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ABSTRACT BOOK

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XV International Conference “Problems of Corrosion and Corrosion Protection of Materials“ (Corrosion-2020) was held at Lviv Palace of Arts on October 15-16, 2020. This Book of Abstract contains the results of studies are devoted to fundamentals of corrosion and corrosion assisted mechanical fracture; hydrogen and gas corrosion; new corrosion resistant materials; thermal spray, electroplated and other coatings; inhibitor, biocidal and electrochemical protection; testing methods and corrosion control; corrosion protection of oil and gas industry and chemical equipment.

In the authors edition.

CONFERENCE TOPICS:

- fundamentals of corrosion and corrosion assisted mechanical fracture;
- hydrogen and gas corrosion;
- new corrosion resistant materials and coatings;
- inhibitor and biocidal protection;
- electrochemical protection;
- testing methods and corrosion control;
- corrosion protected equipment of the oil and gas, chemical and energy industries.

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INFLUENCE OF CHROMIUM SALTS ON CORROSION OF INCOLOY 800 H/HT ALLOY IN FLUORIDE EUTECTIC MELT FLINAK

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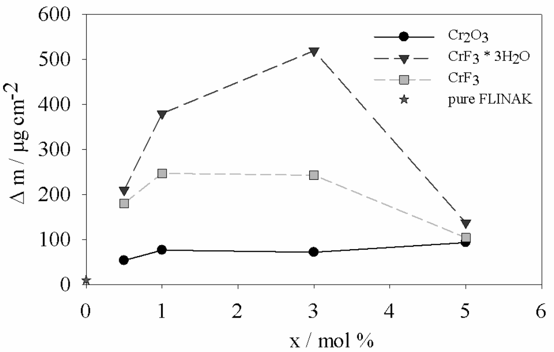
The effect of three chromium salts – potential impurities was analysed with the assumed effect of increasing the corrosion efficiency of eutectic mixture FLINAK on model alloy Incoloy 800H/HT. The occurrence of similar mixtures using superalloys is predicted in the future for 4th generation molten salts nuclear reactors and have been studied by various authors from different perspectives [1, 2, 3]. Salts containing bound chromium, oxygen, fluorine and water (namely $CrF_3.3H_2O$, CrF_3 and Cr_2O_3) were used to observe their corrosiveness through dependence on the weight loss of the samples. One of the main ideas of this work was search for corrosion suppressor that could be added into the system to reverse or slow down overall corrosion process. Experiments consisted of static tests, with samples (diameter 12 mm, thickness 1.2 mm) placed in prepared mixtures (25 g) with different salt concentrations (x = 0, 0.5, 1, 3, 5 mol %). A glove-box furnace with an argon atmosphere was used. The SEM analyses of the surfaces shown corrosion attack on all samples. The surfaces of the samples, which was exposed to concentrations of more than 1 mol % of hydrated CrF_3 appeared to be most damaged with comparison against all other FLINAK mixtures. The SEM-EDX cross-sections shown dealloying of the elements from surfaces, mainly chromium and iron, which is in agreement with general corrosion theory. The process of forming corrosion products was demonstrated by WD-XRF complementary analysis of the mixtures after corrosion. The higher chromium and iron content in the mixtures meant a higher weight loss of material. Gravimetric analysis shown strong dependence of weight changes on concentration of added salts. It has been found that there is always a different corrosion resistance of the material depending on the concentration of cation and / or anion present in the corrosion mixture. The corrosion rate of the material with acidic or hydrated salts is several times higher than that of oxides. It is assumed that the main corrosion mechanism involves the formation of gaseous HF, which preferably reacts with the alloying element to form more volatile or soluble corrosion product depending on Gibbs formation enthalpy. In the case of addition of oxides to molten mixture, this may be a factor that may help to suppress the corrosion reaction when it's detected in power plant's rapid protection system in the future.



