SO₄, boron in the amount of 0.003% did not adversely affect the resistance against IGC, and 0.03% B contributed to the emergence of the susceptibility of steels to IGC.

The modes of deformation and heat treatment based on the principle of grain boundary engineering of materials are proposed, which increase the resistance of steels against IGC.

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POSSIBILITIES OF USING BASALT SCALES FOR COMPOSITE MATERIALS AND ANTI-CORROSION PROTECTION

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Most products and materials are subject to corrosion damage under the influence of environmental factors during operation in real conditions of use (temperature changes, humidity, exposure to aggressive substances, electromagnetic radiation, etc.). To protect materials and structures from the negative effects of the external environment, inorganic, organic, organoelement substances and their compositions are used.

This study proposes the use of scale-like materials based on melts from rocks (basalt scales) as fillers for various types of composite materials and anticorrosion coatings.

During the research, scales obtained from basalt melt by forming a film under the action of centrifugal force and its grinding by a stream of compressed air into discrete scales. The resulting scales contain particles of various shapes with a thickness of 1.0 to 4.5 μ m and a size of 0.1 to 5.0 mm. In the initial state, basalt scales have a vitreous structure, with a relatively smooth surface, but with some defects in the form of unmelted inclusions and submicrotrisks.

When conducting research, flakes obtained from basalt melt by forming a film under the action of centrifugal force and crushing it into discrete flakes by a compressed air stream were used. The resulting scale contains particles of various shapes with a thickness of 1.0 to 4.5 μ m and a size of 0.1 to 5.0 mm. In the initial state, basalt scales have a vitreous structure with a relatively smooth surface, but with some defects in the form of unmelted inclusions and submicrocracks. The density, thickness and number of surface defects depend on the composition of the rock, the method of production, the thickness of the formed scales and the speed of molding. The chemical composition of the scales includes up to 50% wt. SiO₂ and 14-15% wt. iron oxides (FeO+Fe₂O₃). The chemical composition depends on the reaction property of fillers, resistance to aggressive factors, durability.

One of the factors affecting the production technology and properties of composites and coatings containing scales is the particle surface. Physical and mechanical properties, corrosion resistance, durability and other characteristics of materials and coatings, in particular, depend on the surface layer of the scale.

To study the influence of temperature on the structure and properties of the solid surface of the scale-like filler and increase the adhesion of basalt scales to the binder and the coated surface, its thermal activation was carried out at temperatures from 400 to 900 °C. According to the data of thermographic and X-ray studies in the temperature range of 600-900 °C, the processes of crystallization and transition of divalent iron to trivalent iron take place. The data obtained when determining the chemical resistance of basalt scales in alkali and acid solutions showed that there is an increase in its alkali and acid resistance by 20–25% after heat treatment, which is obviously also due to the transition to a higher coordination number (FeO \rightarrow Fe₂O₃).

The corrosion process was studied on a polymer composition based on basalt scales applied to a metal plate. Analysis of the obtained results indicates that the most effective protective properties have coatings with heat-treated scales.

Thus, the results of the research indicate the possibility and prospects of using basalt scales in protective and anti-corrosion compositions.

INFLUENCE OF THE COMPOSITION OF THE ELECTROLYTE FOR SOLID ANODIZING OF ALUMINUM ON THE CORROSION RESISTANCE OF SYNTHESIZED ANODIC COATINGS

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Aluminum alloys are widely used in industry due to their high structural strength and casting properties, low specific gravity and melting point. However, these alloys are characterized by low abrasive wear resistance, which significantly prevents their wide use as a wear-resistant material. The method of hard anodizing is technologically simple and relatively cheap, but it has a significant drawback - through porosity that lead to sub-film corrosion in the form of localized damage – pitting. This does not make it possible to fully use the protective potential of the oxide structure in corrosive technological environments.

The anodizing technology can be improved by changing the composition of the electrolyte, in particular by introducing oxygen, hydrogen peroxide, etc. into the reaction zone, in order to achieve an increase in the growth rate of the coating, its hardness and wear resistance. However, the effect of increasing the content of oxidants in the working electrolyte are not fully understood. Therefore, the purpose of this work was to establish the influence of the composition of the electrolyte for hard anodizing of aluminum on the corrosion resistance of the synthesized anodic coatings.

The solid anodizing process of the aluminium AD0 was performed at a temperature of -4... 0°C for 60 min. The base electrolyte was a 20% aqueous solution of H_2SO_4 . A current density of 5 A/dm2 was maintained during the anodizing process. Hydrogen peroxide (H2O2) at concentrations of 30, 50 and 70 g/l was added to the electrolyte to determine the effect of strong oxidants on the characteristics of the anode layers. In some cases, the electrolyte was purged with ozone-air mixture at the rate of 5 mg of ozone per 1 l/min.

The structure of anodic coatings was studied on a Zeiss EVO-40XVP electron microscope using an INCA Energy 350 X-ray microanalysis system. It was found that with an increase in the concentration of H_2O_2 in the base electrolyte from 0 to 70 g/l, the thickness of the oxide layer increases by almost 50% – from 75 to 110 μ m. Therefore, the concentration of 70 g/l H_2O_2 is optimal. Additional blowing of the electrolyte with the optimal content of H_2O_2 with an ozone-air mixture in the anodizing process does not increase the thickness of the anode layer. Blowing of the base electrolyte increases it by only 15% (up to 90 µm). Potentiodynamic polarization measurements at a sweep rate of 1 mV/s were performed to evaluate the effect of the electrolyte composition on the formation of the anodic coating on the aluminum on its corrosion electrochemical behavior in 3% NaCl aqueous solution. Exposure of coated samples in the medium lasted from 1 hour to 21 days. It was established that the corrosion resistance of synthesized anodic coatings is most reduced by the introduction of hydrogen peroxide into the base electrolyte. With an increase in its concentration from 30 g/l to 70 g/l, corrosion currents increase by 30% and 74%, respectively. Additional blowing by ozone of the electrolyte, which contained 70 g/l of hydrogen peroxide, lead to increase the corrosion currents twice. The presence of hydrogen peroxide and ozone reduces the thickness of the barrier layer coating through which oxygen and aluminium ions penetrate and combine to form an oxide layer. This is confirmed by increased values of corrosion current density (correspondingly lower corrosion resitance) in coatings synthesized in electrolytes containing ozone or hydrogen peroxide.

DEVELOPMENT OF NICKEL-BASED COMPOSITE COATINGS WITH INCREASED CORROSION-MECHANICAL PROPERTIES Halaichak S., Vynar V., Mardarevych R.

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Currently, as an alternative to electrolytic chromium plating, various coating technologies are offered, in which chromium is replaced by nickel alloyed with various chemical elements [1-3]. It is of interest to study the simultaneous effect of corrosion and friction factors on alloyed electrochemical coatings based on nickel, which would make it possible to obtain surface layers on steels with high wear resistance and corrosion resistance. Therefore, the purpose of this research is the development of nickel-based composite coatings doped with Molybdenum (to increase corrosion resistance) and Boron (to increase wear resistance), establishing optimal heat treatment modes (improving the physical and chemical properties of the coatings) and investigating tribo-corrosion properties of coatings in corrosive environments.

The optimal electrolysis conditions for the synthesis of Ni-Mo-B galvanic coating were established: $C(NiSO_4 \cdot 7H_2O) = 0.2 \text{ mol/l}$, $C(Na_2MoO_4) = 0.4 \text{ mol/l}$, $C(Na_3C_6H_5O_7) = 0.3 \text{ mol/l}$, m(B) = 50 g/l, $J_k=3 \text{ A/dm}^2$, t = 60 °C, pH9 (ammonia buffer). A three-component coating was obtained. Chemical composition according to EDX analysis, mass %: 6.39 B, 70.85 Ni and 22.76 Mo.



Fig. 1. SEM image of Ni-Mo-B coating initial (*a*) and after heat treatment at 950 °C for 2 hours (*b*).

On the initial coating (fig.1*a*), the SEM image showed the developed (branched) surface of amorphous boron particles

that were evenly distributed in the nickel-molybdenum matrix. After heat treatment at 950 °C for 2 h in an inert environment, all boron particles were almost completely "dissolved", shells of boride grains were formed around them, and upon interaction with the matrix, borides of different chemical composition were formed

In the process of research, we managed to electrochemically synthesize a threecomponent nickel-molybdenum-boron coating, using its suspension as a source of boron. The prospect of further research is to develop the possibilities of their deposition using a chemical method and to study their physical, tribocorrosion properties and mechanisms of their deposition.

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INVESTIGATION OF CORROSION RESISTANCE OF METAL SURFACES PROTECTED BY POLYMER FILMS

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For metal product protection, volatile corrosion inhibitors based on amines are used, which are introduced into the preservation material in the form of sprayed powder, alcohol solutions, and suspensions [1-3]. However, intensive evaporation of inhibitors may occur causing a rapid loss of protective properties. Such methods of anti-corrosion treatment of the surfaces of metal products have a general disadvantage: a short period of validity, non-ecological, the need for surface preparation, and additional conservation using other anti-corrosion agents. Therefore, it is more promising to use volatile inhibitors by dissolving them in a synthetic organic matrix - vaseline, transformer oils, plastics based on polyvinyl chloride and fluoroplastic, etc.

Compared to protective oils and powder coatings, polymer inhibited films have better anti-corrosion properties. This is mainly due to the additional effective barrier action of the polymer film, which not only separates the oxidant from the metal surface but also prevents excessive consumption of the volatile inhibitor. Long-term protection of metal products, even in particularly difficult microclimatic conditions of storage, is ensured with relatively small (up to 2 wt. %) additions of the inhibitor to the polymer base. Visible corrosion processes on the surface of the steel preserved with a modified polyethylene film, are practically absent in hermetic conditions and the appropriate microclimate inside the package. Loss of the coating tightness leads to the avalanche-like appearance of corrosion centers. It was established that the warranty period of protection of steel surfaces with inhibited polyethylene films is determined by the properties of the coatings and is primarily associated with an increase in the defectivity of protective anti-corrosion coatings [4].

In this study, the appearance of primary corrosion centers on the surface of steel was found during the storage of metal products in closed warehouses after 9-12 months when protected with an uninhibited polymer film. In the case of protection with an inhibited and modified (inhibitor + plasticizer) film, primary corrosion centers appeared after more than 2 years of storage. At the same time, the most effective initial effect in the composition of the polyethylene matrix was revealed for the cyclohexylamine benzoate inhibitor. In addition, effective long-term protection by the dicyclohexylamine benzoate inhibitor was established. Effective inhibition of the corrosion process during continuous use of protective materials based on polyethylene films modified with dicyclohexylamine benzoate inhibitor and plasticizer (dioctyl sebacate, dioctyl phthalate, bis(2-ethylhexyl) phthalate) was found. Focal indicators of steel surface corrosion processes is low up to 5-7 years.

Based on the established regularities, ways of preserving the consumer properties of metal products during their conservation and packaging with protective materials using corrosion inhibitors are proposed.

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CORROSION RESISTANCE OF THE SURFACE OF TITANIUM ALLOYS MODIFIED BY PLASMA-ELECTROLYTIC OXIDATION

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The actual task of chemical material science is to develop scientific basis of the controlled synthesis of the newest materials, in particular thin-layer composite coatings.

Among the known heterooxide systems significant practical interest are plasmaelectrolyte coatings on titanium alloys containing transitional metal oxides. This is due to the possibility of their application as electrochemical and catalytic active materials for electrochemical and heterophasic transformations, wear-resistant and protective systems. The diversity of technological environments of their operation conditions makes it necessary to study the parameters of corrosion resistance of synthesized materials in different mineralization and aggressiveness environments. This has defined the direction of this work.

Heterooxide coatings on titanium alloys (VT1-0) were formed in diphosphate electrolytes by PEO method in galvanic mode. Doping of the synthesized systems with oxides of transition metals was carried out by adding of transition metals (Co, Mn) in cationic form to the electrolyte. PEO of titanium was carried out at current densities 1–5 A/dm². The time of PEO was 30 min. The elemental composition of the obtained materials was determined by INCA Energy 350. The morphology of the coatings was studied using ZEISS EVO 40XVP. The topography and roughness of the modified surface were set with the AFM NT-206. The corrosion properties of the synthesized systems were determined by the methods of polarization resistance and impedance measurement.

It is known that the composition of the electrolyte and the modes of PEO affect the composition, morphology and roughness of the modified surface. In addition to the target dopant metal, oxides of phosphorus and potassium are included in the composition of the synthesized coatings. The formed heterooxide coatings have an unevenly developed globular surface [1].

By testing the synthesized plasma-electrolyte systems in a chloride-containing environment, it was established that the corrosion resistance indicators for the systems Ti/TiO_2 , CoO_y are higher than the indicators of the systems Ti/TiO_2 , MnO_x . It is shown that varying the content of the active component in the composition of the coating also affects the indicators of corrosion resistance. It was determined that the increase in the amount of manganese in the composition of the surface layers $TiO_2 \cdot MnO_x$ causes a decrease in corrosion resistance. Results of corrosion tests of systems $TiO_2 \cdot MnO_x$ and $TiO_2 \cdot CoO_y$ in Ringer's solution and in an alkaline environment (2 mol/dm³ NaOH) also testify to higher corrosion resistance of cobalt-containing systems.

It was established that, in addition to the quantitative composition of PEO systems, the porosity of the formed oxide layer and the topography of its surface, in particular the grain size, influence their corrosion resistance [2]. As the porosity increases and the structure of the surface layers is crushed, the corrosion resistance decreases. This occurs due to an increase in the true surface area and the number of active centers with increased surface energy, which act as foci of corrosion destruction.

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EPOXYPOLYMER COMPOSITIONS FOR PROTECTIVE COATINGS

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Recently, human activity has increased the aggressiveness of the environment. For example, in the industrialized regions of Ukraine there is precipitation with an acidity in the range of pH 4.0 ... 4.5, containing oxides of sulfur and nitrogen, so the problem of protection of structural materials from corrosion is quite relevant. The most affordable and effective corrosion prevention is paint and varnish polymer coatings. During operation, due to the action of water, as well as aggressive environments, the coating degrades. Inhibitory pigments are added to increase the service life of such protective coatings, but manufacturers of paints and varnishes are trying to replace toxic pigments in organic coatings with environmentally friendly and satisfactory protective efficiencies.

Along with this problem, there is another creation of polymer coatings with maximum stability, resistance to corrosion. Promising modifiers for the synthesis of composite materials can be carboxyl-containing petroleum polymer resins (PPRs), which are obtained from recyclable wastes of oil, its fractions and gas, capable of film formation, have high water and chemical resistance. Because the epoxy coating, having in its structure reactive epoxy and hydroxyl groups, interacts with water molecules, swelling and losing adhesion. When studying the properties of the synthesized epoxy-oil-polymer composition, it was found that epoxy and carboxyl-containing resins interact with the formation of three-dimensional structures, as indicated by studies of the gel fraction, IR spectroscopy and differential thermal analysis. The process of creating such compositions is multi-stage and has not been thoroughly studied, but allows to obtain spatially crosslinked oligomeric materials with new properties.

Feedstocks for PPRs are obtained from cracked petroleum fraction. These resins are used in a wide variety of materials including adhesives, printing inks, hot-melt coatings, rubber articles, caulks and sealants, floor coverings, textiles, paints and varnishes, and plastics and chewing gum. They are rarely the sole component in a particular application, but rather are compounded with elastotomers, plastics, waxes, and oils provide spesial properties for a particular use. For example, large volume uses for APRs are in the: rubber industry, printing inks, adhesives and coatings.

The molecular weight of functionalized PPRs were determined cryoscopically in benzol; the softening points were determined using ring-and-ball apparatus; the colour for an iodometric scale (IMS) were defined using a solution of resin in benzol; bromine number, acid number and alkali neutralization were founded utillizing a titrimetric method. Structure of sintetized functionalized APRs and in combination with epoxy resins the mark ED-20 were determined by chemical and spectroscopic (IR- spectroscopy) methods. Resins are uses as expensive and deficient products of natural origin, for example, of oil and rosin in alkidyc lacquers, for the lacquer-paint materials production.

As a result of the conducted researches the expediency of introduction of carboxylcontaining PPRs into epoxyamine composition for improvement of its operational characteristics due to interaction of additional carboxyl groups with epoxy oligomer is substantiated. The optimal content of carboxyl-containing PPRs has been established, which provides an increase in the duration of protection of the structural coating.

LONG-TERM CORROSION RESISTANCE OF THE CrN CATHODIC ARC COATINGS

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The main requirement of a ceramic coating applied to a carbon steel (or cast iron) nuclear waste disposal canister is the prevention, over a period of \geq 10000 years, of access of bentonite and/or Clay pore waters to the substrate via cracking or leaching [1]. Ceramic coating solutions for SF/HLW disposal canisters appear to be less mature than metallic coatings. Physical Vapour Deposited (PVD) coatings have good corrosion protection compared to coatings that are deposited by traditional spraying. Chromium nitride (CrN) has been proven to be one of the most successfully and extensively used PVD coatings in industry due to its high hardness, excellent wear and remarkable corrosion resistance [2]. The demand for high quality coatings in the recent years has led to an intensive research in further evolution of chromium-based coating family [3].

The purpose of this work is to investigate the influence of deposition parameters on the long-term corrosion resistance of CrN coatings on a mild steel (St.3). Ceramic CrN coatings up to 30 μ m thick with different substrate bias voltages (-50, -150 and -300V) were deposited by cathodic arc evaporation. The deposited coatings are stoichiometric chromium nitride with high adhesion to the substrate and high mechanical properties: hardness 21 – 23 GPa and Young's modulus 315 – 340 GPa. Long-term corrosion tests of coated samples were carried out in a 3% NaCl solution for 300 hours.

Table 1. Photographs of the coated samples after corrosion testing in a 3% NaCl solution



The steel sample without coating is intensively oxidized already in within the first 24 hours, the oxide on the surface of the sample is poorly bound and goes into solution. After a long exposure, the entire surface of the sample is covered with pitting and a thick layer of rust. The samples with CrN coatings that were deposited at -50 V and -300 V have individual pitting corrosion, and the samples that were deposited at -150 V show no traces of corrosion after testing for 300 hours. Thus, chromium nitride coatings can be used for the corrosion protection of mild steels in water.

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APPLICATIONS OF CERAMIC-BASED FILM HEATERS WITH HEAT-RESISTANT INSULATING COATINGS <u>Kovbasiuk T</u>.¹, Duriagina Z.^{1,2}, Kulyk V.¹, Kostko O.³ ¹Lviv Polytechnic National University ²John Paul II Catholic University of Lublin, Poland ³LLC «PKVP «KREDUV» taras.m.kovbasiuk@lpnu.ua

Applying of electric current as a source of thermal energy in the conditions of increasing scarcity of natural energy resources is becoming more important. The development of environmentally friendly electric heaters with low inertia for heating of premises, trains, and municipal electric transport vehicles (cabins and carriages for trains, trams, and trolleybuses) is one of the energy conservation problems. The production technology of film heaters is currently expensive and low productive. This technology is based on a multiple screen printing technologies (fig. 1) followed by the complicated heat treatment. This work focuses on the development of alternative production technologies and materials for film heating elements creation.