1. V. Pavlik, M. Kontrik, M. Boca Corrosion behaviour of Incoloz 800H/HT in the fluoride molten salt Flinak + MFx (MFx = CrF3, FeF2, FeF3 and NiF2) // New J.Chem. – 2015. – Vol. 39. – P. 9841–9847.
2. N.S. Patel, V. Pavlik, M. Boca High-Temperature Corrosion Behavior of Superalloys in Molten Salts – A Review // Crit. Rev. Solid State Mater. Sci. – 2017. – Vol. 42. No. 1. – P. 83–97.
3. V. Pavlik, P. Barborik, M. Boca, Z. Vaskova Interaction of metallic zirconium and its alloys Zry-2 and E110 with molten eutectic salt of LiF-NaF-KF containing zirconium fluoride components // Chem. Pap. – 2016. – Vol. 70. – Iss. 2 – P. 197–205.

CORROSION RESISTANCE OF $[(Zn\text{-}Ni)_1/(Zn\text{-}Ni)_2]_n$ COATINGS IN COMPARISON WITH Zn-Ni ALLOY COATINGS

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Multilayer coatings consisting of periodically alternating layers of different compositions with a thickness of about 100 nm each and obtained by various physical methods show improved functional properties both as compared with corresponding alloys and metal coatings. The opportunity to improve the performance of coatings solves the urgent task of resource saving in many industries. Electrochemical methods of metals and alloys deposition have advantages associated with the use of simpler equipment and the ability to treat parts of various shapes and sizes.

The zinc-nickel alloy used to protect steel parts from corrosion [1-3] is an example of the influence of both chemical and phase composition on the properties of the resulting coatings, including their protective properties.

Zinc-nickel alloy coatings were deposited from a pyrophosphate-citrate electrolyte on low-carbon steel samples in the galvanostatic mode. Multilayer coatings consisting of layers of alloys of different chemical and phase compositions were deposited using a two-pulse galvanostatic method. The corrosion behavior of samples with multilayer coatings was compared with alloy coatings of the same thickness and having nickel content corresponding to both the average nickel content in multilayer coatings and composition of the sublayers of multilayer coatings.

After exposure in 0.5 mol L^{-1} NaCl solution for half an hour, the corrosion potentials of multilayer coatings with average nickel content in the range of 9.8-22.3% practically do not differ from the corrosion potentials of freshly deposited Zn-Ni alloy coatings with the same nickel content.

Long-term monitoring of the stationary potentials of coated samples, with periodic updating of the NaCl solution, reveals significant differences in the kinetics of corrosion dissolution of the coatings. As zinc dissolves from the coating, the potentials of all coatings increased with time shifting to the potential of the steel substrate, after which the sacrificial protection nature of the coating ends. The shape of this dependence is practically same in the case of multilayer and single-layer coatings containing 9.8% nickel. The time until the potential of the steel base reaches in both cases did not exceed a week. Coatings with nickel content close to the composition of γ-phase reached the potential of the steel substrate in 8 days, while it took about 20 days for multilayer coatings. Both single-layer and multilayer coatings with excess nickel content with respect to the γ-phase remained sacrificial for 38 and 67 days, respectively.

1. A. Tozar, I.H. Karahan Structural and corrosion protection properties of electrochemically deposited nano-sized Zn–Ni alloy coatings // Appl. Surf. Sci. – 2014. – Vol. 318. – P. 15–23.
2. El. Hajjami, M.P. Gigandet, M. De Petris-Wery, J.C. Catonne, J.J. Duprat, L. Thiery, F. Raulin, N. Pommier, B. Starck, P. Remy Characterization of thin Zn–Ni alloy coatings electrodeposited on low carbon steel // Appl. Surf. Sci. – 2007. – Vol. 254. – P. 480–489.
3. C.A.M. Dutra, J.W.J. Silva, R.Z. Nakazato Corrosion Resistance of Zn and Zn-Ni Electrodeposits: Morphological Characterization and Phases Identification // Mater. Sci. Appl. – 2013. – Vol. 4. – P. 644.