Fig. 1. Applications of screen-printing technologies [1]

The electrophysical and exploitation properties of insulating coatings based on BaO-SiO₂-ZnO or PbO-ZnO-B₂O₃ glass-ceramic materials obtained by the method of thick films have been investigated. The possibility of their use for high-temperature dielectric materials in electrical engineering was shown. Methods for creating resistive coatings based on glass-ceramic materials with the addition of metal borides was developed [2]. A set of methods for creating a film electric heating element on ceramic and cermet bases was demonstrated. Examples of using the created electric heaters in devices used for heating electric transport vehicles (Ukrainian Railways, Electron transport company, etc.) were given [3].

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THE EFFECTS OF GAS NITRIDING ON CORROSION RESISTANCE OF TITANIUM AND TITANIUM ALLOYS

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Owing to their good mechanical and corrosion properties, titanium (Ti) alloys are used in diverse industries e.g., marine, aerospace, chemical, biomedical, while various types of Ti alloys were employed for that. α -Ti is commercially pure (CP) Ti, which shows a good corrosion resistance, but mechanical strength is low compared with other Ti alloys. The most employed Ti alloy in all industries is Ti–6A1–4V. It is an alternative to CP Ti because of its better mechanical and anticorrosion properties. Despite the previously mentioned advantageous properties, the use of Ti and its alloys is limited due to high costs of manufacturing. Nowadays, Ti powder metallurgy (PM) methods are being actively developed to overcome this limitation [1].

The main aim of present study was to investigate the corrosion behaviour of CP Ti and Ti–6Al-4V, manufactured by PM, and to propose a method for improving anticorrosion characteristics. For the study we used 20 wt.% HCl because corrosion problems affects Ti mainly when the electrolyte contains Cl⁻ions [2].

The studied material had a porosity of about 1%: the total porosity was determined by the ratio of the measured density of the material to the theoretical density of CP Ti (4.51 g/cm³) and Ti–6Al–4V alloy (4.43 g/cm³), respectively. The influences of manufacturing technology, phase-structure state and the expedient of gas nitriding for corrosion resistance were investigated; gravimetric corrosion studies, optical and scanning electron microscopy, for this goal were used.

Material	K , g/m²·h			
Time of exposition	15 days	30 days		
CP Ti	1.0523	1.2269		
Gas nitrided CP Ti	0.001			
Ti-6Al-4V	0.6563	0.7283		
Gas nitrided Ti-6Al-4V	0.0052*	0.2674		
*Notation: 12 days immersion				

Table 1. Corrosion rate of CP Ti and Ti–6Al–4V alloy manufactured by PM after immersion in 20 wt.% HCl

The higher corrosion resistance of Ti–6Al–4V compared to CP Ti can be explained by the presence of β –Ti, which was formed as a result of the alloying of β -stabilizers (V). It is worth noting that as a result of the proposed gas nitriding, the corrosion resistance of CP Ti and Ti–6Al–4V alloy increased. Moreover, the corrosion rate during the first 15 days decreased by 2 times. Such protection can ensure the good operation of products working in contact with this acid, as well as biomedical implants, protecting them from the action of Cl⁻ ions, which are present in all physiological solutions. In addition, it was assumed that the nitrided layer will reduce the negative impact of V and Al on the body. Both are the toxic elements, whereas dissolution of V and Al ions can cause Alzheimer's disease, genotoxicity and peripheral neuropathy [3].

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NEW MATERIALS FOR NUCLEAR FUEL CLADDING (ATFC): CURRENT STATE AND PROSPECTS

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Zirconium alloys are used as a base material of fuel claddings in the PWR and BWRtype nuclear reactors all over the world. The Zr-based alloys are widely applied due to their low thermal-neutron capture cross-section, good mechanical properties and high waterside corrosion resistance at normal operating temperature up to 350 °C. However, after severe nuclear accident at Fukushima NPP in Japan in 2011, the issue of fuel stability and reactor safety has attracted much attention in the world. As a result, the concept of accident tolerant fuel (ATF) has been developed with improved performance in normal operation, both in design and in design basis accidents [1]. After near a decade of research, three main categories of accident tolerant materials for the cladding emerged (Coated zirconium alloys, Monolithic FeCrAl alloys, Silicon carbide composites) [2]. The Zr-based alloys with Cr coatings, obtained by the methods of physical deposition, reveal protective properties in different tests in laboratory conditions [3].

The aim of implementation of accident tolerant materials is to make the fuel and the cladding more robust and tolerant to sudden rise in the temperature to levels above 1000 °C. That is, implementation of ATF materials will considerably reduce the risk of plant operation. The implementation of resilient materials will allow longer plant operation and extend the periods between refueling that will also decrease the cost of plant operation [2].

The world's leading nuclear fuel manufacturers, such as Westinghouse, Framatom and General Electric are intensively testing new claddings in research and commercial reactors. Westinghouse and Framatom made the choice in favor of the Cr-coated zirconium alloys and SiC composites, and General Electric in benefit of Cr-coated zirconium alloy and FeCrAl alloy cladding.

The review presents the results of the NSC KIPT advanced developments in the field of protective materials for fuel rod claddings manufactured of zirconium alloy Zr-1Nb. The results of corrosion tests in the environment with the composition and under parameters of the VVER-1000 primary coolant and under the parameters of accidents associated with overheating of the core (up to 1200 °C) are given. The main conclusion was made on the basis of the obtained results that the coatings made of metallic chromium, FeCrA1 and CrNiMo alloys possess high protective properties at temperatures of normal operation and reduce the corrosion rate of Zr-1Nb alloy by more than 10 times at temperatures up to 1100 °C in a water vapor environment (accidents). Also the review presents the results of a comparative analysis of the main characteristics of the coatings, applied with the technology mastered at the NSC KIPT, with the known characteristics of the coatings of the Westinghouse, Framatom and General Electric companies.

The ATF materials projects and their implementation could become the impulse that the nuclear industry needed to wake up and develop this clean and safe source of energy.

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INVESTIGATION OF THE INFLUENCE OF BORIDE ADDITIVES ON THE CORROSION RESISTANCE OF POWDER CHROMIUM STEELS <u>Kyryliuk Y.¹</u>, Bagliuk G.¹ ¹Frantsevich Institute for Problems in Materials Science of the NAS of Ukraine

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The corrosion resistance of chromium steels largely depends on the chromium content in the solid solution of ferrite or austenite. In the work, in order to obtain chromium carbides, instead of high-value chromium carbide Cr_3C_2 , cheap and non-deficient high-carbon ferrochrome (Fe-Cr) was used, and iron was used as the starting metal component, which in the process of liquid-phase sintering and interaction with high-carbon ferrochrome is transformed into chromium ferritic-austenitic steel. The corrosion resistance of materials in a 3% NaCl solution, a 30% NaOH solution and a 20% HNO₃ solution at room temperature was investigated using an accelerated method. The depth of corrosion penetration and the corrosion score were determined [1]. The work investigated the corrosion resistance of Fe – (Fe-Cr) materials alloyed with Ni₃B (3.5, - 8.7) and TiB₂ (0.38-2.2) (%, wt.) additives, the results of the research are shown in fig. 1.



b

Fig. 1. Corrosion resistance of steel system Fe–(Fe-Cr) doped with TiB₂ additives (a) Ni₃B (b)

From fig. 1 (a) shows that increasing the amount of TiB₂ additive from 1.48 to 2.2 (%, wt.) significantly improves the corrosion resistance of materials in 30% NaOH and 20% HNO₃. In a 30% NaOH solution, samples with 1.48 and 2.2 (%, wt.) TiB₂, which have a 1-point resistance (fully resistant), have the best corrosion resistance. This behavior of composites doped with TiB₂ additives can be caused by the presence of up to 2% Ti in their composition, which dissolves in austenite and ferrite, as confirmed by the results of local X-ray spectral analysis, and increases the corrosion resistance of carbide steels. As can be seen from fig. 1 (b) in a 30% NaOH solution, materials doped with 5.2 and 6.9 (%, wt.) of Ni₃B showed the greatest corrosion resistance, corresponding to score 1 (fully resistant). The obtained results can be explained by the increased density of samples of these materials, which is 7.3-7.4 g/cm³.

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CORROSION RESISTANCE OF HARD ALLOYS VN20 AND VNK15 IN ENVIRONMENTS OF DIFFERENT AGGRESSIVENESS <u>Matviichuk O.¹</u>, Vynar V.², Hnatenko I.¹, Botvinko V.¹ ¹Bakul Institute for Superhard Materials of the NAS of Ukraine ²Karpenko Physico-Mechanical Institute of the NAS of Ukraine o.o.matviichuk@gmail.com

Composite materials based on tungsten carbide are characterized by high hardness and wear resistance, due to which they are used in many industries for the manufacture of various elements of structures and tools, especially sliding bearings and other parts of friction pairs [1]. In particular, in practice, hard alloy VN20 of the WC-Ni system with a nickel content of up to 20% by mass is widely used for the manufacture of seals, which is capable of working in environments with frictional interaction at high specific loads. In order to increase tribotechnical characteristics, this alloy is alloyed with various elements, however, its corrosion resistance is often reduced [2], which requires additional tests.

The electrochemical behavior of the VN20 alloy (WC -80%, Ni – 20%) and the VNK 15 alloy (WC–85%, Ni – 9%, Co – 6%) was studied. The materials were obtained by sintering under optimal conditions for each alloy at temperatures of 1340...1420°C in a hydrogen environment [2]. Porosity of no more than 0.02% of pores up to 10 μ m in size is allowed for alloys. After sintering, the surface of the samples was ground and polished to a roughness of R_z = 2.5m. Electrochemical studies were performed on a Pi 50-1-1 potentiostat using a three-electrode scheme with a silver chloride reference electrode and an auxiliary platinum electrode. Media – 3% NaCl solution, 1n H₂SO₄, 1m HCl and NACE solution (saturated with hydrogen sulfide) [3]. Crevice corrosion was studied in pairs with stainless steel 304 and titanium VT 1-0. Microstructure studies and analysis of surfaces and corrosion products were carried out on an EVO 40XVP scanning electron microscope with a micro-X-ray spectral analysis system using an INCA ENERGY 350 energy dispersive spectrometer.

It was established that the bending strength of the VN20 alloy is 160 kgf/mm², and the hardness is 78 HRA. Doping the alloy with cobalt increases the bending resistance to 180 kgf/mm², and the hardness to 84 HRA.

It is shown that in all environments, the electrode potential for the VNK15 alloy is more positive, compared to the VNK20 alloy. The potential values are in the range -0,158....-0,242 V. In the solution of NaCl, HCl and NACE (saturated with hydrogen sulfide), the alloys dissolve in an active state and the density of active dissolution and corrosion currents for the VNK15 alloy is lower than for the VN20 alloy, the corrosion current density is in range \sim 4·10-4.....3·10-4. In the sulfate solution, a repassivation section is observed on the anodic curve in the range of potentials -0,250...0,800 V, and the passivation current density for the VN20 alloy is 0,028 mA/cm², while it is 0.11 mA/cm² for the alloy with cobalt.

Studies of resistance to crevice corrosion of composite materials in a 3% solution for 60 days showed that in cases of contact with stainless steel 304 and titanium VT 1-0, local damage occurs on the surface of hard alloys. Their nucleation and intensive growth begins mainly near pore defects and inclusions that are not dissolved in the bond. There is no significant difference between damage on the surface of VN 20 and VNK15 alloys.

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CORROSION PROPERTIES OF ELECTROLYTIC COBALT METALOXIDE COMPOSITES

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The problem of anticorrosion protection is that the industry is based on the use of equipment made mainly of iron-based steels and alloys, despite the widespread use of composite materials with high chemical resistance. Usually, the production of composite coatings is based on the formation of coatings from electrolyte suspensions due to coprecipitation of dispersed particles of different nature compatible with base metals. Incorporation of particles of the second phase into the composition of synthesized coatings significantly increases their consumer and operational characteristics, however, it is problematic to ensure the stability and aggregative stability of colloidal solutions [1]. In order to solve this problem with regard to metal oxide composite electrochemical coatings CECs, we applied the methodology of obtaining the oxide phase as intermediates of electrochemical reactions when used as the starting ingredients of oxometalates [2].

A preliminary assessment of the effect of the chemical composition of the composite coatings Co-Mo-WOx, Co-Mo-ZrO₂, Co-W-ZrO₂ on their corrosion behavior shows that the stationary potential (corrosion potential) significantly depends on both the composition and morphology of the coating, as well as on acidity of the corrosive environment. It should be noted that the corrosion of all investigated CECs based on cobalt alloys proceeds with oxygen depolarization regardless of the acidity of the solution.

Corrosion behavior of Co-Mo-WOx, Co-Mo-ZrO₂, Co-W-ZrO₂ coatings in environments of different acidity against a background of 1M sodium sulfate was evaluated by recording and further analysis of cathodic and anodic polarization dependences. Based on the values of the polarization resistance, the depth index of the corrosion rate kh was calculated. The analysis of the results shows that the most significant difference in stationary electrode potentials for each group of CEC is observed when the composition of the model medium is changed. The dependence of the potentials on the pH of the solutions is particularly pronounced, which additionally allows them to be positioned as type II metaloxide electrodes.

The most positive corrosion potentials of the investigated CEC samples are in environments with a minimum pH value, and the most negative ones are in an alkaline solution. This happens due to the fact that, according to their chemical properties, tungsten and molybdenum are able to form acidic oxides stable in acidic environments in the presence of an oxidant. The behavior analysis of zirconium-containing KEPs shows that the zirconium content practically does not affect the corrosion resistance of the systems, which can be explained by its small amount.

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CORROSION PROTECTION BY THERMAL SPRAYING Lampke Th.¹, Rupprecht Ch.², Schuberth S.³, <u>Pokhmurska H.⁴</u> ¹Institute of Materials Science and Engineering Chemnitz University of Technology, Germany ²Coating technology department at the Institute for Machine Tools and Factory Management, Technical University of Berlin ³CeWOTec Co., Germany ⁴Lviv Polytechnic National University hanna.pokhmurska@mb.tu-chemnitz.de

In the first part of presentation the description of the mail methods of thermal spraying of coatings according the international standard DIN EN 657, including the main points of Thermal Spray Basics, Definitions, materials, processes as well as application possibilities in Corrosion protection against atmospheric corrosion, active and passive corrosion protection, cost-effective wire processes, zinc, zinc-aluminum application, protection against high-temperature corrosion and combined protection against corrosion and wear, such as hard chrome substitutes, hard metals, composite materials.

The main methods of investigations of the corrosion properties of thermally sprayed coatings are also described following the discussion of the Thermally Sprayed coatings applications Advantages and Limitations.

CORROSION BEHAVIOR OF Ni-TiO₂ COMPOSITE COATINGS ELECTRODEPOSITED IN ELECTROLYTES BASED ON A DEEP EUTECTIC SOLVENT

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The development and implementation of green hydrogen energy requires the creation of new, cheap, affordable and highly efficient electrocatalysts for water electrolysis. One of the promising ways to solve this problem is the electrochemical deposition of coatings of alloys and composites based on nickel. Among the large number of possible options, considerable attention is drawn to electroplated nickel-titanium dioxide composites [1]. Ni– TiO₂ electrodeposits can be synthesized from traditional aqueous colloidal electrolytes, a significant disadvantage of which is their aggregative and sedimentary instability. Therefore, the electrochemical deposition of Ni–TiO₂ composite coatings in a new environmentally friendly and affordable type of ionic liquids, the so-called deep eutectic solvents, looks very promising in this context [2]. An important step in creating electrocatalysts is to assess their corrosion resistance, which determines the duration of their uninterrupted operation.

In this work, we investigated the corrosion behavior of Ni and Ni–TiO₂ coatings (with the content of the dispersed phase of 5 and 10 wt.%) deposited from an electrolyte based on a eutectic mixture of ethylene glycol and choline chloride containing dissolved nickel(II) chloride, water additive and TiO₂ dispersed phase (nanopowder Degussa P 25). An aqueous solution of 3% NaCl was used as a corrosive medium and the evaluation of corrosion parameters was performed by methods of linear voltammetry and electrochemical impedance spectroscopy. It was established that the introduction of titanium dioxide particles into the nickel matrix and the increase of their content in the coating leads to a shift of the corrosion potential towards positive values, a decrease in the corrosion current density and an increase in the polarization resistance. The observed effects of improving the corrosion resistance of composite coatings are due to the barrier action of particles of the dispersed phase and the formation of a large number of corrosion micro-cells that are evenly spaced in the metal matrix and contribute to hinder local corrosion [3].

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APPLICATION OF FLUORINATED GRAPHENE FILM AS A PROTECTIVE COATING TO REDUCE METAL CORROSION IN COASTAL AREAS

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This work describes the use of fluorinated graphene film as the main anti-corrosion coating for metals in coastal areas with a high salt content. The main side problem during the experiments was that the graphene film also acted as a highly conductive coating on the test samples in a 30% NaCl solution. The author proposed to reduce such a destructive effect on iron, to use a graphene film made from reduced graphene oxide. It is known that graphene oxide has an extraordinary electrical conductivity, which can make it difficult to use it as a covering material for iron surfaces.

Introduction. One of the main problems today is the corrosion of iron in aggressive coastal areas. The reason for such corrosion is the high content of NaCl in these zones, which contributes to the appearance of rust on iron and iron-containing surfaces [1]. By researching open literary sources, it was found that when graphene is fluorinated, the coefficient of electrical conductivity decreases sharply, and from this, we will be able to use fluorinated graphene film (Fig. 1) as an anti-corrosion protection of iron surfaces against the formation of rust.

Formulation of the design model. To conduct an experiment on iron corrosion protection, 2 iron plates measuring 50 x 30 x 5 mm (1 x b x h) were made, one of which was covered with a fluorinated graphon film. After that, each of the samples was placed in a special solution containing 30% NaCl, which was heated to a temperature of 70 degrees Celsius. Such samples were subjected to electrolysis to accelerate the development of corrosion rust on the surface of the material for 14, 20 and 24 hours. The same experiment was carried out, at a temperature of 100 degrees Celsius, for the same time as mentioned above. During such an experiment, it was found that samples 2 and 4, and coped with the task, so it was decided to increase the time for all samples to 60, 80 and 120 hours, one more sample was added to the experiment, which, unlike the other samples, was not polished. At the end of the experiment, it was found that the samples that were not covered with a film of fluorinated graphene and the untreated sample were subjected to very strong destructive corrosion with manifestations of rust and the formation of bumps on the surface [2]. After analyzing the samples, was found that the samples that were covered with an anti-corrosion film, unlike the samples that were not protected, did not succumb to corrosion in the form of rust and retained their original appearance [3].

Conclusions. Iron samples that were not covered with a protective coating, after 120 hours in an aggressive NaCl environment, were destroyed by rust (corrosion) and lost their original characteristics and appearance. At the same time, samples with anti-corrosion protection preserved them. And this means that such a method of protecting materials in coastal areas will be sufficient to preserve the original state of materials and environmentally friendly in extraction and use in mass production, even when making a film from reduced graphene oxide (rGO).

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HIGHLY PRODUCTIVE ELECTROSLAG ANTI-CORROSION SURFACE WITH TWO ELECTRODE TAPES

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To protect parts of power and chemical equipment against corrosion surfacing of highalloy corrosion-resistant metal on low-carbon or low-alloy steel is widely used. Experience shows that the most effective method for surfacing such equipment is electroslag surfacing with two strips, which provides high productivity (\geq 40 kg/h) and a minimum proportion of the base metal in the deposited metal (8-10%). This makes it possible to obtain the required chemical composition of the deposited metal already in the first layer.

PWI jointly with the China-Ukrainian Institute of Welding (CUIW, Guangzhou, China) carried out work on the creation of equipment and the development of technology for anti-corrosion electroslag surfacing with two electrode tapes in China.

The machine for electroslag surfacing with two electrode tapes developed in China consists of KM 2530 welding manipulator, on the transverse traverse of which a welding machine with a mechanism for feeding two tapes and a device for supplying and removing flux; inverter power source KAIYUAN ZD5-2000 with a rated welding current of 1650 A at duty cycle = 100%; roller stand for surfacing of cylindrical parts KT5000; computer control unit.

The load capacity of the roller stand KT5000 is 5000 kg, the diameter of the welded parts is 500...3500 mm, the range of circumferential speeds of rotation of the part is 134...1340 mm/min. The current supply to the workpiece is carried out through the drive rollers using sliding contacts.

As a result of the research, it was found that a stable electroslag process using two ESAB 309LNb ESW tapes with a cross section of 0.5x60 mm is achieved under the following modes: I = 1400...1500 A; U = 32...33 V; V = 14...17 m/h; tape feed speed - 70...80 m/h; gap between the tapes - 16 mm; surfacing productivity - 37.5 kg/h.

Metallographic studies have shown that the samples deposited in the specified modes are characterized by good formation of deposited beads and a minimum proportion of the base metal in the deposited metal within 7...9 %.

The mechanical properties of the weld metal of the 309LNb stainless steel type are given in the table.

Mechanical properties at 20 °C				
Ultimate strength, Yield strength,		Relative	Relative	
МРа	MPa	elongation δ , %	contraction ψ , %	
504-506 (≥510) [*]	286-297 (≥205)	44,0-49,0 (≥25)	64,0-69,7 (≥60)	

Table. Mechanical properties of weld metal type stainless steel 309LNb.

* - in parentheses are the mechanical properties of 309LNb stainless steel.

The research results show that the strength characteristics of the metal deposited with ESAB 309LNb ESW strips are at the level of properties of stainless steel 309LNb.

The results obtained are used in the development of materials and technologies for anti-corrosion surfacing of parts of power and chemical equipment in China.

LONG-TERM CORROSION RESISTANCE OF THE Cu, Cr AND Ti COATINGS DEPOSITED BY CATHODIC ARC EVAPORATION

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The concepts for deep geological disposal in Finland, Sweden, Canada, Korea and Switzerland propose copper as outer barrier material for containers [1]. Also, several other metallic materials have been investigated as candidates for containers, such as carbon steel, stainless steels, nickel and titanium alloys [2]. Titanium, chromium, and copper are well known materials for corrosion protection [3]. Good protective properties of Cr coatings were demonstrated under normal operation conditions: autoclave tests in PWR and BWR simulated medium [4]. Candidate titanium coating solutions for application to carbon steel nuclear waste disposal canisters are immune to microbially induced corrosion. Issues for application of titanium, chromium and copper as protective coatings on steel substrates: the required thickness to exclude through porosity, the effect of through defects and irradiation on corrosion resistance are open.

The purpose of this work is to investigate the influence of deposition parameters and thickness on the long-term corrosion resistance of the Cu, Ti and Cr coatings on a mild steel (St.3).

Metallic Cu, Ti and Cr coatings from 5 up to 50 µm thickness with different substrate bias voltages (-25, -50 and -300 V) were deposited by cathodic arc evaporation in vacuum at residual pressure 0.001 Pa. According to the EDS analysis, the concentration of impurities in the coatings is at a level of less than 1 at.%. Adhesion was determined using the Daimler–Benz test (Rockwell indentation at load 1500 N) and coatings have high adhesion to steel substrates, at the level (HF1–HF2) without any cracking of the coating in the surrounding of the crater. Long-term corrosion tests of samples with coatings were carried out in a 3% NaCl solution for 300 hours studying the surface by optical microscopy.

The steel sample without coating is intensively oxidized already in the first 24 hours, the oxide on the surface of the sample is poorly bound and goes into solution. After a long exposure, the entire surface of the sample is covered with pitting and a thick layer of rust. Traces of pitting corrosion in coatings with a thickness of 5 - 15 μ m appear after 140 hours of testing. Traces of pitting corrosion for coatings with a thickness more than 30 μ m, deposited at bias voltage -25 V arise after 296 hours of testing, and no corrosion traces were observed for coatings deposited at bias voltages -50 and -300 V.

Thus, metallic Cu, Ti and Cr coatings deposited by the cathodic arc evaporation method at a substrate potential of at least -50 V and a thickness of at least 30 μ m have high long-term corrosion resistance on mild steel in 3% NaCl solution.

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METAL OXIDE NANOCOMPOSITES - ELECTROCHEMICAL SYNTHESIS AND PROPERTIES

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The problem of creating new materials with a wide range of functional properties, as a global trend in electrochemical materials science, quite often faces a number of scientific and technical problems. Thus, one of the problems when applying composite electrochemical coatings (CEC) is the need to stabilize electrolyte solutions, which include the second phase of the composite (oxides, carbides, nitrides, polymer, carbon particles, etc.) in the form of nano- or finely dispersed particles, or is a colloidal solution. In other circumstances, the problem is managing the process of creating both the main matrix of the CEC and the dispersed phase, since they can be created according to the principle of "bottom-up" [1]. and "top-down" [2]. In view of this state of affairs, we formulated the latest principle of synthesis of metal oxide composites, which consists in the inversion of the nature of the main matrix of CEC [3]. In addition, we substantiated the processes of creating metal oxide composites (MOC) based on metals of the ferrum family (Fe, Co, Ni), which incorporate an oxide phase formed by refractory metals (Mo, W, V, Zr). It was proved [4]. that in the latter case, the coating takes place from complex electrolytes, which by their nature are true solutions, and the oxide phase, which is incorporated into the MOC composition, is formed as a result of incomplete cathodic reduction of oxometalates $(WO_4^2, MOQ_4^2, VO_4^{3-}...)$, i.e. there is an intermediate of the electrode reaction. The creation of MOC according to this principle solves the problem of stabilizing the electrolyte solution, and the control of the content of the second phase is carried out by using controlled electrolysis and varying its parameters. It was on this basis that we created a series of metal oxide nanocomposites.

Binary and ternary MOCs of the composition M1-M2-MOx were synthesized in the Fe-Mo, Fe-W, Co-Mo, Fe-Co-Mo, Co-Mo-W, Co-Mo-Zr, Co-W-Zr systems. Coatings were formed from aqueous solutions in the presence of ligands in which citrate and/or diphosphate ions were used. Electrolysis was carried out both with a unipolar current and with the use of a pulse mode with a current density in the range of 1-10 A/dm² and variation of the pulse-pause duration ratio. A quantitative composition of the coatings was defined using the X-ray fluorescent method and the portable spectrometer "SPRUT" with a relative standard deviation of 10^{-3} to 10^{-2} . The obtained data were verified by the electrodisperse X-ray spectroscopy using the electron-probe microanalyzer Oxford INCA Energy 350. Coatings with a thickness of 25-30µm were tested in corrosive environments with different pH levels by measuring polarization dependences and/or electrode impedance spectra. For these purposes the hardware complex based on the Versa STAT 4 potentiostat was used.

According to the results of systematic studies, coatings were ranked according to the influence of alloy-forming components, their content and ratio in the composition of MOS on the parameters of chemical resistance - the potential and current density of corrosion with the determination of the depth indicator of the corrosion rate.

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FORMATION AND ELECTROCHEMICAL PROPERTIES OF CHROMOXIDE COATINGS OBTAINED BY NON-STATIONARY ELECTROLYSIS

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AISI 304 steel is an important structural material due to its properties such as excellent strength, ductility and corrosion resistance. However, the wear resistance of stainless steel is quite low. In addition, it is well known that this material is extremely sensitive to pitting corrosion under certain conditions. Chrome oxide coatings formed on stainless steel allow to expand the functional properties of the surface and increase the range of its applications [1-2]. This is due to the special properties of this metal, including its resistance to heat, wear, corrosion, abrasion and low friction. Despite the fact that researchers are looking for some alternatives to hexavalent chromium, today chromium oxide coatings are still necessary for very demanding industries [2].

Electrochemical deposition using non-stationary current regimes can be an effective method of improving the characteristics of metal oxide coatings, compared with galvanostatic mode [3]. The ability to control the parameters of the electrochemical process allows to influence the structural (crystal structure, crystal size, cracking, morphology) and physical properties (appearance, hardness, wettability, corrosion resistance) of the obtained coatings, their deposition rate [3-4].

The aim of this work is to study the electrochemical properties of chromium oxide coatings on AISI 304 steel obtained by non-stationary electrolysis.

The formation of oxide coatings was carried out in pulsed modes using unipolar and bipolar current forms in a two-electrode cell with a system of continuous stirring at $j_k = 100 \text{ A/dm}^2$, $j_a = 25 \text{ A} / \text{dm}^2$, pulse duration 0.25-1 sec, pause duration 0.25 -1 sec. The process was performed from the electrolyte [1] at a temperature of 25 °C.

The morphology and elemental composition of the obtained coatings were examined using a ZEISS EVO 40XVP scanning electron microscope with INCA Energy 350 microanalysis system. The results indicate that the coatings have a fine crystalline structure and consist mainly of elements such as oxygen and chromium.

Impedance spectroscopy was used to study the structure of the synthesized coatings. Measurements were performed in 3% NaCl using a system of potentiostat IPC-pro and a frequency analyzer FRA in the range of 0.03 Hz - 50 kHz [2]. The obtained dependences of the parameters of the system "metal-oxide-electrolyte" indicate that the formed metal oxide coatings have fewer defects compared to the non-oxidized sample, as evidenced by the relatively low value of $tg\delta_0$.

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FORMATION OF PEO COATING ON Ti-6AI-4V ALLOY WITH HARDENED DIFFUSION LAYER

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The protective and stable oxides are able to provide good corrosion resistance of titanium alloys in the physiological environment of the human body. Plasma electrolytic oxidation (PEO) is an effective method to control the thickness, composition and topography of the oxide film, and can be used to modify the surface of titanium implants. This method of surface engineering allows to form uniform coatings on substrates with relatively complex geometries in environmentally friendly electrolytes.

However, it should be considered that the disadvantage of titanium alloys is the high tendency to contact seizure that prevents their use for the manufacture of endoprosthetic joint replacement (hip and knee endoprostheses). Therefore, it is efficiently to use the method of thermodiffusion saturation from controlled gas atmosphere, which is based on the formation of hardened gradient diffusion layer, which provides high adhesion between the coating and the metal matrix.

Thus, the combination of methods of thermodiffusion saturation and PEO can open new opportunities in the formation of functional coatings on titanium alloys for medical purposes. Therefore, the aim of this work is to evaluate the corrosion resistance of PEO coating on Ti-6Al-4V alloy with pre-formed oxygen diffusion layer in Ringer's solution at 37°C.

The oxidation of the alloy was carried out in O_2 +Ar (0,02 Pa) at 750°C for 5 h. The subsequent PEO was performed in 0.1 M H₃PO₄ at 20 V for 5 min. The current density was 100 mA/cm².

It was determined that the PEO coating formed on the pre-oxygen-saturated surface of Ti-6Al-4V alloy provides higher value of OCP in Ringer's solution (Fig. 1 a), which leading to lower thermodynamic tendency towards corrosion. It was shown that the anodic dissolution of the coating is occurred at at lower currents (Fig. 1 b). It was established that after potentiodynamic polarization the oxygen content on the surface of the PEO coating increases from 25.91 at. % to 29.49 at. %, i.e. it is observed the additional oxidation of the surface, which confirms its higher corrosion resistance in the physiological environment.



Fig. 1. Open circuit potential vs time curves (a) and polarization curves (b) of Ti-6Al-4V alloy after thermodiffusion saturation by oxygen (1) and subsequent PEO (2) in Ringer's solution at 37°C.

ADVANTAGES OF USING THE EXOTHERMAL ADDITION CuO-AL AS A COMPONENT OF CORE FILLER IN FLUX-CORED WIRES FOR HARDFACING <u>Trembach B.</u>¹, Holovchuk M.², Trembach I.³, Subbotina V.⁴, Knyazev S.⁴ ¹PJSC "Novokramatorsky Mashinostroitelny Zavod" ²Karpenko Physico-Mechanical Institute of the NAS of Ukraine ³Donbas State Engineering Academy ⁴National Technical University «Kharkiv Polytechnic Institute» btrembach89@gmail.com

Different hardfacing technologies are used to increase the service life of the parts and working devices of mining machines in the mining industry. During the recent years, more attention was focused on the flux-cored wire, having many advantages, such as high welding efficiency and good weldability. The global energy crisis requires modern science to develop new welding materials providing high strength and satisfactory impact strength of the metal subject to hardfacing, and to ensure high energy efficiency and good workability.

An interest to the use of exothermic additions in the welding materials composition during the recent years increases. The main advantage of exothermal additions introducing is to ensure uniform melting of the metal shell and flux cored wire filler and to reduce the need for electrical energy due to the heat generated during exothermic reaction. Various systems of exothermic additions are used nowadays. CuO-Al exothermic addition has significant advantages among them. Studies by Trembach and co-authors showed the significant benefits (productivity and energy efficiency increasing, the weld bead morphology improvement etc.), using the CuO-Al system as an exothermic addition. However, it is important to increase the resistance to abrasive, corrosive and tribocorrosion wear of the materials used for hardening by hardfacing. Boron-containing alloys Fe-C-Cr-B-X (where X alloying element) are the mostly widespread for the wear resistance increasing. However, these alloys are characterized by low ductility (tendency to cracking) and low corrosion resistance, despite the high chromium content. As well as the use of CuO-Al system exothermic addition provides alloying of the metal with copper, it is interesting to study its influence on the hardfacing metal properties. It is proved that it is easy to weld the steel, strengthened by precipitaion with a high content of Cu, due to the good balance of strength and ductility. The aim of the work was to study the effect of partial replacement of chromium (Cr) with copper (Cu) in the Fe-C-Cr-B-Ti alloy on the resistance to abrasive and corrosive wearing. Experimental studies were made to compare an influence of exothermal addition introduction in the flux cored wire filler on the structure, phase composition, mechanical properties of the deposited metal and abrasive wear resistance. Deposited metal microstructure made by standard FCAW-S with a high chromium content consists of carbide eutectic and borides grid with ferrite inclusions. Carbide eutectic consists of chromium carbides Cr_7C_3 , residual austenite and cementite. In turn, with the partial replacement of chromium with copper (by 8 wt.%), the microstructure of the weld metal changed. It is a grid of boride eutectic (M2B and ferrite) with inclusions of titanium carbonitrides (Ti(C,N) connected with the matrix. The matrix of deposited metal is an austenite with local secgregations of carboborides M₃(C, B). The hardfacing process and the study of mechanical properties showed a positive effect of chromium with copper replacement in the amount of 8 wt.% in the Fe-C-Cr-B-Ti alloy. Formation of hot cracks was not observed in the deposited metal. Elastic properties were increasied despite the microstructure change. A comparison of the corrosion current density Icorr and the electrode potential of the corrosion Ecorr, measured for samples deposited FCAW-SS-140Cr13Si1MnBTi and FCAW-SE-110Cr4Cu7TiVBA1 (with an exothermic additive), showed an increase in flowability to corrosion. Thus, these corrosion current density values Icorr decreased from 1.525 mA/cm² to 0.166 mA/cm², and E_{corr} increased from 0.359 mV to 0.631 mV. That is, a significant increase in corrosion resistance was observed. Thus, the use of exothermic additions represents a high efficiency method for deposited metal hardfacing, technological and operational characteristics improvement.
CORROSION BEHAVIOR OF ELECTROLYTIC CoRe ALLOY AT LONG-TERM EXPOSURE IN AN ALKALINE MEDIA

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Electrolytic coatings with rhenium alloys are a promising electrocatalytically active material for use in electrolyzers for producing hydrogen from alkaline solutions. Corrosive behavior of electrocatalysts in an aggressive environment, not only during operation (at the cathode potential), but also during idle periods, is an important technological aspect.

The electrodeposition of CoRe alloys was carried out in a citrate-pyrophosphate electrolyte of the following composition, mol·1⁻¹: CoSO₄ - 0.1; KReO₄ - 0.01; Na₃C₆H₅O₇ - 0.2; K₄P₂O₇ - 0.2; at a current density of 20 mA·cm⁻² and a temperature of 50°C in the galvanostatic mode using a constant current source LIPS-35. A copper plate with an area of 1 cm² was used as the working electrode and platinum was the anode. Corrosion tests were carried out by impedance spectroscopy in the frequency range of 5.0 kHz – 10 mHz (voltage was applied sinusoidally with an amplitude of 5 mV) while keeping the sample in a solution of 1.0 mol·1⁻¹ KOH at a temperature of 25°C for 10 days. The morphology and chemical composition of the samples were studied using a JSM-6700F field emission scanning electron microscope equipped with a JED-2300 energy dispersive spectrometer (JEOL).

The resulting coating contains 22.3 at.% rhenium, is uniform and shiny, while the study of micrographs shows that the alloy is stressed and has microcracks, which is a characteristic feature and problem of deposition of refractory metals alloys with iron subgroup metals.

Impedance measurements taken once a day show the change in the corrosion resistance of the coating from the initial value of $1.05 \text{ k}\Omega \cdot \text{cm}^2$ in accordance with the equivalent circuit R1(Q1R2); then - the formation of the initial oxide layer during the first day, the resistance of which was 37.7 k $\Omega \cdot \text{cm}^2$ in accordance with the equivalent circuit R1(Q1(R2(Q2R3))); the course of the corrosion process in the pores and the compaction of the oxide layer with a corrosion resistance of 25.6 k $\Omega \cdot \text{cm}^2$ according to the scheme R1(Q1R2)(Q2R3); stabilization of the process and the absence of significant changes after six days and beyond - the corrosion resistance of the protective oxide layer was 26.2 - 34.9 kOhm $\cdot \text{cm}^2$.

When analyzing the chemical composition of the sample after corrosion testing, one should take into account the features of various areas - the surface of the coating and microcracks. In both cases, the formation of an oxide phase is observed, and, in microcracks, the formation of agglomerates $1-2 \mu m$ in size with a composition of 76.4 at.% - O, 0.25 at.% - Re, the rest is cobalt, and on the plane - a fibrous structure, the composition of which is because of the limitations of the EDX method, it can only be shown approximately (57.6 at.% - O, 4.9 at.% - Re, the rest - cobalt). The combination of data from impedance spectroscopy and EDX analysis allows us to conclude that the corrosion process proceeds until the coating surface is filled with an oxide phase, which blocks further dissolution of metals and consists mainly of cobalt oxide.

ELECTROCHEMICAL BEHAVIOR OF THE MA5 MAGNESIUM ALLOY WITH ALUMINIUM COATINGS SPRAYED BY DIFFERENT METHODS AFTER THEIR PLASMA ELECTROLYTIC TREATMENT

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Plasma-electrolytic oxidation (PEO) is a relatively new type of surface treatment and strengthening of metal materials, which makes it possible to obtain multifunctional oxide ceramic coatings with a unique set of properties, including wear-, corrosion-, heat-resistant, electrical insulating and decorative coatings.