IMPROVEMENT OF CORROSION RESISTANCE OF NICKEL AND NICKEL–COPPER ALLOYS VIA THEIR ELECTROPOLISHING IN A DEEP EUTECTIC SOLVENT

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Deep eutectic solvents (DESs), as a novel generation of room temperature ionic liquids, are considered to be a very promising medium to develop environmentally safe, high-performance and available processes in different branches of industry [1, 2]. DESs are composed of eutectic mixtures of different components, they are liquid at room temperatures and have an ionic character. It was earlier shown that DESs can be used as electrolytes for the environmentally safe processes of electrochemical polishing of different metals and alloys.

Among various metals that can be treated by electropolishing, nickel and its alloys occupy a special place due to their valuable physicochemical and service properties.

This work was devoted to the investigation of electropolishing of pure nickel and nickel-copper alloy (51% Cu + 49% Ni, the so-called "German silver") in a deep eutectic solvent, ethaline. Ethaline is a eutectic mixture of ethylene glycol and choline chloride (66.67 mol.% and 33.33 mol.%, respectively).

It was established that the quality of electropolishing treatment that is characterized by the roughness coefficient mainly depends on the electrochemical polishing duration, applied potential and electrolyte temperature. The electrochemical polishing duration should be about 20–30 min. At smaller values of anodic treatment duration, the extent of surface leveling is weakly pronounced; at greater time, the metal surface would be excessively etched.

The applied potential affects the roughness coefficient after the treatment in a complicated manner. The main trend implies that better results (i.e. lower roughness coefficient) are observed when the potential lies in the range of a passive state of the metal. Electropolishing at the potentials corresponding to the area of active anodic dissolution causes only slight surface leveling.

Electrolyte temperature proved to be the most important factor determining the finished value of roughness coefficient. Electropolishing at relatively low temperatures (about 20°C) ensures satisfactory surface leveling and provides decreasing the roughness coefficient and smoothing the surface morphology. An increase in temperature leads to the reduction of electrolyte viscosity and hence to the worsening of the surface quality after anodic treatment in ethaline. When the temperature approaches about 40–50°C, the surface leveling cannot be achieved at any values of electrode potential and processing time for both nickel and nickel-copper alloy.

Electropolishing of Ni and Ni–Cu alloy in ethaline appreciably affects the corrosion performance of the treated metal surface. The corrosion resistance was evaluated by means of electrochemical impedance spectroscopy in 3% NaCl aqueous solution at 25°C. It was determined that there is a good correlation between the achieved roughness coefficient and polarization resistance of the corrosion reaction calculated from the recorded Nyquist plots. The less the roughness coefficient of the electropolished surface, the greater is the value of polarization resistance. This may be explained by the fact that electrochemical polishing ensures preferential removal (dissolution) of the surface areas corresponding to the microdefects that facilitate corrosion damage of a metal [3].

1. E. L. Smith, A. P. Abbott, K. S. Ryder Deep eutectic solvents (DESs) and their applications // Chem. Rev. – 2014. – Vol. 114. – P. 11060–11082.
2. A. P. Abbott, K. S. Ryder, U. König Electrofinishing of metals using eutectic based ionic liquids // Trans. Inst. Met. Finish. – 2008. – Vol. 86. – P. 196–204.
3. A. A. Kityk, V. S. Protsenko, F. I. Danilov, O. V. Kun, S. A. Korniy Electropolishing of aluminium in a deep eutectic solvent // Surf. Coat. Technol. – 2019. – Vol. 375. – P. 143–149.

EFFECT OF ELECTROPOLISHING OF METALS AND ALLOYS BY USING A DEEP EUTECTIC SOLVENT ON THEIR CORROSION CHARACTERISTICS

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Electropolishing is an electrochemical technique based on controlled partial anodic dissolution of a metal surface to achieve a reduction in surface roughness and hence an increase in optical reflectivity. Common procedures of metals and alloys electropolishing involve corrosive electrolytes at high temperatures [1, 2]. An eco-friendly promising and highly efficient alternative to “classical” polishing electrolytes can be based on a deep eutectic solvents (DESs). DESs are characterized by the availability of components, ease of synthesis, environmental safety, biodegradability, a wide window of electrochemical stability, thermal and chemical stability, etc. [3]. A unique combination of high viscosity and high electrical conductivity makes DESs a suitable medium for anodic surface treatment of metals and alloys.