The operational properties of oxide ceramic coatings on aluminum alloys have a significant advantage compared to PEO coatings on Mg, Ti, Zr, Ta alloys. Sputtering of coatings from aluminum alloys on magnesium alloys with subsequent PEO treatment makes it possible to obtain oxide ceramic coatings with properties at the level of PEO coatings on aluminum alloys. Using such a complex approach allows to create oxide ceramic coatings on other alloys that are not amenable to PEO treatment, for example, on steels and cast irons. However, an important characteristic affecting their corrosion resistance is porosity, which depends on the spraying method.

The purpose of the work was to find out the behaviour of magnesium alloy MA5 with aluminum coatings sprayed by different methods followed by plasma electrolytic treatment.

Aluminum coatings were deposited on a substrate made of magnesium alloy MA5 (0.3 wt.% Mn, 7.8 wt.% Al, 0.4 wt.% Zn, the rest Mg) by detonation and thermo-vacuum methods.

The structure and properties of aluminum coatings largely depend on the method of their application. The structure of vacuum coatings (thermo-vacuum deposition) is similar to the structure of annealed aluminum. The structure of coatings formed by detonation spraying of aluminum alloy AMg3 powder is due to the presence of aluminum oxides. Such coatings have higher hardness.

The characteristics of corrosion processes were investigated in the potentiodynamic mode and it was established that the corrosion resistance of the investigated coatings significantly exceeds the MA5 alloy ($E_{corr} = -1.584$ V; $i_{corr} = 420 \cdot 10^{-3}$ mA/cm2). It was found that the corrosion resistance of the detonation coating is twice as high as that of the MA5 alloy, but the layer synthesized on the PEO coating neutralizes this effect. This is due to the growth of the PEO coating through the sprayed coating to the base and the presence of through-pores in it. This eventually causes peeling of such a combined coating. The opposite electrochemical behaviour was observed on the surface of the thermo-vacuum sprayed coating without and with the presence of a PEO coating on it. In this case, the corrosion currents are 25 times and 2 orders of magnitude smaller, respectively. Such a significant difference in the corrosion resistance of aluminum coatings is due to their porosity and structural defects, which is due to the peculiarities of the technological process.

ALTERNATIVE SYNTHESIS METHODS OF NANOCOMPOSITES BASED ON IRON AND TITANIUM OXIDES DOPED WITH AURUM

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The increasing interest in nanosized composite materials synthesis is associated with the expansion of their practical application due to the combination of the physicochemical properties of their constituent initial components. In particular, the iron and titanium oxides doping with the gold makes the obtaining composites with magnetic, photocatalytic, optical (plasmon) properties, biocompatibility, and activity in biological media possible [1]. At the same time, an important aspect that affects on the properties of such nanostructures is the choice of a synthesis method that makes it possible to prevent the entry of accompanying components of solutions, for example, anions of inorganic salts, into the structure of nanocomposites. In this case, a perspective way to solve the chemically pure materials obtaining problem can be the adaptation of corrosion processes as a source of the aqueous form of iron [2] or the usage of organic precursors, the destruction of which can occur at elevated temperatures [3].

The aim of this work is to characterize Fe_3O_4 &Au and TiO_2 &Au nanocomposites that are obtained, respectively, by the method of rotational corrosion dispersion (RCD) and thermal destruction of titanium tetraisopropoxide in the presence of a HAuCl₄ solution.

According to the XRD analysis, thermal decomposition of titanium (IV) isopropoxide in the presence of Au^{3+} (T = 600°C) leads to the formation of anatase and gold phases (Fig. 1a). The composition of nanopowders formed by RCD methods includes magnetite and gold particles. The air contact of such structures results in the oxidation of uncoated areas of the magnetite surface and the formation of lepidocrocite admixture (Fig. 1b). According to the EDS data, in both cases, the inclusion of gold atoms into the structure of the oxide core takes place. Fig. 1c shows the SEM image of TiO₂&Au composite particles. The composite structure is characterized by uniformity and nanometer dimensions; the CSR of anatase, which forms the core of the composite, is 16 nm. Similar structures were obtained by the RCD in the presence of gold aquaforms, CSR of magnetite core was 21 nm [2].



Fig. 1. The XRD patterns of the composite structures: a - TiO_2 &Au, b - Fe_3O_4 &Au, and c - the SEM image of TiO_2 &Au nanocomposite particles. Numbers correspond to: 1 - TiO_2 , 2 - γ -FeOOH, 3 - Fe₃O₄, 4 - Au⁰.

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Inhibitors and anti-corrosion pigments

SHIFTING THE PARADIGM OF CORROSION INHIBITION RESEARCH, SHOWCASE MAGNESIUM

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For more than a decade, the field of corrosion inhibition has been under pressure due to an urgent need to find environmentally friendly alternatives to carcinogenic chromates. The traditional way of identifying corrosion inhibitors typically involves empirical preselection of one to three candidate compounds followed by their intensive characterization. Although this route offers important insights into the inhibition mechanism, it rarely provides optimal inhibition performance. The lead inhibitors are rarely explored further, e.g., as additives or pigments distributed in protective coatings. Additionally, this low throughput testing route is time-, labour-, and resource-intensive. Conspicuously, testing conditions such as specific alloy composition and its treatment history, surface condition, testing electrolyte, and inhibitor concentration are typically not conducive to direct comparison of multiple studies. Years of experimenting result only in incremental improvement.

By leveraging reliable high-throughput testing and machine learning methods used in other areas of science and technology, we aim to accelerate the exploration of the vast space of small organic chemical compounds by combining accelerated testing with computational modelling.

The lecture will present the results of a systematic search for magnesium corrosion inhibitors by traditional experimental and computational machine learning methods. The experimental database, the largest up to date, [1] enabled development of predictive machine learning models of quantitative structure-inhibition relationships. Subsequent experimental validation demonstrated the high potential of computational methods for rapid, accurate, and cost-effective discovery of corrosion inhibitors [2, 3]. This approach also fast tracks the search for efficient, alloy specific corrosion inhibitors and can be used for testing coated substrates, thus bringing selected inhibitors closer to the application phase.

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ANTI-CORROSION PIGMENTS FOR PAINTS BASED ON ALUMINOSILICATE NANOCONTAINERS

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Today, the most effective inhibiting pigments for paints are chromates, but they are toxic, pollute the environment and are difficult to dispose of. There is an urgent need to find environmentally friendly materials to replace them. Known zinc-phosphate pigments have insufficient protective properties due to their low solubility in the environment. The main idea of the research is to develop scientific approaches to the creation of new anti-corrosion pigments, in which zeolites will act as nanocontainers for intercalation of the inhibitory phase based on phosphates of zinc and/or alkaline earth metals, as well as source of cations – cathodic corrosion inhibitors.

The purpose of the work is to create scientific bases for the technology of synthesis of highly effective complex corrosion inhibitors with a combination of nanoscale component and aluminosilicate matrix in one structure, to study the effectiveness of their protective action on metal, and development of inhibitory compositions for organic coatings.

Research methods – electrochemical impedance spectroscopy, potentiodynamic polarization, gravimetry, SEM, EDX analysis, XRD-analysis, mechanochemical synthesis, thermal analysis, photometry, quantum chemical methods PM7 and DFT.

The conditions and modes of obtaining complex inhibitory pigments by modifying zeolite Na-A with calcium, zinc and manganese phosphates by mechanochemical method were investigated. Correlation dependences between structure, chemical composition, dispersion of pigments and their electronic structure, specific surface area and desorption characteristics in environment are obtained. Mechanisms and regularities of inhibition of corrosion processes on the surface of steel and aluminum alloy by pigments are established. It is shown that the inhibitory efficiency of pigments depends on the quantitative ratio of their components, production conditions, chemical composition and nature of the protected metal [1-3]. The relationship between the electronic characteristics of aluminosilicate nanocontainers, their interaction with nanosized phosphates and the anti-corrosion activity of the synthesized pigments has been established. The obtained pigments can be promising inhibitory components of paint primers for the protection of aluminum alloys and steels in industrial atmosphere.

Acknowledgments

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CORROSION INHIBITION OF ALUMINUM ALLOY IN CHLORIDE SOLUTION BY COMPOSITION BASED ON NATURAL BIOPOLYMER

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Alloys of the Al–Cu–Mg system are widely used in various industries. Under normal conditions, the surface of duralumin is covered with an oxide film, which to a certain extent protects the alloy from corrosion in many neutral and weakly acidic environments, as well as in atmospheric conditions. However, it is more defective on the surface of intermetallic inclusions, which often causes local corrosion of the metal.

It is known [1] that organic compounds obtained from vegetable raw materials are effective corrosion inhibitors of aluminium and its alloys. Guar gum (GG) is a natural water-soluble nonionic polysaccharide extracted from the seeds of the guar plant *Cyamopsis tetragonolobus* of the legume family. It was previously shown [2] that in a chloride environment, the effectiveness of metal corrosion inhibition by this biopolymer is insufficient. Therefore, in this work, an attempt was made to strengthen the protective effect of GG on an aluminium alloy in a neutral chloride solution by combining it in one composition with the potassium salt of sorbic acid (PS).

In the study, samples of D16T aluminium alloy with a working surface area of 1 cm^2 were used. A 0.1% sodium chloride solution served as a corrosive medium, to which GG and PS were added, both as individual substances and their compositions with a total concentration of 2 g/l. Impedance spectra were recorded on a Gill AC potentiostat.



Fig. 1 – Frequency dependences of the impedance modulus of the D16T alloy after 3 h (a) and 24 h (b) exposure in: 1) 0.1% NaCl; 2) +2 g/l GG; 3) +2 g/l PS;
4) GG+PS (1:1); 5) GG+PS (1:3); 6) GG+PS (3:1)

The obtained results showed (Fig. 1 *a*) that the value of the impedance modulus at a frequency of 0.1 Hz of alloy samples after 3-hour exposure in a chloride solution with the addition of 2 g/l of PS is the lowest $(9.3 \cdot 103 \ \Omega \cdot cm^2)$. With simultaneous use for inhibiting the corrosion solution of GG and PS, with different ratios of components in the composition, the impedance modulus of the aluminium alloy increases by an order of magnitude. After 24 h (Fig. 1*b*) of exposure, the values of the impedance modulus of the alloy in all solutions decrease in several times. However, the ratio of the protective properties of the composition of GG + PS (1:1) in comparison with other solutions is preserved. The protective effect of the composition can be explained by the synergistic interaction of its two components. It is obvious that with the simultaneous introduction of GG and PS into the solution, an adsorption film is formed on the surface of the alloy, which is more perfect and covers most of the electrochemically active areas.

Thus, it was established that the effectiveness of corrosion inhibition of aluminium alloy by guar gum in a 0.1% NaCl solution is significantly increased by its combination in one composition with potassium sorbate. The optimal ratio of the components of the composition, at which the value of the charge transfer resistance is maximal and corresponds to the highest corrosion resistance of the aluminium alloy, is 1:1.

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POLYVINYLPYRROLIDONE PROTECTION PROPERTIES FOR CARBON STEEL IN NACE MEDIUM AND MODEL RESERVOIR WATER

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The oil and gas industry is one of the largest consumers of water, especially in the case of low flow wells. At the same time, the need to use reliable inhibitory equipment protection is increasing. In this regard, the development of innovative formulations of environmentally safe corrosion inhibitors is an urgent and promising task. When drilling for oil and gas, ecosafe polymers are used as emulsifiers and dispersants, such as carboxyl methyl cellulose, polyvinylpyrrolidone, etc. [1]. The surface activity of such compounds allowed us to assume the possibility of using them as corrosion inhibitors in NACE environments and model reservoir waters.

Polyvinylpyrrolidone (PP) of two molecular weights of 12600 and 28000 at three concentrations 0.2, 0.5 and 1.0 g/dm³ influence on the corrosion rate of steel 20 in the NACE environment and model reservoir water was investigated. It was established that the maximum inhibition of the steel corrosion rate is observed at a PP concentration of 0.5 g/dm³ in both mediums. A further increase in the concentration of the inhibitor to 1.0 g/dm³ reduces the degree of protection more significantly in the NACE solution than in reservoir water (Fig. 1). PP with a higher molecular weight exhibits higher protective properties, which is characteristic of polymers capable of adsorbing both linearly and in a ball.

PP in reservoir water shifts the corrosion potential of steel 20 towards more negative values, although this shift is not synchronized with the change in concentration. In the NACE solution, there is a certain refinement of the potential under the influence of higher molecular PP. The determined densities of corrosion currents correlate with gravimetric data and the nature of the polarization curves indicates the mixed nature of the protective effect of PP. In the future, PP can be used as component of inhibitor compositions.



Fig. 1. Influence of concentration and molecular weight of PP (■ - 12600; ■ - 28000) on protection degree of 20 steel in solutions: *a*) NACE; *δ*) model precipitate water.

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THE CORROSION RESISTANCE OF ALUMINUM ALLOY IN MEDIUM INHIBITED_BY ENVIRONMENTALLY FRIENDLY PIGMENTS Danyliak M.-O.¹, Khlopyk O.¹, Zin I.^{1,2} ¹Karpenko Physico-Mechanical Institute of the NAS of Ukraine ²Lviv Polytechnic National University Lviv danyliak-olena@ukr.net

The corrosion resistance of D16T alloy in corrosion solution with the addition of zeolite/Ca(H₂PO₄)₂ and zeolite/Zn(H₂PO₄)₂ inhibiting pigments was studied by gravimetric method (see table 1). Sample preparation, removal of corrosion products and formulas for calculating the corrosion rate K_m and the degree of inhibitory protection Z are given in [1]. The pigments were synthesized by mechanochemical method at a ratio of zeolite to calcium and zinc dihydrogen phosphates of 1:3 and 1:1, respectively.

The corrosion rate of aluminum alloy in 0.1% NaCl solution due to the use of zeolite/phosphate pigments after 10 days of exposure decreased by about 6 times, which indicates their high anti-corrosion efficiency. As the exposure time of the samples in a corrosive medium increases to 20 days, the K_m of the alloy decreases due to the combined action of inhibitors and the formation of a layer of corrosion products on its surface.

Table 1. Corrosion rate $(K_m, g/cr$	$n^{2}\cdot h$) and protection degree (Z, %) of aluminum a	lloy D16T
	in 0.1% NaCl solution	

	Exposure time					
Medium	10 days		20 days			
	K_m	Ζ	K_m	Ζ		
0,1% NaCl solution	$2,86 \cdot 10^{-6}$	-	$3,76 \cdot 10^{-6}$	-		
0,1% NaCl solution + zeolite/Ca(H ₂ PO ₄) ₂	$4,88 \cdot 10^{-7}$	82,9	$2,16\cdot 10^{-7}$	94,3		
0,1% NaCl solution + zeolite/Zn(H ₂ PO ₄) ₂	$4,53 \cdot 10^{-7}$	84,2	3,91·10 ⁻⁷	89,6		



Fig. 1. Photos of the aluminum alloy surface after 20 days of exposure in 0,1% NaCl solution: a - uninhibited; b - inhibited with zeolite/Ca(H₂PO₄)₂; c - inhibited with zeolite/Zn(H₂PO₄)₂

Thus, the corrosion rate of D16T alloy is significantly reduced in the extracts of synthesized inhibiting pigments, which is apparently due to the adsorption of inhibitory ions on the alloy surface, followed by the formation of a protective film.

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CORROSION INHIBITION OF THE STEEL BY ENVIROMENTAL FRIENDLY SALT OF CARBOXYLIC ACID

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Corrosion inhibitors are one of the most practical and cost-effective methods of anticorrosion protection. The aim of work was to study the corrosion inhibition of steel by sodium citrate - sodium salt of citric acid. The corrosion resistance of $09\Gamma 2C$ steel was investigated by electrochemical impedance spectroscopy (EIS) method. An equivalent electrical circuit, which included solution resistance R_s , charge transfer resistance R_{ct} and double layer capacitance as constant phase element (CPE), was used to calculate the components of the impedance (Figure 1).



It was established that the value of the charge transfer resistance of the steel sample increases with an increase in the content of sodium citrate in the solution and at a concentration of 2.5 g/l exceeded this indicator by 3 times compared to an uninhibited solution of 0.1% NaCl. This result can be associated with the adsorption of sodium citrate on the steel surface due to its hydroxyl and carboxyl functional groups. The introduction of sodium citrate as a corrosion inhibitor into the corrosive solution contributes to the decrease of the CPE, which corresponds to the double layer capacitance of steel. The parameter n of CPE characterizes the degree of geometric and energy heterogeneity of the metal surface. A decrease in the value of n due to an increase in the duration of exposure to 24 h indicates a change in surface heterogeneity, which can probably be associated with the formation of both a protective film and a partial accumulation of corrosion products on the steel surface (Table 1).

different concentrations of social entrate										
C, g/l	R _s ,Ohms·cm ²		R_{ct} , Ohms·cm ²		CPE, s^n /Ohms·cm ²		n			
	3 hours	24 hours	3 hours 24 hours		3 hours	24 hours	3 hours	24 hours		
0	206	192	866	836	$1.79 \cdot 10^{-3}$	$2.06 \cdot 10^{-3}$	0.71	0.66		
1.0	155	164	1540	1257	$0.25 \cdot 10^{-3}$	$1.61 \cdot 10^{-3}$	0.73	0.55		
1.5	122	133	2323	1313	$0.18 \cdot 10^{-3}$	$1.70 \cdot 10^{-3}$	0.79	0.64		
2.0	114	116	2269	1694	$0.29 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.74	0.60		
2.5	99	110	2677	1859	$0.39 \cdot 10^{-3}$	$1.20 \cdot 10^{-3}$	0.73	0.65		

Table 1. Impedance characteristics of 09F2C steel after exposure in 0.1% NaCl solution with different concentrations of sodium citrate

Sodium citrate is an environmental friendly substance and may be promising in creating inhibitory compositions for the anti-corrosioin protection of mild carbon steels in neutral chloride-containing environments.

ANTI-CORROSION PROPERTIES OF COMPOSITE INHIBITING PIGMENT BASED ON NATURAL CALCIUM SILICATE AND ZINC MONOPHOSPHATE <u>Khlopyk O.¹</u>, Zin I.^{1, 2}, Bilyy L.¹, Duriagina Z.², Datsko B.¹

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It is promising to obtain composite anti-corrosion pigments of the "inert core + active shell" type. This allows to reduce their cost and ensures high anti-corrosion efficiency due to the formation of an active inhibitory shell on a cheap sparingly soluble core. In order to obtain a composite inhibitory pigment, a mechanochemical modification of wollastonite with zinc monophosphate was used to form the "calcium silicate core - phosphate shell" system. The purpose of the study was to establish the inhibitory efficiency of the new composite pigment in relation to the corrosion of aluminum alloy.

Samples of D16T aluminum alloy were used in the study. A 0.1% NaCl solution served as a corrosive medium, to which wollastonite, zinc monophosphate, their simple mixture, and the composite pigment "wollastonite/phosphate" were added at a concentration of 1 g/l. The composite pigment was obtained by mechanochemical modification of wollastonite with zinc monophosphate in a high-energy Retsch PM100 planetary mill. The mass ratio in the grinding mixture between zinc dihydrogen phosphate and wollastonite was 1 to 3. Impedance spectra of the aluminum alloy were recorded on a VersaStat 3 potentiostat/galvanostat.

It was established (Fig. 1) that the value of the impedance modulus at a frequency of 0.1 Hz ($Z_{0.1}$) of alloy samples after a week of exposure in an uninhibited chloride solution is 2.0·10³ Ohms·cm², and when wollastonite or zinc monophosphate is added separately to the corrosive medium, it does not exceeds 9.0·10³ Ohms·cm². With the simultaneous introduction of both substances into the corrosive solution, $Z_{0.1}$ of the aluminum alloy increases to 2.0·10⁴ Ohms·cm². The greatest increase in the $Z_{0.1}$ parameter of the alloy is observed when the composite pigment "wollastonite/phosphate" is added to the chloride solution (Fig. 1). The increased protective effect of the composite can be explained by the interaction of a more active phosphate shell on the inert core compared to solid zinc orthophosphate.



Fig. 1. – Frequency dependences of the impedance module of an aluminum alloy after a week exposure: 1) 0.1% NaCl:

2) +1 g/l wollastonite; 3) +1 g/l zinc monophosphate; 4) +1 g/l of zinc monophosphate and wollastonite mixture at 3/1 mass ratio; 5) +1 g/l composite pigment "zinc monophosphate/wollastonite" at 1/3 mass ratio

According to data of electrochemical impedance spectroscopy, the new composite pigment has high protective properties, its characteristics are superior to a simple mixture of calcium silicate with zinc orthophosphate and it is promising for use in paint coatings.

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INVESTIGATION OF SORPTION CAPACITY OF SYNTHETIC ZEOLITE IN RELATION TO PHOSPHATES OF DIVALENT METALS

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Salt-modified zeolites are promising materials that can be used as anti-corrosion pigments in paints and varnishes [1, 2]. This is due to their high ion exchange and sorption properties, which gives the prospect of generating an inhibitor only when the corrosive environment comes to the metal surface, causing subfilm corrosion [3].

Energy dispersion analysis of phosphate-modified zeolites of metals for 60 and 120 min indicates intercalation into their structure of phosphorus and calcium, zinc and manganese (Table 1). It is shown that with increasing dispersion time from 60 to 120 min the Ca content increases slightly from ~ 8.82 to 8.88%, wt., While Zn and Mn decreases from ~ 10.32 to 9.92% and ~ 13, 87 to 12.15%, wt. in accordance. A similar trend with a time from 60 to 120 min is observed for the content of P. Therefore, the optimal time of dispersion is 60 min.

Table 1. Data from EDX analysis of modified zeolites with salts of $Ca(H_2PO_4)_2$, Zn $(H_2PO_4)_2$, Mn $(H_2PO_4)_2$.

	Chemical composition, %, mass									
	Na-A	Ca(H	$I_2PO_4)_2$	Zn(H ₂	$PO_4)_2$	$Mn(H_2PO_4)_2$ ·				
	120 min	60 min	120 min	60 min	60 min 120 min		120 min			
0	54,10	55,47	56,05	51,19	50,58	51,15	50,93			
Na	9,90	4,89	4,65	6,9	6,86	4,1	5,1			
Al	14,36	6,64 6,21		7,59	8,59	6,68	7,31			
Si	20,98	10,66	10,66 10,61		12,13	9,66	11,78			
Ca		8,82 8,88								
Mg		0,84 0,79								
Р		12,48	12,48 12,2		11,57	14,36	12,51			
Zn				10,32	9,92					
Mn						13,87	12,15			
Fe	0,65	0,2	0,61	0,34	0,35	0,18	0,22			

The results of photocolorimetric sorption characteristics of modified zeolites showed that the concentration of extracted phosphate ions in 0,1% NaCl increases in the range of Na-A/Zn(H₂PO₄)₂ – Na-A/Ca(H₂PO₄)₂ – Na-A/Mn(H₂PO₄)₂, which is associated with the formation of phosphate films of different chemical composition, which have different product of solubility $PS(Zn_3(PO_4)_2)=9,1\cdot10^{-33}$, $PS(Ca_3(PO_4)_2)=2,0\cdot10^{-29}$, $PS(Mn_3(PO_4)_2)=1,0\cdot10^{-25}$. Their maximum concentration is reached within 48 hours; after which it increases slightly. On the alloy D16T and steel 08G2S there are different dependences of the desorption of phosphate anions over time. This is due to differences in electrochemical characteristics.

Acknowledgments

This work was performed within the project $N_{2020.02/0063}$ "Synthesis and properties of new complex anti-corrosion pigments for paint coatings based on aluminosilicate nanocontainers" of the National Research Foundation of Ukraine.

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INHIBITION OF MICROBIAL STEEL CORROSION BY QUATERNARY SALTS OF IMIDAZOCHINOLINIUM

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A significant part of the corrosion damage to metal structures in many natural and industrial environments is caused by microbial corrosion. In particular, sulfate-reducing bacteria play a special role in accelerating metal corrosion. The metabolic activity of sulfatereducing bacteria as part of the corrosion-active group determines the intensity of the corrosion process on the metal surface. Heterocyclic compounds containing quaternary nitrogen, having a biocidal effect on sulfate-reducing bacteria, are promising inhibitors of microbial steel corrosion.

The aim of this paper is to study the process of microbial corrosion of low-carbon steel in the presence of imidazochinolinium quaternary salts. 2,3-diaryl-4,5-dihydro-imidazo[1,2alchinolinium-3 bromides were tested as biocides and inhibitors of microbial corrosion of low carbon steel induced by bacteria of strain Desulfovibrio sp. M 4.1. Sulfate-reducing bacteria of strain Desulfovibrio sp. M 4.1 were isolated from the sulfidogenic natural group of sandy soil formed in the ferrosphere adjacent to the surface of the gas pipeline, and identified by molecular biological methods. Antibacterial properties of bromides were identified by the method of agar diffusion using wells in agar, into which alcoholic solutions of the studied salts with a concentration of 0.25%, 0.5%, 1.0% were added. Gravimetric corrosion analysis was carried out in hermetic containers with samples of low-carbon steel St3ps in a sterile nutrient medium of Postgate "B", inoculated with bacteria of Desulfovibrio sp. M-4.1 strain. The number of sulfate-reducing bacteria cells in plankton and biofilm was determined by the tenfold dilution method when the appropriate cell suspension was seeded on Postgate nutrient medium "B". The number of cells was calculated using McCready tables, developed on the basis of methods of variational statistics. The sulfate-reducing activity of bacteria was defined.

It was established that sulfate-reducing bacteria of *Desulfovibrio* sp. M 4.1 strain are sensitive to 2,3-diaryl-4,5-dihydro-imidazo[1,2-a]chinolinium-3 bromides. Under the action of imidazochinolinium quaternary salts (concentration 1%), the inhibition zones of bacterial growth have the diameters of 25.7 - 45.5 mm. Quaternary salts of imidazochinolinium completely suppress the growth of sulfate-reducing bacteria of *Desulfovibrio* sp. M-4.1 strain in plankton and significantly affect the formation of biofilm (the number of cells decreases by 6-8 orders compared to the control sample) under conditions of microbial corrosion. Suppression of the sulfate-reducing bacteria of *Desulfovibrio* sp. M-4.1 is 84.6% - 92.4%. 2-(para-tolyl)-3-(41-methoxyphenyl)-4,5-dihydro-imidazo[1,2-a]chinolinium bromide demonstrated the best protective effect. This substance can be promising for further research as an inhibitor of microbial corrosion of low-carbon steel induced by sulfate-reducing bacteria.

ANTICORROSION AND BACTERICIDAL ACTION OF 9,10-DIHYDROANTHRACENE SALTS

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The totality of literature data on the study of the anticorrosion activity of organic compounds is convincing evidence that this scientific area has great reserves for expanding the scope of the use of heterocyclic compounds and their main functional derivatives, including 9,10-dihydroanthracene salts, as effective corrosion inhibitors.

The anticorrosion activity of salts was studied by the gravimetric method (10% HCl solution; t = 30 0 C; $\tau = 1$ h; C_{ing} = 0,5 g/l; reference - Ing "Donbass"). Identification of Steel 3 samples was carried out by X-ray fluorescence analysis, % wt.: Fe – 98,48034; Mn – 0,47359; Si – 0,40000; Cu – 0,30000; C – 0,2-0,3; Cr – 0,09226; Ni – 0,07321; P – 0,04300; S – 0,03724. The bactericidal effectiveness (environment - technical H₂O, meat-peptone agar; $\tau = 48$ h; t = 27 0 C; C_{ing} = 0,4 g/l) of salts was determined as the ratio of the number of microorganisms (colony counting method) in the control to the number of microorganisms in the sample with the inhibitor.

The anticorrosive and bactericidal action (table) of 9,10-dihydroanthracene salts was studied: 9,10-di-(*N*-pyridinium)-9,10-dihydroanthracene-dichloride hydrate (I), 9,10-di-(*N*-isoquinolinium)-9,10-dihydroanthracene-dichloride hydrate (II), 9,10-di-(*N*-methylmorphoinium)-9,10-dihydroanthracene-dichloride hydrate (III).

Protection	Structure of compound					
effectiveness, %			H ₃ C, + CI H - CI H - 25H.0			
	+ 1,5 H ₂ O + ci ⁻ I	+ CI- II				
Anticorrosion	97,9	98,8	98,3			
Bactericidal	94,6	96,7	89,4			

Table. Protective action of 9,10-dihydroanthracene salts

An analysis of the results showed that all the studied compounds are effective corrosion inhibitors of steel in an acidic environment and are superior to the industrial inhibitor "Donbass" (Z = 96,3%) in terms of protective effect. A definite dependence by influence of substituents at positions 9- and 10- dihydroanthracene is not observed.

Apparently, the protective effectiveness of substituted dihydroanthracene is related to their ability to restore the oxidized metal surface due to hydrogen which is formed during dehydrogenation. Compounds (I) - (III) are superior in biocidal activity to the inhibitor of biological fouling "Vazin" (at C = 0.4 g/l the effectiveness of the bactericidal action is 49.3%).

Moreover, 9,10-dihydroanthracene salts have a biocidal effect on all components of the industrial H_2O microflora (aerobic bacteria *Pseudomonas, Bacillus mycoides*, as well as sulfate-reducing bacteria) and may find application as inhibitors of steel biocorrosion in circulating water supply systems.

NEW ECOLOGICALLY SAFE NATURAL CORROSION INHIBITORS FOR STEEL PROTECTION

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A high concentration of sodium chloride in water can cause the destruction of metal products (pipelines, ships, etc.) as a result of corrosion cracking. Therefore, the aim of the work was to evaluate the corrosion resistance of steel st3 in 0.1% aqueous solution of NaCl at 25 and 50°C for 7 days, as well as the protective ability as rhamnolipid inhibitors (RL) and trehalose lipid (TL) surfactants obtained in Department of PhChFF InPOCC NAS of Ukraine; technical glycerin – a by-product in the technological process of obtaining biodiesel; ethyl-(ETS) and allylthiosulfonates (ATS) – synthetic analogues of garlic phytoncides, synthesized at the Department of TBASPB of the Lviv Polytechnic National University.

In Table 1 was shown the best results of using individual substances and compositions in various versions as corrosion inhibitors at a temperature of 20° C and 50° C in 0.1% NaCl aqueous solution, selected from the results of a wide range of studies.

-				
Nº	Variant	Corrosion rate, $K_m \times 10^{6-}$, g/cm ² ·h	Protection level, Z, %	Depth rate of corrosion, <i>P</i> , mm/year
1	Control, 20°C	4,17	-	0,0530
2	Control, 50°C	7,13	-	0,0908
3	RL 0,1 g/dm ³ +0,5 g/dm ³ Tween 2:1, 20°C	1,27	69	0,0161
4	RL 0,1 g/dm ³ +0,15 g/dm ³ Tween 2:3, 20°C	1,59	61	0,0203
5	TL 0,5 g/dm ³ +0,25 g/dm ³ ATS, 20°C	0,10	98	0,0012
6	TL 0,5 g/dm ³ +0,25 g/dm ³ ETS, 20°C	0,05	99	0,0006
7	RL 0,1 g/dm ³ +0,5 g/dm ³ Tween 2:1, 50°C	0,22	96	0,0028

Table 1.	Impact	on corrosio	n of stee	l st3 o	f selected	compositions	in 0.1%	6 NaCl
			auneone	coluti	on			

The analysis of the obtained results shows that the most effective protective properties relative to steel st3 from the studied options for the compositions of synthetic and biogenic surfactants at NaCl concentration of 0.1% and a temperature of 20°C are mixtures of RL with Tween-80 at a ratio of 2:1 and 2:3 (Table 1). When the temperature rises to 50°C, a mixture of RL with Tween-80 with a ratio of 2:1 has the preferred protective properties. For the studied compositions of RL with Tween-80 at a ratio of 2:1 and 2:3 (Table 1) and 2:1 and 2:3, a synergism of action was observed, which enhanced the protective properties of each individual component. It was shown that compositions of trehalose lipids with allylthiosulfonate and ethylthiosulfonate in a ratio of 0.5:0.25 g/dm³ protect steel st3 by 98% and 99%, respectively (Table 1).

Thus, the results of the conducted research testify to the possibility and perspective of using the compositions developed by us to protect metals from corrosion in mineralized water environments.

INFLUENCE OF CARBOXYLMETHYLCELLULOSE ON CORROSION-ELECTROCHEMICAL CHARACTERISTICS OF 20 STEEL IN NACE SOLUTIONS AND MODEL RESERVOIR WATER

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An urgent problem today is the development of effective ecological means of protecting the metal fund against corrosion and corrosive-mechanical destruction, in particular, the search and creation of "eco-friendly" corrosion inhibitors. Such inhibitors are promising substitutes for toxic reagents of pyridines, quinolines, chromates, etc. Solutions of carboxyl methyl cellulose (CMC) have emulsifying, dispersing properties, form films on the surface of metals, and can also slow down corrosion processes in some environments [1].

The study of the influence of the molecular weight of CMC and its concentration on the corrosion rate of medium-carbon steels showed the following. In the NACE solution during mixing, the corrosion rate of steel 20 at concentrations of 0.2 and 0.5 g/dm³ depends little on the molecular weight of CMC. The degree of protection is at the level of 52-54%. But at a concentration of 1.0 g/dm³ of CMC with M.m. 14800, the degree of protection is 10% higher than for CMC with M.m. 7000.



Fig. 1. Influence of concentration and molecular weight of CMC (■ - 7000; ■ - 14800) on protection degree of 20 steel in solutions: *a*) NACE; *δ*) model reservoir water.

In the model reservoir water, increasing the concentration of CMC increases the degree of protection, but the efficiency of a higher molecular weight product is lower than that of a low molecular weight product. Perhaps this is related to a change in the configuration of a long polymer chain, namely, folding into a globule. In general, the protective capacity of CMC in reservoir water is higher than in NACE solution.

Electrochemical studies have shown that CMC is a mixed action inhibitor. Shifting the potential towards more negative values, they inhibit both partial reactions with a greater influence on the cathodic process. At the same time, corrosion currents are reduced by an order of magnitude. The obtained electrochemical indicators are correlated with the results of gravimetric tests.

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A NEW INSIGHT INTO CORROSION INHIBITION MECHANISM OF STEEL IN NEUTRAL SOLUTION BY "GREEN" PLANT EXTRACT: EXPERIMENTAL AND THEORETICAL APPROACH

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A large number of mechanisms were anticipated for steel in neutral medium. In the literature of recent years 2018-2021, more and more studies have begun to appear, where the authors proved that the process of inhibition of plant extracts is more complex, phased with chemical transformation of the component composition of the extract in solution and/or on the metal surface this is in fact a modern and up-to-date view of the mechanism of inhibitory action. For the first time, grape, apricot, peach and tomato pomace extracts, obtained by mixture of solvent as corrosion inhibitor in neutral media of 0.5 M NaCl solution was found. The results indicated that the green" plant extract act as "pro-inhibitor" corrosion of the steel in neutral solution. This behavior of the grape, apricot, peach and tomato pomace extracts in water solution can be explained by the fact that due to the multicomponent composition of plant extract organic compounds in aqueous solution are able to:

-To formation of condensation reaction products of anthocyanins and flavan-3-ol with/or without aldehydes (Flavanol-anthocyanin adducts);

- To formation of adducts of transformation (polymerization) of flavan-3-ol and aldehydes (flavanol-aldehydes adduct).

The main compounds of the extracts during 48 hours polymerize to form waterinsoluble compounds, such as catechin-furfuraldehyde dimer, catechin-syringaldehyde dimer, procyanidin B3-furfuraldehyde and cyanidin 3-O-glucoside furfuryl-catechin adduct were formed. The polymerization products have much more carbon atoms in the skeletal structure, arranged in an aromatic pattern, plus some hydroxyl groups and additional of aromatic groups. Such structures of compounds have a large ability of being strongly bonded to metal surfaces via oxygen heteroatom and π - π interactions. Quantum-chemical calculations were used to predict the adsorption/inhibition properties of some of the main compounds of the extract and compounds formed as a result of chemical conversion (Fig.). This work is helpful to contributes to enlarge the state of the art interpretation/explanation understanding mechanism of action exactly of green corrosion inhibitors in neutral solution.





Catechin- syringaldehyde trimer

Cyanidin 3-O-glucoside furfuryl-catechin

Fig. The ESP distribution of the molecules

MULTIFUNCTIONAL INHIBITORY COMPOSITIONS BASED ON "GREEN" ORGANIC COMPOUNDS AND ORGANOSILANE

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Multifunctional combinational corrosion inhibitors of steel based on extracts of plant raw materials and organosilane 3-aminopropyltriethoxysilane have been developed, which provide a synergistic effect of anticorrosive action in corrosive-aggressive water and air environments (Z = 99%). Corrosion-electrochemical and IR spectral studies (Fig. 1.) in combination with atomic force and scanning electron microscopy with EDX surface analysis showed that the synergistic effect of increasing the inhibitory properties of plant extracts in corrosive-aggressive air and water-salt environments is possible due to the introduction of organosilane (Fig. 2.). It was found that the increase in inhibitory efficacy with the combined action of combinations of plant extracts with 3-aminopropyltriethoxysilane occurs due to chemisorption processes with the formation of siloxane (Si-O-Si) (Si-OC) and metalsiloxane (Si-O-Fe) which promotes the formation on the metal surface of a polymer-like film consisting of molecules of plant extract/compounds, their chemical transformation and the products of their copolymerization with organosilane.



Fig. 1. FT-IR spectra displayed on the surface of the carbon steel, the treated volatile compounds of the plant extracts +APTES (a) and in the neutral solution (b)



Fig. 2. SEM images of the steel surface after 24 and 48 h exposure for TPE+APTES film-forming from volatile phase and neutral solution.

GUANIDINE-CONTAINING ALKYL-SUBSTITUTING OLIGOMER AS A METAL CORROSION INHIBITOR

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Today, corrosion, in particular its variety - microbial-induced corrosion), is one of the biggest problems in the construction and fuel and energy industries, the annual losses from which reach from 3 to 6% of the country's GDP. This problem requires the search for new, more effective inhibitors, the use of which will be cost-effective. Guanidine-containing alkyl-substituted oligomer based on aliphatic oligoepoxide is a newly synthesized substance with a known bactericidal effect, which gives it prospects for use as an inhibitor of microbial corrosion. The aim of this work was to synthesize an oligomeric alkyl-substituted guanidinium bromide and study its Anticorrosive properties to metal.