We stated that a deep eutectic solvent Ethaline, which based on choline chloride and ethylene glycol mixed in a molar ratio of components of 1:2, respectively, can be used at room temperatures as a polishing electrolyte for improving anticorrosion properties of aluminium [4], aluminium alloy (AlMg), stainless steels (Mn AISI, AISI 304 and 316 Ti) and bronzes A 22 and A 712 (Table 1).

Table 1. Corrosion parameters for different alloys in 10 wt.% NaCl solution at 298 K calculated from Tafel's plots

Alloy		Corrosion parameter			Alloy		Corrosion parameter		
		E_{corr}, V	i_{corr}, A cm^{-2}	CR, mm/year			E_{corr}, V	i_{corr}, A cm^{-2}	CR, mm/year
AlMg	*unp.	-0.984	8.600×10^{-7}	0.0096	A 712	unp.	-0.226	1.396×10^{-5}	0.1699
	el.	-0.789	5.765×10^{-7}	0.0064		el.	-0.204	1.295×10^{-5}	0.1576
AISI 304	unp.	-0.238	3.329×10^{-6}	0.0386	A 22	unp.	-0.304	1.176×10^{-5}	0.1635
	el.	-0.024	1.876×10^{-6}	0.0218		el.	-0.241	8.447×10^{-6}	0.1174
Mn AISI	unp.	-0.315	1.118×10^{-5}	0.1313	AISI 316 Ti	unp.	-0.143	1.624×10^{-6}	0.0186
	el.	-0.261	4.894×10^{-6}	0.0575		el.	-0.017	4.964×10^{-7}	0.0028

*unp. – unpolished, el. – electropolished

It was shown that electrochemical anodic treatment of alloys in Ethaline can be used as effective method for improving not only the surface appearance (to increase gloss, reduce roughness and amount of surface defects) and some physico-mechanical properties (to increase microhardness, wear resistance, etc.) but also corrosion resistance. It is important to note that this method of surface treatment is fast, affordable, resource-saving and environmentally friendly.

1. A.S. Mansour, T.H. El-Sherify Electropolishing of single-phase Cu-Sn alloys in H_3PO_4 // Surf. Technol. – 1981. – Vol. 13. – P. 325–329.
2. C.-C. Lin, C.-C. Hu, T.-C. Lee Electropolishing of 304 stainless steel: Interactive effects of glycerol content, bath temperature, and current density on surface roughness and morphology // Surf. Coat. Technol. – 2009. – Vol. 204. Iss. 4. – P. 448–454.
3. E.L. Smith, A.P. Abbott, K.S. Ryder Deep eutectic solvents (DESs) and their applications // Chem. Rev. – 2014. – Vol. 114. – P. 11060–11082.
4. A.A. Kityk, V.S. Protsenko, F.I. Danilov, O.V. Kun, S.A. Korniy Electropolishing of aluminium in a deep eutectic solvent // Surface and Coatings Technology. – 2019. – Vol. 375. – P. 143–149.

PHYSIC-MECHANICAL PROPERTIES OF IRON BASED NANOCEP

Sakhnenko N.[1], *Ved' M.*[1], *Yermolenko I.*[1], *Yar-Mukhamedova G.*[2], *Karakurkchi A.*[1]
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Electrochemical with the application of thin-film coatings are quite common in the industry of high-tech countries. Nanocomposite electrolytic coatings were deposited on a substrate made of gray cast iron widely used for piston rings and other machine parts. Coatings with alloys Fe-Mo or Fe-W were obtained from a citrate electrolyte of the composition given in [1, 2]; the pH was in the range 3.0–4.5; temperature of 20–30 ºC. The coatings were formed in two modes: by direct current (dc) with varying current density i of 2.5–6.5 A/dm^2, and by pulse current (pc) with an amplitude of 2.5–8.5 A/dm^2 with a pulse duration t_{on} of 5 ms and pause time t_{off} of 20 ms [3, 4].