The synthesis of an alkyl-substituted guanidine-containing oligomer was carried out in two stages. At the first stage, alkyl – substituted guanidine was obtained. and alkyl bromide $Alk=C_{10}H_{21}$ in methanol at a temperature of 50^oC and a molar ratio of components of 1:1, at the second stage, a reaction was performed between aliphatic oligoepoxide DEG-1 and alkyl-substituted guanidine at a temperature of 50^oC for 2-3 hours and a molar ratio of components of 1:2.

The synthesized oligomer showed bactericidal properties against heterotrophic bacteria - destructors of protective coatings of pipelines *Bacillus subtilis* 138 and *Rhodococcus erythropolis* 102: the growth inhibition zones of which were 25-30 mm and 35-40 mm, respectively, depending on the concentration of the oligomer.

To study the anticorrosive properties of the newly synthesized guanidine-containing oligomer, collector cultures of sulfate-reducing bacteria SRB *Desulfovibrio* sp B-.1103, *D. Desulfuricans* DSM642, *D. vulgaris* DSM644 were used, stored in the Ukrainian collection of microorganisms of the D. K. Zabolotny Institute of microbiology and virology of the National Academy of Sciences of Ukraine. For comparison, the effectiveness of the compound was compared with inhibitors - DPH (a quaternary ammonium compound based on N-decylpyridinium chloride) (KPI, Ukraine) and Armohib CI-28 (based on Diamine Ethoxylate) (Akzonobel, Holland). When applying the guanidium oligomer, similar to DPH, only dozens of SRB cells were detected. The calculated biocidal efficacy of DPH, Armohib CL-28, and the newly synthesized guanidine-containing oligomer was 99.99-100%, 63.0-95.89%, and 99.99%, respectively.

The corrosion rate of steel in the control variants with SRB and without the introduction of inhibitors was $0.15 - 0.35 \text{ mg/cm}^2 \cdot h$, the addition of an oligomer to the culture medium reduced the corrosion rate to $0.075 - 0.079 \text{ mg/cm}^2 \cdot h$ under the influence of three SVB strains. According to the weight loss data of steel samples, the degree of protection of the metal from microbial corrosion in the presence of guanidinium oligomer had a lower degree of protection of 60.15 - 63.17 %, but the oligomer also exhibited anti-corrosion properties The data obtained indicate that the guanidine-containing oligomer based on aliphatic oligoepoxide has good biocidal and anticorrosive properties and is promising for use as a means of combating microbial corrosion.

THE DEPARTMENT OF CORROSION AND CORROSION PROTECTION Karpenko Physico-Mechanical Institute of NAS of Ukraine



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The Department of Corrosion and Corrosion Protection conducts the following research and testing of materials in corrosion environments:

- Corrosion resistance testing of materials and coatings in various aggressive environments using standardized methods (potentiodynamic polarization method, gravimetry, electrochemical impedance spectroscopy, climate chamber, etc.).
- Synthesis of metal corrosion inhibitors and testing of their anti-corrosion effectiveness, development of inhibiting pigments and protective metallic and organic coatings.
- Investigation of physical and mechanical properties of paint coatings on metals by standard methods: adhesion, flexural strength, impact strength, etc.
- Corrosion-mechanical studies of materials in aggressive environments (corrosionfatigue tests of metals and alloys, determination of resistance of steels to stress corrosion cracking in different environments).
- Tribological and tribocorrosion tests of metals and alloys in different environments according to standardized and original methods.
- Preparation of samples and specimens for metallographic, X-ray structural, X-ray fluorescent, and other physicochemical methods of analysis using a planetary ball mill Retsch PM 100 (Germany), installation for spraying samples of magnetron type JFC-1600 (JEOL, Japan), grinding equipment LABOPOL-5 (Denmark).
- Investigation of the surface of materials and determination of their chemical composition using optical microscopy and scanning electron microscope Zeiss EVO 40-XVP (Germany) and energy dispersion spectrometer INCA Energy 350 (Oxford, England).
- Quantitative analysis of the characteristics of roughness and waviness of the surfaces of materials using a profilograph-profilometer "Calibr S-265".
- Determination of hardness and microhardness of materials and their structural and phase components.
- Determination of hydrogen concentration in metals by vacuum extraction method.
- Synthesis of hydrogen sulfide and production of model hydrogen sulfide media for research and testing of metals and alloys using a laboratory generator of high pressure hydrogen sulfide (1-15 atm).

Testing methods and corrosion monitoring

APPLICATION OF ELECTRICAL RESISTANCE SENSORS FOR REAL-TIME CORROSION MONITORING IN ATMOSPHERE

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Corrosion monitoring is a powerful tool to evaluate environmental corrosiveness, material corrosion behavior and protectiveness of coatings and inhibitors and, consequently, predict service lifetime, prevent rapid failures and study corrosion processes of metallic materials. Although a variety of corrosion monitoring techniques has been developed in last decades, their applicability is limited under atmospheric conditions which can significantly vary in terms of relative humidity (RH), temperature, presence of aggressive pollutants, dust particles and water droplets.

The resistometric corrosion monitoring technique is based on the electrical resistance (ER) measurement of a thin metal track on a non-conductive substrate and exposed in aggressive environment. As the track thickness decreases due to corrosion, ER increases, and the difference between initial and actual ER directly reflects the material loss and corrosion rate. Compared to other monitoring methods, the resistometric technique is simple in terms of sensor preparation and data interpretation, provides direct real-time corrosion rate values, and is applicable both in dry and aggressive humid atmospheres.

Resistometric sensors were used to study corrosion processes outdoors and in laboratory tests. First, zinc sensors were exposed in eight accelerated corrosion tests developed by the automotive industry to study the effect of test parameters on metal corrosion. Actual corrosion rates in each particular test phase were measured and the effect of test parameters on corrosion was evaluated using multivariate regression. Along with the crucial effect of the highly aggressive chloride deposition phase, duration of the climate change phases, pH and material history impacted the corrosion process most significantly.

In order to evaluate the effect of surface pre-treatment on further corrosion response, carbon steel sensors with pre-treated or pre-corroded surfaces were exposed under cyclic climatic conditions. Fast activation of pre-corroded surfaces was observed after RH increase; on the contrary, surface treatments, such as surface passivating agents or sealants, showed good protective ability of the material.

Two carbon steel sensors, one as-produced and one placed on a painted panel, were exposed in outdoor urban conditions for a year to evaluate the effect of time of wetness difference caused by the substrate on steel corrosion rate. The results revealed the accelerative effect of the painted panel due to the longer wetting time, especially in summer and autumn when temperature and humidity fluctuations during the day are the most significant.

The experiments proved the resistometric technique to be a powerful method for realtime corrosion monitoring both outdoors and in a laboratory. Along with the use of asreceived clean open-surface sensors, sensors with the surface modifications, such as protective pre-treatment and pre-corrosion, were successfully tested, showing an interesting potential of the technique for a wide range of scientific and industrial applications.

ELECTROCHEMICAL METHODS FOR SIMULATING BOND STRENGTH DEGRADATION IN REINFORCED CONCRETE

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Reinforced concrete (RC) structures are usually designed for long-term operation, over 50 years. During this time they subject to continuous ambient impacts (temperature changes, acid rains, de-icing salts) and operational loads which influence their structural integrity and serviceability. Bond degradation between rebar and concrete is among main causes of strength loss of RC members. There are two different factors reducing bond strength: reinforcement corrosion and overprotection of RC. Corrosion of reinforcing steel is one of the main reasons of RC structures deterioration [1]. Accumulation of corrosion products at the steel-concrete interface with a larger volume than the volume of original iron causes internal stresses promoting cracking and spelling of concrete cover. Cathodic protection of RC structures by impressed current is efficient for corrosion suppression of reinforcing steel especially when an installation is operated in chloride-contaminated environment. However, application of cathodic current can lead to hydrogen generation and its further absorption by metal. The role of hydrogen in structural integrity of RC structures is not limited by hydrogen embrittlement of steel reinforcement [2]. Taking into account the long-term operation of RC structures, material degradation should also be considered. Transformations of dislocation substructure, an increase in dislocation density, failure of cementite in pearlite grains, micro crack growth along the grain boundaries have been revealed in operated hot-rolled reinforcing steel [3]. Hydrogen absorbed by steel can facilitate these processes thus contributing to steel degradation. However, almost all hydrogen recombines and evolves as gas at the surface of the reinforcement surrounded by concrete. A possible destructive effect of just this hydrogen on bond strength at the interface reinforcement-concrete is worth considering.

The electrochemical approach is used for accelerated RC structures degradation: anode polarization for corrosion simulation of the reinforcement, and cathodic impressed current for its hydrogen charging.

It was revealed that intensive dissolution of steel embedded in concrete under anode electrochemical conditions leads to cracking of RC specimens and extensive filling of formed cracks with corrosion products. Spreading of corrosion products suppresses a potential rise of their expanding pressure near the interface concrete–reinforcement thus delaying concrete cover cracking. However, significant outflow of corrosion products from the interface could weaken bond strength.

Prolonged application of cathodic current results in bond strength degradation in RC. The causes of the bond weakening could be not only ion migration in concrete due to impressed current but also hydrogen evolution at the steel–concrete interface. Special attention should be paid to the potential impact of stresses produced in concrete by hydrogen moving outwards from the interface through the concrete matrix, which suggests hydrogen-induced cracking in concrete.

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MAGNETOMETRIC ASSESSMENT OF THE INFLUENCE OF CHEMICAL ELEMENTS IN THE PROCESS OF CORROSION OF AUSTENITIC FE-CR-NI ALLOYS

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Various methods are used to study pitting corrosion, which made it possible to obtain significant results [1]. The magnetometric method, based on establishing a correlation between the corrosion rate and the specific magnetic susceptibility of austenite, with a low content of d-ferrite, was applicable to AISI 304 steel [2]. Despite numerous studies of corrosion processes, the emerging problems require new approaches to studying the role of both individual and combined elements in the pitting corrosion of austenitic chromium-nickel steels [3].

The samples were selected from sheet (thickness 1 mm) industrial supplies of the 06Cr22Ni28MoCuTi alloy (5 melts). Specific magnetic susceptibility χ_0 was determined by a magnetometric unit (Faraday balance). The corrosion rate of alloy samples was determined in a mixture of concentrated hydrochloric and nitric acids (HCl:HNO3 3:1) at t = 30 °C. An analysis of the experimental dependences of the corrosion rate *K* on the paramagnetic susceptibility χ_0 of austenite (before corrosion tests) of different melts, but one brand of alloy 06Cr22Ni28MoCuTi, which does not contain δ -ferrite (Fig.) shows: the greater the χ_0 , the greater the corrosion rate *K*, that is, there is an opposite dependence [3] compared to austenitic chrome-nickel steels that contain δ -ferrite. Hence, by studying the magnetic properties of austenite, it is possible to obtain information about the behavior of austenite under the influence of external factors, for example, about its corrosion resistance.



Fig. Trends in changes in the corrosion rate of *K* in a mixture of concentrated acids: chloride and nitrate (HCl:HNO3 3:1) and the specific paramagnetic susceptibility χ_0 of austenite of various melts of the 06KH28MDT alloy that do not contain δ -ferrite

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TECHNIQUE FOR DETERMINING CORROSION-ACTIVE AREAS OF FERROMAGNETIC MATERIALS UNDER EFFECT OF MAGNETIC INHOMOGENIOUS

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The influence of the magnetic field on the course of electrochemical reactions attracts a lot of attention. Under the effect of a constant magnetic field, there is a significant acceleration of corrosion and the appearance of vortex structures of electrolyte during the movement of reaction products are observed [1, 2].

The dissolution of a ferromagnetic sphere-like shaped sample manufactured from 100Cr6 steel in 7% nitric acid solution in an external inhomogeneous magnetic field was investigated. An inhomogeneous magnetic field was created by a neodymium magnet positioned under electrochemical cell, the magnitude of magnetic field directly above the magnet was 0.2T. The electrochemical cell is illuminated by LED lamp and a semiconductor red laser with a wavelength of 650 nm.

During the reaction, the rotation of the electrolyte around sample in the horizontal plane was observed. In white visible light, the rotation of reaction products end electrolyte is visible only in the immediate vicinity of the sample. In the mixed light, the distribution of the reaction products, which have the shape of a spiral untwisting around the sample is observed. In pure laser light, a granular structure also known as speckles is observed.

To determine the corrosion-active areas, the dependence of the intensity of each pixel of the video image of corrosion process on time was determined, followed by the determination of statistical characteristics and Fourier transformation (in order to determine the characteristic frequencies of the electrolyte movement) [2]. The most chemically active areas were distinguished by the minimum specular contrast in laser radiation, and by statistical data in the visible irradiation.

Characteristic frequencies are most clearly manifested when observed in incoherent white light. A mixture of white light and red laser radiation makes it possible to see in more detail the spatial distribution of reaction products. This technique does not distort the course of the reaction and can be adapted to determine the corrosion active areas and the frequency characteristics of the electrolytes, gases and small objects movement without direct influence on the environment under study. And to determine the areas with the most intensive course of the reaction.

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INCREASING THE EFFICIENCY OF MAIN PIPELINES DIAGNOSTIC EXAMINATIONS USING NON-CONTACT CURRENT MEASUREMENTS <u>Dzhala R.</u>^{1,3}, Verbenets' B.¹, Dzhala V.¹, Kostiv V.², Kychma A.^{3,4}, Lozovan V.¹, Melnyk M.¹, Savula R.², Shevchuk T.^{1,3} ¹Karpenko Physico-Mechanical Institute of the NAS of Ukraine ² Ukrainian Transmission System Operator ³National University "Lviv Polytechnic" ⁴Research and Production Enterprise "Integrator" dzhala@ipm.lviv.ua

Underground and underwater pipelines (UP) transport gas, oil, water, raw materials and products of the chemical industry. Environmental influences cause corrosive damage to pipelines. This leads to accidents and disasters, causes supply interruptions and loss of transported products, environmental pollution. To increase the reliability and prolong the service life of metal pipelines, corrosion protection (CP) with insulating coatings and cathodic polarization is used. In order to prevent corrosion damage, it is necessary to adjust the CP on time and in the appropriate places, which requires periodic diagnostic examinations of the UP.

UP diagnostic examinations are traditionally carried out by contact electrometric methods, the main disadvantages of which are the laboriousness of ensuring a sufficient number of reliable contacts of the voltmeter with the UP metal and the soil, the local type of control and insufficient informativeness. The efficiency and informativeness of UP examinations are significantly increased by the use of non-contact current measurements (NCM).

New methods and devices of NCM were developed at the Physical and Mechanical Institute of the National Academy of Sciences of Ukraine. Azimuthal, radial and invariant systems of NCM sensors are proposed. Equipment for determining the placement of UP, noncontact measurements of depth of occurrence and current of UP has been manufactured. Measurement results and geographic coordinates are automatically recorded in the device's memory. Then they are transferred to the computer for further processing and documentation. An information and measurement system and technology for non-contact UP examinations have been created.

NCM make it possible to intensify the process of diagnosing the technical condition of the UP's CP, to carry out integral, differential and local control, to determine new parameters (which were difficult or impossible to determine by means of contact electrometry) to assess the suitability of objects for operation. Quantitative evaluations of the distribution of the CP current between the threads and branches of the pipelines according to the results of the NCM show the state of the CP (insulation and electrochemical protection) in different sections of the pipelines, since the current distribution is most sensitive to the resistance of the insulation and the medium.

According to the results of research and development and field tests and pilot operation, the potential economic effect of using a set of NCM for non-contact inspections of underground pipelines amounts to 1.6 million hryvnias for 1 set of NCM equipment per year.

According to BVS, we quickly identify the place of unsatisfactory insulation of the PT, we look for the transition resistance "pipe-ground" in different sections of the PT; and the use of additional measurements of potentials make it possible to detect the transient specific resistance of the insulating layer and the polarization resistance, which can be used to estimate the corrosion rate in real operating conditions.

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MONITORING OF THE CORROSION STATE OF SUPPORTING UNITS OF ABOVE-GROUND SECTIONS OF GAS PIPELINES

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A significant part of the territory of Western Ukraine falls within the Carpathian and Carpathian regions, as a result of which the profiles of the routes of most gas pipelines (GPs) have significant height differences and cross riverbeds and swampy areas. The supporting nodes of the overhead sections of the GPs (Fig. 1) are a spatial reinforced concrete structure that is operated under the action of static and dynamic loads in a corrosive environment. Based on a literature review [1] and the experience of long-term operation of GPs [2], their individual sections passing through water obstacles and swampy places are subject to intensive corrosion processes and local defects appear, including under the collars of support nodes. Thus, for GPs of long-term operation, it is necessary to periodically monitor their technical condition and, if necessary, carry out repair and restoration work of the support nodes of overhead crossings. For this purpose, the authors proposed a technology for repairing the support nodes of the above-ground sections of the GPs without stopping gas transportation using mobile lifting devices. On the basis of the conducted studies, the defects of the sections of the supporting nodes of the GPs on the overhead crossing were identified (Fig. 2 and Fig. 3), the degree of their danger was determined and the methods of their repair were proposed. The proposed method of repair and restoration works allows to carry out repairs of support units of GPs in hard-to-reach places (river beds and floodplains, swampy areas, etc.) without the use of heavy lifting equipment (cranes, pipelayers, etc.).



Fig. 1. Overground passage of GPs across the river



Fig. 2. Corrosion condition of the surfaces of the constituent elements of the support unit



Fig. 3. Corrosion defects were found in the body of the pipe in the area of the support unit

The simulation of the stress-strain state of the support nodes of the above-ground sections of the GPs was carried out based on the condition that the pipeline is simultaneously an element of the building structure, which is subjected to vertical and horizontal loads from its own weight, temperature changes, wind loads, and a technological element that is subjected to the action of internal pressure. Recommendations have been developed to minimize the impact of detected deviations and corrosion damage of the elements of support nodes on the further trouble-free operation of overhead crossings of GPs.

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THE USE OF NEURAL NETWORKS FOR ANALYSIS OF THE PROCESS OF CORROSION FRACTURE OF ARMATURE IN NANOCONCRETE Yuzevych V., Lozovan V. Karpenko Physico-Mechanical Institute of the NAS of Ukraine vitalulozovan@gmail.com

Concrete, the most common material in the world, is a multiphase composite material that ages over time. Concrete with nanoparticles is named nanoconcrete. To ensure greater strength of concrete structures, a reinforcing frame is placed in the thickness of the concrete at a minimum distance from the walls of the concrete element. However, such actions increase the risk of corrosion of armature and, as a result, violation of the integrity and fracture of the concrete structure. The most common cause of rusting of steel armature in nanoconcrete is the corrosive fracture of its structure under the influence of the environment, namely, the loss of the load-bearing capacity of the component parts of the common structure. In concrete structures, industrial buildings, bridge structures, piers and other objects, destruction of the protective layer of nanoconcrete and corrosion of armarute can be detected after 4-5 years [1, 2].