The microhardness of the coatings with thickness of 25–30 μm was determined on a PMT-3 device with a load of 50–100 g. The tribo-technical properties of coatings were evaluated by the friction coefficient f_{fr}. Wear resistance was determined by tests on a 2070 SMT-1 serial friction machine with gradual loading of conjugated samples from 0.2 kN to 0.8 kN according to the "disk-block" scheme and a reciprocating friction machine.

As was established the pc deposition produces nanoCEP Fe-Mo(W)MO$_x$ with a more perfect surface and a higher content of alloying components that contributes to an increase in the corrosion resistance of coatings compared with ones deposited at dc mode. These assumptions are totally confirmed by the corrosion indices of substrate material and those of Fe-Mo(W) based composites formed on cast iron (Table 1).

Table. 1. The corrosion indices of cast iron and Fe-Mo(W)-MO$_x$ coatings

pH of test medium	Cast iron		dc mode		pc mode			
			Fe-Mo-MoO$_2$		Fe-Mo-MoO$_2$		Fe-W-WO$_2$	
	E_{cor}, V	K_{h}, mm/year	E_{cor},V	K_{h}, mm/year	E_{cor},V	K_{h}, mm/year	E_{cor},V	K_{h}, mm/year
3	–0.34	1.98	–0.30	0.038	–0.31	0.030	–0.24	0.04
7	–0.55	1.15	–0.47	0.04	–0.49	0.035	–0.35	0.039
10	–0.35	0.30	–0.58	0.028	–0.60	0.021	–0.037	0.028

Studies proved that the wear resistance for the restored with coatings Fe-Mo(W)-MO$_2$ surface is of 1.7–1.8 times higher than for gray iron cast samples. The mass change of the samples Δm during tests indicates wear of the surface when the parts are worn. It is completely predictable that the wear resistance of W-containing CEP, like other mechanical properties, is higher compared to molybdenum-based ones. Hence, the physical and mechanical properties of CEP based on the Fe-Mo(W) alloys allows us to view them as the promising materials for the technologies used for the hardening of the parts made of cast iron and low-carbon steel and these can also be used by the maintenance services to repair and upgrade worn out surfaces that are operated in the environment of a different corrosiveness.

1. Ved' M. V., Sakhnenko N.D., Karakurkchi A.V., Yermolenko I.Yu., Electroplating and functional properties of Fe-Mo and Fe-Mo-W coatings //Is. of Chem. and Chem. Tech.. – 2015. – № 5-6 . – P. 53–60.
2. Ermolenko I.Yu., Ved' M.V., Karakurkchi A. V. Et al. The electrochemical behavior of Fe^{3+}-WO$_4$ $^{2-}$-Cit^{3-}and Fe^{3+}-MoO$_4$ $^{2-}$-WO$_4$ $^{2-}$-Cit^{3}systems // Issues of Chem. and Chem. Tech. – 2017. – № 5-6 (98). – P. 4–14.
3. Yar-Mukhamedova G., Ved M., Sakhnenko N., Nenastina T. Electrodeposition and properties of binary and ternary cobalt alloys with molybdenum and tungsten // App. Surf. Sci. – 2016. – Vol. 445. – P. 298–307.
4. Ved, M.V., Sakhnenko, M.D., Karakurkchi, H.V. et al. Functional properties of Fe-Mo and Fe-Mo-W galvanic alloys Materials Science.– 2016. – 51(5). – P. 701–710.

CORROSION RESISTANCE OF 17Mn1Si STEEL IN THE ENVIRONMENT WITH DIFFERENT HYDROGEN SULFIDE CONCENTRATIONS

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A high concentration of hydrogen sulfide in petroleum products can cause destroying of pipelines as a result of hydrogen sulfide stress corrosion cracking. The local corrosion on the bottom of the pipeline and the deposition of iron sulfides are the most dangerous. Standards for the concentration of hydrogen sulfide in transported oil products have been developed, what provides the safe working conditions for employees of the oil refining industry. However, the increased incidence of pipeline systems that comply with existing regulations indicates that these requirements have become -insufficient to ensure operational reliability. Therefore, the purpose of the paper was to study the effect of different hydrogen sulfide concentration and exposure time on the corrosion nature and corrosion resistance of 17Mn1Si pipe steel.

Electrochemical studies of steel were carried out in a NACE solution of 5% NaCl + 0,5% CH_3COOH + H_2S (in various concentrations: 0, 50, 750, 1500 mg/l). Ag/AgCl reference electrode and platinum auxiliary electrode were used for electrochemical tests. METAM PB-2 optical microscope was used for metallographic studies.

If hydrogen sulfide content in a NACE solution increases from 50 to 750 and 1500 mg/l, the corrosion current density of steel grows respectively from 1,2 to 1,5 and 1,8 times and electrode potentials shift from 583 mV to the negative side. When the concentration of hydrogen sulfide in the solution is 1500 mg/l, the largest potential shift (640 mV) is observed (Table 1). The shift of the electrode potential of the steel to the negative side can be associated with adsorption $(HS)^-$ ions on the electrode surface [1, 2].

Table. 1. Electrochemical peremeters of 17Mn1Si steel in NACE solution with different concentration of hydrogen sulfide

H_2S concentration, mg/l	$-E_{cor}$, mV	i_{cor}, mA/cm^2	Tafel constant, mV	
			b_a	b_c
0	583	0,040	64	104
50	604	0,047	68	107
750	615	0,079	59	106
1500	640	0,126	69	115

The Tafel constants b_a and b_c change ambiguously. They reduce with increasing of hydrogen sulfide content up to 750 mg/l and increase slightly at the concentration of hydrogen sulfide 1500 mg/l. Blistering occurs on the surface of the tube steel at the maximum H_2S concentration, which can lead to corrosion-mechanical destruction. Therefore, using of 17Mn1Si pipe steel at a hydrogen sulfide concentration of 1500 mg/l is unacceptable due to the low corrosion resistance and the high risk of steel destruction.

1. The influence of cyclic loading on fracture resistance of pipe steels and their weld joints in hydrogen sulphide environments / M. S.Khoma, M. R.Chuchman, V. R. Ivashkiv, H. M. Sysyn // Mater. Sci. – 2013. – Vol. 49. – P. 52–57.
2. Khoma M. S. Problems of fracture of metals in hydrogen-sulfide media // Mater. Sci. – 2014. – Vol. 46. – P. 190–200.

INFLUENCE OF AN ALTERNATING MAGNETIC FIELD ON THE ELECTROCHEMICAL CHARACTERISTICS OF AMORPHOUS ALLOYS IN SULFURIC ACID

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Currently, almost all areas of technical application of Fe-based amorphous metallic alloys (AMA) are based on the unique combination of corrosion, magnetic and mechanical properties which make amorphous materials one of the key elements in modern information technologies. It is also important to study the effect of various types of modification, in particular, by the alternating magnetic field on their electrochemical properties in acid solutions.

Investigating the influence of the alternating magnetic field on the properties of amorphous alloys based on Fe, it is necessary to take into account the peculiarities of magnetic properties of the base metal and doped metals.

It was investigated the effect of surface modification of amorphous alloys $Fe_{78,5}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$, $Fe_{73,1}Cu_{1,0}Nb_{3,0}Si_{15,5}B_{7,4}$ in alternating magnetic field (AMF) (50 Hz) and its influence on the alloys corrosion resistance in 0.5 M H_2SO_4 aqueous solution. For the first time, electrochemical characteristics of amorphous Fe-based alloys with various dopants in aqueous sulfuric acid solutions were determined by chronopotentimetry and cyclic voltammetry.