The factors that initiate and intensify the negative process of fracture include, first of all, the water permeability of concrete, the penetration of aggressive gases and salts into it, as well as the tendency to carbonization (gradual loss of alkalinity). Two main schemes of development of corrosion processes of reinforced concrete structures can be noted. According to the first, the corrosion armature begins after the fracture of the concrete in the protective layer, that is, the reason for the damage to the structure lies in the insufficient stability of the concrete. The development of corrosion according to the second scheme begins with the armature, when the nanoconcrete does not have sufficient protective properties, but is not destroyed under the influence of the environment, which in this case is not aggressive towards it. The fracture of nanoconcrete occurs under the pressure of rust growing at the interface with the fracture, that is, it is purely mechanical in nature. Usually, this type of fracture of concrete structures occurs as a result of the action of moist air or periodic humidification, especially if the atmosphere is polluted with aggressive gases.

It is known that in most cases the corrosion of metals occurs by an electrochemical mechanism, which requires the following conditions [3]:

- the presence of a potential difference on the surface of the metal;
- the presence of an electrolytic connection between areas of the metal surface with different potentials;
- active state of the surface on the anodic areas, where metal dissolution is carried out;
- the presence of a sufficient amount of depolarizer, in particular oxygen, necessary for the assimilation of excess electrons on the cathode areas of the metal surface.

The aim of the work is to analyze the parameters of corrosion fracture of nanoconcrete using neural networks taking into account analytical functions. It is important in this context to establish, on the basis of a computational experiment, the correct input data, between which there are implicit relationships and regularities. We propose to use robustness criteria and a neural network with an analytical function, which is well developed and tested.

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CORROSION MONITORING OF PAINT COATING EVOLUTION USING CORRELATION SPECKLE INTERFEROMETRY

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Corrosion monitoring of paint films temporal evolution under influence of aggressive environment is one of the urgent tasks for nondestructive testing of materials and constructive elements degradation. Known techniques of speckle interferometry and dynamic speckle pattern analysis perform the control changes of paint films surface characteristics [1] and determining the level of swelling of the paint film due to the absorption of water vapor [2].

We studied the influence of liquid aggressive medium on a polyurethane paint coating (PPC) and analyzed the temporal evolution of its surface, using the method of correlation speckle interferometry. To this end, we made several samples of PPCs applied to steel substrates. For the interaction of the PPC with a 3% NaCl solution, beakers without a bottom were attached to the PPC surface. Studying the influence of this solution on the PPC surface were performed using an optical-digital experimental setup based on a speckle interferometer constructed according to the Twyman-Green interferometer scheme.

Correlation speckle interferograms (CSIs) of the PPC surface were registered before the experiment, as well as after 7, 14 and 21 days of NaCl solution action. Before the experiment, we registered the first speckle interferogram (SI) of the surface in initial state and the second one after the surface heating to $40 \div 50^{\circ}$ C. The CSI was obtained by pixel-by-pixel subtraction of these recorded SIs. At the end of each seven-day cycle, i.e., after 7, 14, and 21 days, the solution was drained, the PPC was dried, and then a series of CSIs were obtained in the same way as the CSI before the start of the experiment, i.e., by heating the PPC surface.

Since the PPC surface reflects only the part of the laser radiation, and the other part is scattered inside the coating layer, the SI were blurred. As a result, the correlation fringes on CSIs become fuzzy and noisy. For further processing of the obtained CSIs, two equidistant parallel vertical profiles were selected in all CSIs to form the intensity distributions of correlation fringes along them. To evaluate the temporal evolution of normal surface deformation during influence of the NaCl solution on the PPT and increasing in the number and size of corrosion defects along the two chosen profiles, the distances between correlation fringes maxima and minima along these profiles were measured. Because the correlation fringes were corrupted by high frequency noise, a low-pass Gaussian filtering of the fringe profiles was performed to increase the accuracy of measuring the distances between fringes. Measurements results allow calculating the surface normal displacements d and differences between correlation fringes displacements Δl along the profiles. To estimate the deformation level of the LFP surface, we use the dependence of the relative maximum displacement $\Delta l_{\rm max}/d_{\rm max}$ between correlation fringes on the time of NaCl solution action ($d_{\rm max}$ is the maximum surface displacement). The resulting dependence increases almost linearly. To assess the corrosion defects growth, the dependence of their total size along two profiles on the time of NaCl solution action was built. This dependence tends to grow exponentially.

Thus, the new technique of corrosion monitoring of the PPC surface under continuous action of NaCl solution is developed. This technique enables estimating the temporal evolution of the deformations and corrosion defects on the PPT surface.

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COMPARATIVE ANALYSIS OF THE TEST METHODS OF CORROSION CRACKS PROPAGATION

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The intensive development of the chemical, power, oil and gas and other industries, as well as the exhaustion of the design life time of the existing equipment of long-term operation, stipulated the operators and scientists to dirct their efforts to solution of the problem of ensuring their reliability and durability. This especially applies to equipment and products operating in corrosive working environments with the simultaneous action of static and other types of load. The simultaneous action of these factors causes premature fracture, the most dangerous of which are corrosion cracking of materials and corrosion fatigue.

Non-destructive test methods are used to diagnose the state of the above-mentioned equipment, and therefore to make decisions regarding its further operation. Among them, the acoustic emission (AE) method has recently taken a prominent place, which, thanks to its high sensitivity and the best ratio of economic costs to efficiency of use, is confidently gaining new areas of use. The paper considers the comparative characteristics of the most common methods of assessing the development of corrosive cracks used in research.

Specimens of rolled steel 9X Φ were used in the experiments. The specimen was placed in a chamber filled with a 3% NaCl working corrosion medium . The temperature of the medium was maintained by a heating element and controlled by a thermotransducer. The loading was carried out with the help of a rigid static mechanism, which made it possible to obtain a given stress intensity coefficient at the crack tip and was measured with a strain gauge dynamometer. Electrochemical parameters in the crack (hydrogen index of the environment pH, and electrode potential of the metal φ) were determined by mini-electrode sensors according to the Dmytrakh–Panasyuk method. Electric signals corresponding to the values of the load *P*, the hydrogen indicator of the pH medium and the electrode potential of the metal φ were recorded using the signal processing and coding unit..

At the same time, AE signals were recorded synchronously with the aforementioned indicators of electrochemical parameters and load. For this purpose, a primary piezoelectric signal transducer was installed on the side surface of the specimen outside the chamber, from which they were fed to the SKOP-8 measuring system. After processing the signals in real time, they were observed and analyzed on a computer.

The AE signal extraction and processing modes were as follows. The operating frequency band of the primary transducer was 160–600 kHz, the gain of the preamplifier was 40 dB, the low-pass filter of the measuring path was 800 kHz, and the high-pass filter was 100 kHz.

During tests, the numerical values of the parameters , λ_i , P_i , pH_i , φ_i , at a fixed moment of time τ_i were recorded. After tests, these data can be printed on a printer in the form of appropriate graphic dependences , $\lambda(\tau)$, $P(\tau)$, $pH(\tau)$, $\varphi(\tau)$, as well as tables.

It was established that the AE method according to the parameter of the signal counting rate allows us to establish the beginning of fracture much earlier than using the φ , pH parameters and optical determination of the propagation Δl of the crack on the side surface of the specimen.

THE USE OF CORROMETERS FOR CONTROLLABLE REAGENT WATER TREATMENT IN HEATING NETWORKS

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In conditions when traditional methods of water treatment are not able to ensure corrosion-safe operation of the heating network, an alternative may be the transition to reagent water treatment. In this technology, reagents of complex action are dosed into the water, forming a protective layer on the metal surface that prevents corrosion and form complexes with hardness salts, stable at high temperatures. The control of the efficiency of dosing of such reagents should be performed according to the actual corrosion rate and requires the installation of corrosion control means.

Testing of the reagent method of water treatment by means of anti-scale and anticorrosion reagent LVH-1.1V with the use of corrosion control devices was carried out at the district boiler house of Kyiv city. To control the corrosion rate, corrosion rate probes DK-2 were installed on the forward and reverse pipelines of the heating network, and on the supply line – before and after the deaerator. Determination of the anti-scale efficiency of the reagent was performed by measuring the change in the hardness of water before and after the heating equipment. The decrease in hardness on the heating equipment is an evidence of scale deposition, while no change in hardness means the absence of scale formation.

To minimize the possible risks of transition of equipment from chemically softened water to tap water treated with reagent, the replacement took place gradually, in 3 stages: 1) 50 by 50%; 2) 30 to 70%; 3) 100% of tap water treated with the reagent. The ratio of softened water to reagent-treated water was changed every 2 weeks during which no decrease in hardness was registered on the heating equipment. The dose of reagent dispensed by the pump was 75 ml per 1 m³ of water.

The results of corrosion monitoring showed that the corrosion rate in the heating network is maintained at 0.1 mm/year. The presence in the reagent of components that promote the dissolution of solid sediments from the inner surface of the pipes, leads to the transfer of sediment into the sludge, increasing the concentration of iron from 1 to 5 mg/dm³ in water. The sludge that deposits on the surface of the electrodes leads to an increase in the measured value and reduces the accuracy of corrosion monitoring. To reduce the intensity of sludge washing, the reagent dose was reduced and regular purging of boiler equipment for discharge of sludge into the sewage was introduced. This led to the normalization of the transparency and iron content in the water, and after cleaning the electrodes of the probes, the corrosion rate reached 0.1 mm/year. The corrosion rate on the feed line due to reagent water treatment was reduced to 0.03 mm/year in non-deaerated water, which is below the allowable level of corrosion in thermal networks – 0.05 mm/year.

Thus, as a result of industrial tests, the transition from traditional water treatment to reagent coolant treatment was worked out. According to the results of real-time corrosion monitoring, the anti-corrosion efficiency of the reagent was determined, and it was shown that feeding the heating network with water treated with the reagent does not increase the corrosion rate. The calculation of economic efficiency has shown that the reagent method of water treatment for heating networks is 13% cheaper than traditional approach and can serve as an alternative to traditional, especially in terms of energy savings.

PARAMETRIC CORRELATION METHODS FOR DETERMINING THE COORDINATES OF CORROSION DAMAGE IN UNDERGROUND PIPELINES Vladimirsky A., Vladimirsky I.

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Heating and water supply systems in Ukraine are characterized by a significant degree of wear. The main part of them was laid down in the last century, more than 50% of the networks have fulfilled their scheduled service life and is used for more than 30 years. Significant deterioration of heat and water supply underground pipelines in Ukrainian cities, on the one hand, and the economic inability to carry out large-scale upgrades of pipelines that have fulfilled their scheduled service life, on the other hand, cause the problem of instrumental determination of actually worn out sections of underground pipelines for their renovation. Of course, the problem of reliability and efficiency of determining the leakage points in underground pipelines is also relevant.

The main cause of leaks, and even more significant gusts of heating networks pipelines, is the corrosion thinning of pipeline walls.

Development of assessing the technical condition of underground pipelines by creating new methods and technical means of determining leaks, corrosion damage and actual heat losses is presented. Low-frequency vibro-acoustic signals propagate along the pipelines for considerable distances and can be registered at a considerable distance. Therefore, they should be considered promising for the diagnosis of underground pipelines in urban conditions, despite the expected problems with the interpretation of results in a complex interference situation. Analysis of the reasons for the existing problems with the reliability of the existing means of diagnosing worn-out underground pipelines shows that they are caused, first of all, by using too simplified models of the processes of propagation of vibrating signals.

The correlation parametric method of passive operative detection and determination of coordinates of leaks and accompanying corrosion damages of sections of underground pipelines [1, 2] is developed. The method takes into account the multi-wave structure of acoustic data and is adapted to work in conditions of small signal-to-noise ratio. The new method is implemented as part of an experimental system for determining damage to underground pipelines. The effectiveness of the method has been proven experimentally. Method allows obtaining high accuracy and reliability. These properties of the developed method are especially relevant for the post-war repair of urban engineering networks.

For targeted remote diagnostics of extended sections of underground pipelines, it is considered expedient to apply the principles of active sensing. The correlation parametric method for determining the coordinates and estimating the degree of pipelines walls corrosion thinning that combines the diagnostic model of the pipeline, obtained through synchronous multichannel registration, arrays of initial acoustic data, space - frequency analysis of the corrected correlation functions is developed. To achieve the greatest distance, echolocation sounding of pipelines is carried out by weakly attenuating acoustic signals in the lowfrequency sound range. The method is based on the use of the developed hardware-software simulation system RASTR-1.

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PROBLEMS OF CORROSION MONITORING OF TECHNICAL CONDITIONS OF MINE DEGASSING PIPELINES

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Corrosion monitoring of underground degassing pipelines is continuous control of steel pipe corrosion velocity under the conditions of aggressive mine environment.

Steel pipes, supplied traditionally for coal enterprises to construct underground degassing systems, are made of simple carbon steel. They have no specific coating. Resulting from underground degassing pipeline operation, the metal pipes suffer from rock mass deformation as well as from negative impact of aggressive mine environment. Hence, spatial pipe bending takes place in addition to deposition of mechanical impurities and moisture as well as internal and external corrosion.

Analysis of technical conditions of degassing systems in the underground mine workings of MA *Pokrovske* (Fig. 1) has registered numerous corrosion damages of the arched metal frames and pipelines laid in them.



1 is arched frame; and 2 is degassing pipeline

Fig. 1. Corrosion of metal structures in the underground mine workings

The detailed studies of the corroded pipeline sections have helped identify partial wall thinning of the metal pipes; caverns and hollows provoking crack formation; mine air inflow; and deposition of mechanical impurities from mine working atmosphere.

The problem of negative corrosion impact on technical conditions of mine degassing pipelines is still understudied. Industry normative documents recommend estimating corrosion velocity in pipeline walls relying upon at least two measurements of wall thickness in terms of the expression

$$\Pi_{e} = \frac{365 \sum_{i}^{n} (\Delta S_{1} + \Delta S_{2} + \dots + \Delta S_{n})}{n \cdot T_{e}},$$

where Π_e is corrosion velocity within the controlled pipe share or a pipeline under operation, mm/year;

 ΔS is difference in thickness of the walls for the control measurement period, mm; 1, 2, ..., n indices are numbers of the control points;

 T_e is operation period between the control measurements, day; and

n is the number of the control measurement points (at least three) from each component of the degassing pipeline (i.e. pipe, removal; and adapter).

Purpose of the research is to identify dependences of changes in technical conditions of underground degassing pipelines upon their corrosive wear during operation under the conditions of uncontrolled action of the mineralized mine water as well as aggressive mine environment.

For the purpose, both program and methods of monitoring and operative control of formation of corrosion areas of metal sections of degassing pipelines have been developed for the actual conditions of mine environment.

Corrosion protection of industrial equipment. Corrosion of alternative energy equipment

CORROSION OF THE RESPONSIBLE ELEMENTS OF WIND ENERGY FACILITIES

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The problem of energy supply to the EU is particularly acute after Russia launched a fullscale war against Ukraine. After the introduction of sanctions against Russia and the recent accident on the Nord Stream pipeline, it is necessary to quickly find a replacement for Russian gas and oil. Two main ways can be identified here. The first is the search for optimal routes and maximum diversification of fossil fuel supply; the second - replacing fossil fuels with renewable energy sources in the short- and medium-term perspective. The second way, in our opinion, is optimal, taking into account the goals of climate neutrality set by the European Union. Achieving this ambitious goal will be helped by the comprehensive development of wind energy. One of the most promising areas for the construction of new wind power facilities is offshore and onshore areas of the continental coast and sea islands (fig.1, a). The wind blows constantly in these areas, ensuring good electricity generation efficiency. Wind energy has become especially widespread in Northern Europe, in particular in the north of Germany and the Scandinavian countries.



Fig. 1. Scheme of wind turbines (a) and monopile support (b) construction [1, 2].

The highest danger of developing corrosion lesions during the operation of wind energy facilities will be in the tidal zone (fig 1, b), as well as in the places of local defects of the protective anti-corrosion coating and around the welded joints of the windmill supports. We modeled the interaction of the defects of the protective coating on the sections of the welded joints of the support of the wind power plant in COMSOL Multiphysics 6.0 and find that the highest risk of corrosion damage occurs in the place of contact between the main metal and heat affected zone of the welded joint. To extend service life of the windmill monopile proposed to use Ni/Cu nanolaminate coatings [3].

Conclusions: The development of wind energy is very relevant considering the reduction of greenhouse gas emissions and the transition to carbon-neutral energy.

Numerical modeling methods show that the highest risk of corrosion damage occurs when the protective coating is damaged at the point of contact between the base metal and the metal of heat affected zone.

To increase the fatigue life of the welded joints of the supports of wind energy installations, proposed to use Cu/Ni nano-coating.

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OPTIMIZATION OF THE CHOICE OF DRILL PIPE MATERIAL DURING THE OF DEEP WELLS CONSTRUCTION IN PROTECTED AREAS

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Today, the oil and gas complex remains the main source of energy resources not only in Ukraine, but also in the world. Among the primary security elements of Ukraine, the "Energy Independence Program" occupies a prominent place, the basis of which is the increase in the volume of hydrocarbon extraction and geological exploration and development of new deposits, and the intensification of the inflow of hydrocarbons to wells at the final stage of the development of deposits operating with the appropriate infrastructure.

At the same time, world experience shows that the rate of consumption of natural resources is high. Laying of new pipelines, intensification of the inflow of hydrocarbons to wells at the final stage of field development, changes in oil and gas pumping modes due to logistical changes in the market, carry potential technological and environmental risks. However, to abandon this means to significantly weaken, and in some sectors even lose, energy independence. Increasing own production of hydrocarbons requires the drilling of deep wells, where the oil and gas production equipment will be exposed to the simultaneous action of high temperatures and a corrosive environment. Therefore, optimizing the selection of materials, especially for drill pipes, is an important scientific and practical task.

The fatigue life of drill pipe is a vital factor affecting the drilling process and safety, while severe fatigue failure of drill pipe under the condition of high temperature containing hydrogen sulfide have been reported frequently in recent years. [1, 2]. According to the experimental results, the economical practicality of different drill pipes is analyzed and compared (Fig.1).



Fig. 1. Scheme of drill pipe material optimization.

The presented work can provide a technological basis for fatigue theory and service conditions of drill pipes.

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THE INFLUENCE OF CO₂ AND H₂S ON THE CORROSION OF PIPE STEELS IN THE OIL AND GAS EXTRACTION INDUSTRY

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Carbon dioxide is a component of produced gas, gas condensates, and associated petroleum gases. Its concentration in gas can vary widely from hundredths of a percent to tens of percent. A more complicated situation is observed when hydrogen sulfide is present. It is known that CO_2 and H_2S gases intensify corrosion, the speed of which can reach several millimeters per year. The H_2S in environments significantly intensifies local corrosion and hydrogenation of steels, which causes specific damage - hydrogen-initiated cracking and hydrogen-induced delamination of tube walls metal (blistering). The standard [1] recommends investigating hydrogen sulfide corrosion in a solution: 5% NaCl solution + 0.5% $CH_3COOH+H_2S$ and does not take into account the role of carbon.

In this work, the influence of carbon dioxide on the corrosion and corrosionmechanical properties of steels in a standard chloride-acetate solution and in model brine water (MBW) was studied.