In investigation of the alloys corrosion resistance by cyclic voltammetry, the rate of scanning potentials is important. The electrochemical characteristics of amorphous alloys were determined at 10 and 50 mV/s rate. Investigation of the corrosion resistance of amorphous alloys by cyclic voltammetry at lower scanning rate makes it possible to evaluate the contribution of slower stages in corrosion processes on the surface of the studied amorphous alloys. It was determined that with the increase of the potential scanning rate, as well as with the increase of the pre-exposure time in an alternating magnetic field, the corrosion potentials shift to the anodic side, in particular, the $Fe_{78,5}Ni_{1,0}Mo_{0,5}B_{6,0}Si_{14,0}$ alloy is passivated. According to the results of electrochemical investigation, the alloy $Fe_{73,1}Cu_{1,0}Nb_{3,0}Si_{15,5}B_{7,4}$ proved to be more corrosion resistant, and the modification in the AMF causes an increase in its corrosion resistance, which is reflected in the shift of the potentials to the anodic side.

After keeping in the alternating magnetic field of the Fe-based alloy samples, the elemental composition of the surface also changes. An increase in Fe content is observed.

Therefore, the corrosion resistance of AMA samples is conditioned by the elemental composition of the samples and the corrosive environment. It was determined that the selection of the duration of keeping in an alternating magnetic field can change the physico-chemical properties of amorphous alloys.

REAL-TIME ONLINE CORROSION MONITORING IN THE FIELD – NEW ECN EVALUATION TECHNOLOGY

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The number of tools for reliable industrial online corrosion monitoring is small and the individual tools face different application limits. This paper reports on an innovative automated small size (hand-held) electrochemical noise (ECN) measuring device with a new ECN diagnosis software (CoulCount) which together allow real-time online corrosion monitoring in practically all fields of industry. The advantage is its easy implementation in industrial processes and its high versatility in application. The corrosion sensor basically consists of two freely corroding electrodes (surface area ca. 1 cm^2 per electrode) made of the metals whose corrosion performance is to be investigated. A reference electrode which always creates problems in long term industrial electrochemical measurements is not needed, although it can be implemented in the sensor for orientating LPR measurements. The measuring electrodes can be similar or dissimilar depending on the individual corrosion problem. This differentiates the CoulCount-method fundamentally from all other classic ECN measurements. Thus, it is likewise possible to monitor the corrosion intensity of a pipeline material or to monitor the efficiency of an inhibitor under conditions of galvanic coupling between different materials. The method works under corrosion conditions in crevices and under deposits. It can be used to monitor the onset of flow induced localized corrosion and, thus, can evaluate critical flow intensities. The paper will give examples on the versatility of the CoulCount-method including examples from oil and gas field application. The electrochemical measuring device which runs on accus and can be recharged even with a car battery, functions as potentiostat, galvanostat and zero resistance ammeter with an output of 300 mV. It contains software for CoulCount-, Linear Polarization Resistance(LPR)-, Electrochemical Potentiodynamic Reactivation(EPR)-, and impedance measurements and is commercially available. With a graphic program the progress of the data collection and the corrosion intensity can be followed in real time on a monitor.

CREEP MODEL OF CONCRETE UNDER SULFATE ATTACK

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In this study, the creep model of concrete under sulfate attack is experimentally and theoretically investigated. The concrete samples were immersed in sulfate solution with different concentration (0%, 3%, 8%), and the deformation of samples were measured by an elongation tester at different corrosion time (shown in Fig. 1). It was found that concrete creep takes place, and such a creep deformation includes damage [1, 2] and viscoelastic deformation. The dominant mechanism for the creep is the action of internal expansive stress produced by the delayed ettringite, which is chemical reaction production between sulfate ions and pore solution in concrete (shown in Fig. 2). By means of micromechanics theory combined with chemical reaction rate equation, the creep constitutive equation is derived, and the creep model depends on two characterized time, one is the relaxation time, and the other is the chemical reaction characterized time. Experimental results indicate that the model could better express the behavior of concrete creep due to sulfate attack.