The 2 pipe steels were researched: 17Mn1Si-U, and P110. Electrochemical studies have shown that hydrogen sulfide, like carbon dioxide, facilitates the cathodic process in model brine water. This depolarization is observed at lower values of the cathode potential. The nature of the anodic curves does not change as a function of hydrogen sulfide concentration. The addition of hydrogen sulfide to carbon dioxide shifts the corrosion potential for P110 steel towards negative values by no more than 30-40 mV. Replacing carbon dioxide with hydrogen sulfide increases the corrosion current for P110 steel by three times. Similar studies were carried out in chloride acetate solution on samples of 17Mn1Si-U steel. The corrosion current in a solution with argon is one and a half times higher than in an environment with carbon dioxide. Electrochemical properties of 17Mn1Si-U steel in environments saturated with carbon dioxide and hydrogen sulfide in different ratios differ slightly. For exposures of 504 h, the corrosion rate of 17Mn1Si-U steel in MBW with carbon dioxide is twice as high as for P110 steel in MBW with hydrogen sulfide. An increase in temperature to 60 degrees and pressure to 60 atm accelerates the corrosion rate by an order of magnitude in pure carbon dioxide compared to hydrogen sulfide-containing mixtures. The kinetics of corrosion processes for 17Mn1Si-U steel in a chloride-acetate solution can be divided into two periods. In the first period, there is the formation of sulfide or oxide films, which, with increasing thickness, increase the diffusion barrier to corrosion processes. Accordingly, the rate of corrosion during this period decreases. The starting rate of corrosion is proportional to the content of hydrogen sulfide in the corrosion solution. A significant increase in the corrosion rate is observed after 100-300 hours, depending on the environment, This is the beginning of the second period. An increase in the rate of corrosion is due to the appearance of phases in sulfide or oxide films. Hydrogen can release on these films by an electrochemical mechanism. The second period is not observed at low concentrations of hydrogen sulfide. Carbon dioxide reduces the corrosion rate by about two times compared to argon. Its effect is neutralized in the presence of hydrogen sulfide. It was also established that the amount of absorbed hydrogen is proportional to the concentration of hydrogen sulfide. Replacing argon with carbon dioxide practically does not change the amount of absorbed hydrogen. Therefore, it can be stated that carbon dioxide has a significant effect on corrosion processes in those environments. It plays the role of the pH determining component in those environments.

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CORROSION IN ALUMINIUM-BASED SACRIFICIAL ANODE – STEEL SYSTEM

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AP4 sacrificial anode alloys with 0.1% Ca and 0.65% Fe additives have been smelted. 5.3 mm diameter and 18 mm height rods have been made of the alloys. A thread has been screwed on the end of the rods. 15.5 mm diameter nuts with corresponding thread have been made of 3 mm thick St3 steel plate. Three groups of experiments have been performed. Ten glass containers with model sea water of the Black Sea were used in the each group. Three samples were placed into the each of the container. There were steel nuts connected to the sacrificial anodes with calcium addition in the first group of the experiments. Steel nuts connected to the aluminium alloy rods with excess iron were examined in the second experimental set. And the third group of the experiments was control: 3 steel nuts without sacrificial anodes were put in each of the ten glasses. The samples were in the aggressive media for up to ten days (240 hours). Specimens were taken from one container for each group of the experiments every day. Rods and nuts were separated from each other and corrosion products were removed. The samples were washed with distilled water and dried. The nuts and the sacrificial anodes were weighed separately. In the control experiment, the steel is actively oxidized with the formation of brown iron (III) oxide and black intermediate iron (II, III) oxide. The sacrificial anodes with calcium addition actively interact with the model seawater forming hydrogen bubbles and a white precipitate of aluminium hydroxide. The rods with iron excess interact with the sea water much weaker, bubbles with hydrogen and aluminium hydroxide sediment are formed much less. Only a slight plaque of iron oxides was observed on the steel samples in both cases. Steel protected by sacrificial anodes corrodes an order of magnitude less than not protected one. Corrosion of the steel with the anodes does not depend on whether the sacrificial alloy is used with the iron or calcium addition: the data for these two cases coincide within the experimental errors. But sacrificial anodes with calcium lose weight faster than that with iron. Thus, calcium hyperactivates the sacrificial anode alloy and reduces its capacity and efficiency.



Fig. 1. Time dependences of specific weight loss of St3 steel and aluminium-based sacrificial anodes.

Black squares and solid black line – corrosion of AP4 + 0.1 wt. % Ca sacrificial anodes connected with steel; black circles and dashed black line – corrosion of AP4 + 0.65 wt. % Fe sacrificial anodes connected with steel; gray up triangles and solid gray line – corrosion of steel connected with AP4 + 0.1 wt. % Ca anodes; black down triangles and black dotted line – corrosion of steel connected with AP4 + 0.65 wt. % Fe anodes; gray diamonds and gray dotted line – corrosion of steel line – corrosion di steel

PARAMETRIC DESIGN OF STEEL STRUCTURE CORROSION PROTECTABILITY BASED ON THE LIMIT STATES <u>Korolov V.¹</u>, Korolov P.² ¹State Higher School "Priazovsky State Technical University" ²LTD "Kartis Building" center sts@ukr.net

The paper explores into the task of selecting of models and practical recommendations for parametric design of structure corrosion protection system (SCPS) based on the principles of limit state calculation. It is shown that corrosion protectability defines the ability of SCPS to meet the given quality, reliability and safety requirement based on organizational and technical measures required for normal operation of an industrial facility thought the life cycle.

Design of corrosion protection for given design cases implies the use of partial reliability factors, which determine serviceability of the structure in normal service during the specified service life. Presented is a logistical structure of constant, temporary and emergency design cases based on corrosion hazard indicators. Methodological approach has been developed to managing technological safety of structures and installations based on level of industrial facility corrosion hazard.

Performed is a systematized description of standard (basic, characteristic) impacts and representative values of corrosiveness negative factors. Design characteristics of corrosion resistance, durability and serviceability of structures and their protective coatings are determined based on experimental data in accordance with the specified procedure of defining tests [1].

In the course of structural design, the level of facility corrosion protectability, classification features of structures and their protective coatings based on criticality rating are taken into account. It is proposed to substantiate design indices of structural durability using the developed procedure, taking into account reliability and availability factors of corrosion protection. Reliability factors of primary and secondary protection take into consideration uncertainty of design models of corrosion protectability in structures and installations. Availability factor of structural steel is taken as a complex index of repairability for analyzing alternatives of structural and process measures of primary and secondary protection.

Substantiated are the stages of SCPS parametric design on the basis of a system analysis of external influence factors, diagnostics and risk analysis and substantiation of corrosion protection tolerances at all stages of the life cycle. Logistical system has been generated for reserve planning of a structure's survivability on the basis of signs of corrosion protectability [2]. A method is suggested for calculating compensation for corrosion losses when comparing competitive advantages of corrosion protection systems. The index of a level of corrosion protection is specified for managing technological safety on the basis of risk reduction.

Results of theoretical and experimental substantiation of limit state criteria are used for developing a system of measures for quality control and safety assurance of steel structures in service.

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Zabezpechennia koroziinoi ta funktsionalnoi stiikosti metalomistkykh kompleksiv i krytychnoi infrastruktury za dopomohoiu innovatsiinykh naukovo mistkykh ekoresursozberihaiuchykh tekhnolohii: monohrafiia // Pid zah. red Pluhina A.A. – Tsentr uchbovoi literatury – 2019. – P. 306.

COMPARATIVE ANALYSIS OF THE SUSCEPTIBILITY OF STEELS PIPELINE ASSORTMENT TO STRESS-CORROSION CRACKING UNDER CATHODIC PROTECTION

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The analysis of susceptibility to stress-corrosion cracking (SCC) of pipe steels grade 09G2S, 17G1S and 10G2FB, from which the main gas pipelines of Ukraine are built, in the conditions of cathodic protection in the model soil environment NS4 is made.

In the range of the mixed fracture mechanism action (from -0.85 V to -1.0 V) the susceptibility of 09G2C steel to SCC and to hydrogenation changes non-monotonically (Fig. 1, a), compared to the potential range more positive than -0.85 V (mechanism of anodic dissolution) [1]. At potentials less than -1.0 V (hydrogen embrittlement mechanism), in which the concentration of hydrogen which is penetrating into steel increases intensively, sharp increasing the inclination steel to SCC is observed, Fig. 1, a.



Fig. 1. Susceptibility to stress-corrosion cracking and to hydrogenation of pipeline steel of different grades under electrochemical cathodic protection in NS4 solution: a - 09G2S; b - 17G1S; c - 10G2FB

For 17G1S steel in the potential range from -0.8 V to -0.98 V (mixed mechanism of corrosion cracking [1]) increases the concentration of hydrogen capable to penetrate into the steel, Fig. 1, b. In this potentials range the susceptibility of 17G1S steel to SCC also increasing, Fig. 1, b. A sharp increase of hydrogen concentration, and a corresponding increasing of susceptibility to SCC was observed for potentials negatively than -0.98 V, Fig. 1, b.

For the steel 10G2FB in NS4 solution at potentials positively than -0.75 V hydrogen penetration is not occur (Fig. 1, c), the coefficient of susceptibility to SCC does not exceed 1.1 (Fig. 1, c). In the potential range from -0.75 to -1.05 V, a significant increasing in hydrogen penetration and nonmonotonic increasing of the susceptibility to SCC 10G2FB steel was observed (Fig. 1, c). It was due to the shifting of the equilibrium of the fracture process from anodic dissolution to hydrogen cracking [1, 2] mechanism. In the potential range (less than -1.05 V), where the concentration of hydrogen which penetrating to the steel changes abruptly, the susceptibility to SCC estimated by the K_S coefficient increasing from 1.11 to 1.25.

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ASSESSMENT OF SOIL CORROSIVENESS FROM THE ACCIDENT SITE OF THE MAIN PIPELINE

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The corrosivity of three soil samples from the accident site of the main gas pipeline made of low-alloy steel 17G1S, taken below the lower forming of pipe (No1), on the right (No2) and on the left (No3) of the pipe for the course of the gas.

Quantitative chemical analysis revealed that the content of water-soluble substances in slightly alkaline soil (pH 7.2 to 7.4) is 0.093, 0.210 and 0.369 g/kg of soil. According to the total content of sulfates and chlorides in water extracts, the corrosivity of soil samples was assessed as «low» (58.4 mg/l), «increased» (252.3 mg/l), «high» (310.6 mg/l). The content of sulfates and chlorides more than 300 mg/l indicates on the high soil corrosivity, from 200 mg/l to 300 mg/l – on the increased soil corrosivity [1].

According to the electrochemical studies' results (Fig. 1) it is determined that increasing of water-soluble substances content in soil probes causes to the changes in corrosion properties, in particular, the corrosion rate varies from 0.050 mm/year in soil with low water-soluble content of substances up to 0.111 mm/year – with high water-soluble content. According to DSTU 4219 [2], soil with such properties is an environment with «average» corrosion activity (corrosion rate from 0.01 mm/year to 0.3 mm/year). The potential of the beginning of hydrogen evolution did not exceed the normalized value of the maximum polarization potential, -1.05 V (c.s.e.) [2].



Fig. 1. Corrosion rate changing of 17G1C pipe steel for 3 hours in different environments determined by the polarization resistance method (a) and polarization curves (b): 1-3 – water extracts of the soil selected in the area of failure of the main pipeline

It is noted that the residual corrosion rate at the minimum protective polarization potential -0.75 V varies from $8.6 \cdot 10^{-3}$ mm/year to 0.014 mm/year, i.e. in the sample with higher content of water-soluble substances technically sufficient protective effect (corrosion rate of steel less than 0,01 mm/year) is not achieved at the minimum protective potential, which may warn about insufficient protection with minimal protective polarization potential in this environment.

It was found that one of the important corrosion factors in the considered corrosion situation is the differences in soil corrosion relative to 17G1C pipe steel at the emergency site of the main pipeline, which led to the formation of macrocorrosion pairs at the interface of different soils and corrosion cracking.

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INDUCED UNDER-DEPOSIT CORROSION OF METAL SURFACES DURING COMBUSTION OF COAL WITH HIGH SALT CONTENT

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It is known that the main source of the formation of deposits (slagging) on the heating surfaces is sulfates of alkaline, alkali-earth metals and iron, and the main cause of underdeposit corrosion of metal surfaces is chlorine compounds, primarily hydrogen chloride. The complexity of the processes of slagging and corrosion, which occur when using various fuel raw materials, determine the need for a more detailed study of each type of fuel, especially one with an increased content of salts, such as salty coal (SC). Experimental studies were carried out on samples of salty coal from Northern Donbass (Table 1).

Coal deposit	A ^d , %	V ^{daf} , %	W ^a , %	Na ₂ O in ash, %	S ^d , %	Cl ^d , %
Bohdanivsk №4	5.0-5.7	42.8	12.7	6.62-7.22	1.2	0.8
Starobilsk №12	7.0-7.7	43.7	20.3	6.43-6.7	2.8	0.7

Table 1. Characteristics of salty coal samples

The study of the intensity of slagging (formation of deposits) on metal surfaces was carried out by the gravimetric method. The development of corrosion processes was assessed by visually determining the morphological features of metal surfaces and the mineral composition of exfoliated layers (scale) using X-ray diffraction analysis. It was established that the formation of deposits on the metal surface occurs when using different types of fuel (biomass waste, wood biomass, different types of coal), but the most significant effect occurs in the case of salty coal [1]. At the same time, the removal of salts from coal by water washing leads to a noticeable decrease in the mass of deposits.

Fig. 1 shows the metal surfaces that were exposed to the combustion products of salty and desalted coal of the Bohdanivsk deposit. The surface of the metal under the influence of the combustion products of the SC is covered (up to 63 %) with scaly formations. At the same time, similar formations on the surface exposed to desalted coal gases cover only 19 % of the surface. A similar picture was observed for Starobilsk deposit, where the surface after exposure to the SC is covered with scaly formations by 70 %, and after desalting by less than 20 %. The mineral composition of exfoliated layers of SC samples is presented in Table 2.



Fig. 1. The influence of salty (a, b) and desalted (c, d) coal on metal surfaces

Table 2. The composition of scale nom metal surfaces					
Coal deposit	Fe_2O_3 , %	Fe ₃ O ₄ , %	FeO, %	FeS, %	NaCl, %
Bohdanivsk №4	35	17	30	16	2
Starobilsk №12	44	25	15	13	3

Table 2. The composition of scale from metal surfaces

1. T. Shendrik, N. Dunayevska, A. Tsaryuk, V. Yelahin, A. Fateyev. Experimental development of approaches to reduce the slagging and corrosive activity of salty coal // Eastern European Journal of Enterprise Technologies. – 2020. – № 6. – P. 124-133.

THE CORROSION RESISTANCE OF THE ALTERNATIVE MATERIALS FOR TOLERANT FUEL ROD CLADDING OF LIGHT WATER REACTORS Zuyok V., Rud R., Tretyakov M., Rud N., Kushtym Ya., Dykyy I., Shevchenko I.

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The Fukushima NPP accident revealed the ultimate danger of the steam-zirconium reaction and gave an impulse to R&D into the development of accident tolerant fuel (ATF). The long-term stable operation of light water reactor fuel rod claddings under the design conditions and severe accidents is vital and high priority task, that is being solved by a large number of scientists. The scientific community considers the replacing of zirconium alloys for the fuel rod cladding with more corrosion-resistant material as a remedy to ensure long-term stability. This material should possess a low neutron absorption cross section, and at high temperature oxidation should not result in the formation of a large amount of explosive hydrogen and the destruction of the cladding.

The ATF must be stable when operating under normal conditions and tolerant to loss of coolant conditions according to the specification of the IAEA. Basing on above, it can be argued that one of the most important characteristics of the fuel rod cladding material is corrosion resistance, in order to maximal prevention the development of severe accidents with loss of coolant.

The advantages of steels in comparison with zirconium alloys are the following: high corrosion resistance in steam-water coolant, no steam-zirconium reaction, wide experience of operation in different types of nuclear reactors, including light water reactors, and the availability of production technology for thin-walled weld-free tubes and components.

The purpose of the study was the evaluation the corrosion resistance of the fuel rod cladding materials of the tolerant fuel for light water reactors alternative to zirconium alloy in the water vapor environment for the selection of the appropriate one.

The high-temperature testing of basic cladding materials for nuclear fuel rods (Zr+1%Nb and E110 alloys), as well as alternative materials for tolerant fuel rod claddings (Cr18Ni10Ti steel and 42CrNiMo alloy), that are capable to maximally prevent the development of severe accidents was carried out in water vapor. Also presented the results of similar tests by the world's leading scientists and a comparative analysis of the corrosion resistance of these materials.

42CrNiMo alloy samples possess the highest corrosion resistance in a hightemperature water vapor among the other considered fuel rod cladding materials. The corrosion resistance of this alloy at 1200 °C is approximately 40 times higher than Cr18Ni10Ti steel and E110 alloy. The corrosion rate of the 42CrNiMo alloy at high temperatures is comparable to the Fechral alloy. Under the conditions of severe design accidents associated with overheating of the core the hydrogen released from the 42CrNiMo alloy claddings would be almost forty times less in comparison with the zirconium alloy.

COMPATIBILITY OF DYSPROSIUM TITANATE POWDER AND PELLETS WITH 42XHM ALLOY IN WATER VAPOR ENVIRONMENT AT TEMPERATURES IN RANGE (600...1200) °C

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Dysprosium titanate is the neutron-absorbing material in the absorbing elements for Rod Cluster Control Assemblies (RCCAs) of the VVER-1000 reactor. The way to increase reliability and efficiency of the absorbing elements that considered by scientific community is replacing absorber powder with pellets. Despite the fact that dysprosium titanate is hermetically placed in claddings manufactured of 42CrNiMo alloy, it has requirements for high-temperature compatibility with neutron-absorbing material in the environment (water vapor) under the parameters of maximum design accident with loss of coolant - LOCA (temperature up to 1200 °C and a pressure of 0.1 MPa).

The paper presents the research results on the interaction of 42CrNiMo cladding material in close contact with powder and pellets of dysprosium titanate. 42CrNiMo alloy tubes manufactured in Ukraine were taken from the batch of which the SS AEM of SE "NNEGC "Energoatom" manufactures the RCCAs for experimental and industrial operation in the VVER-1000 reactor. Dysprosium titanate pellets and powders were used as a neutron-absorbing material, manufactured according to the technology developed at the National Science Center "Kharkov Institute of Physics and Technology".

High-temperature tests were carried out in a water vapor environment in a tube furnace at atmospheric pressure and revealed that at low temperatures (up to 900 °C) during oxidation of 42CrNiMo samples, a uniform straw-colored oxide film without cracks and defects forms on their surface. As the test temperature or exposure time increases, the color of the film changes to black one with low reflectivity, that may indicate its looseness. A rough, matte gray oxide film with a metallic tint forms again on the surface of the absorbing element dummies after testing at a temperature of 1200 °C for 1 hour.

The appearance of dysprosium titanate pellets and powders does not change after testing. After tests at temperatures above 800 °C, the mass gain for the dummies is characteristic depending on the time of the isothermal testing and the temperature. After tests at a temperature of 1200 °C for 1 hour, the mass gain is 120 mg/dm^2 .

The absorbing element dummies did not change their geometric dimensions after testing and were easy to disassemble. Dysprosium titanate powder and pellets could be removed from the cladding after testing with no more difficulty than before testing. Examination of the contact area between dysprosium titanate and 42CrNiMo alloy did not reveal traces of low-melting phases, that confirms the absence of their interaction.

Basing on the obtained data, it was concluded that dysprosium titanate in the form of pellets and powder manufactured at the NFC STE NSC KIPT and 42CrNiMo alloy claddings manufactured at Ukrainian enterprises, are highly compatible in the water vapor environment at temperatures up to 1200 °C.

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