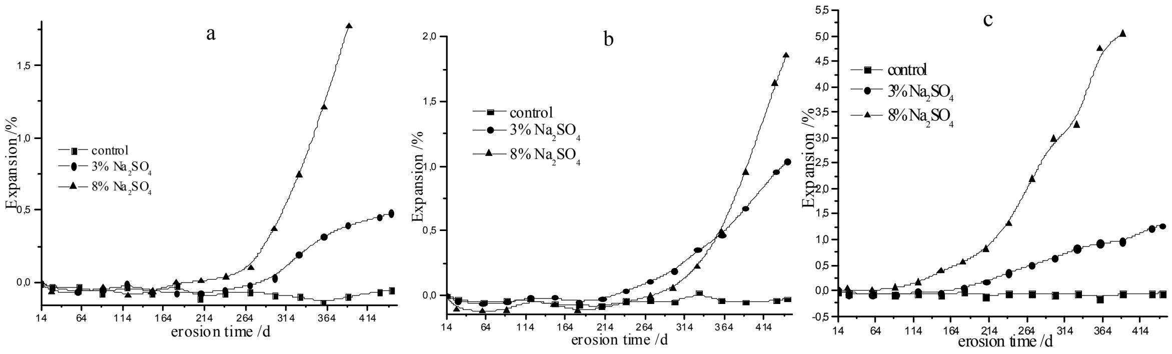

Fig. 1. The expansion of concrete under sulfate attack

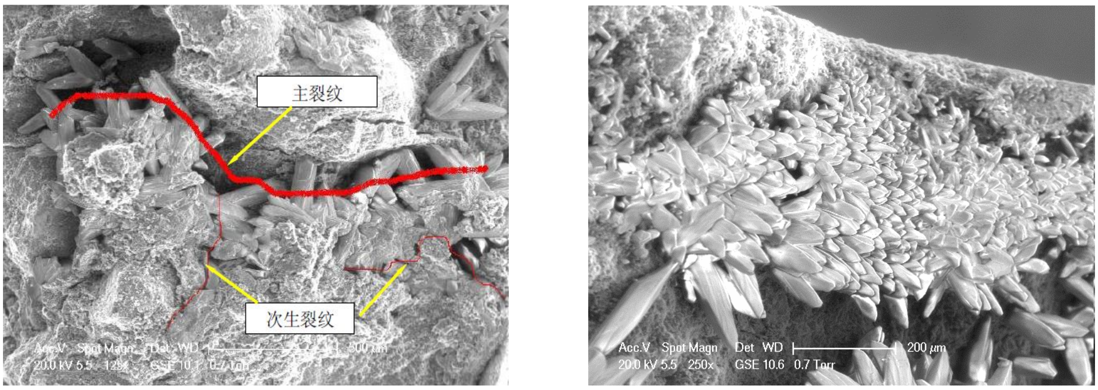

Fig. 2. SEM image of delayed ettringite

1. J. Chen, M. Jiang, J.Zhu, Damage evolution in cement mortar due to erosion of sulphate // Corr. Sci. – 2008. – Vol. 50.– P. 2478–2483.
2. T. Ikumi, S.H.P. Cavalaro, I.Segura, A. Aguado Alternative methodology to consider damage and expansions in external sulfate attack modeling // Cem. Concr. Res. – 2014. – Vol. 63. – P. 105–116.

EFFECT OF HYDROGEN ON INTERFACIAL STRENGTH OF HYBRID COMPOSITE MATERIALS

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Composites reinforced with fibers of synthetic or natural materials have been found to be the most promising and discerning material due to exceptional performance in the numerous fields of applications. Fiber-reinforced polymer composite is characterized not only high strength to weight ratio, but also such properties as high durability; flexural strength; and resistance to corrosion, wear, impact, etc. Composite materials have widely applied in mechanical, construction, aerospace, automobile, biomedical, marine, and many other industries. Performance of composite materials predominantly depends on their constituent elements, manufacturing techniques, and interfacial strength. The point of weakness in such hybrid composites often is the interface between the different materials. These discontinuities will lead to stress peaks when the interface is loaded. Therefore, a special attention is paid to enhancing the interfacial strength of hybrid composites. To improve the interface performance the combination from different joints is intended.

In this paper main factors influencing interfacial strength of hybrid composite materials, including influence of hydrogenation and environmental ageing, are considered and discussed. For experimental characterization, the mode I fracture toughness test was selected as a most sensitive indicator of the material degradation. Typical measurement stand is shown in Fig. 1.

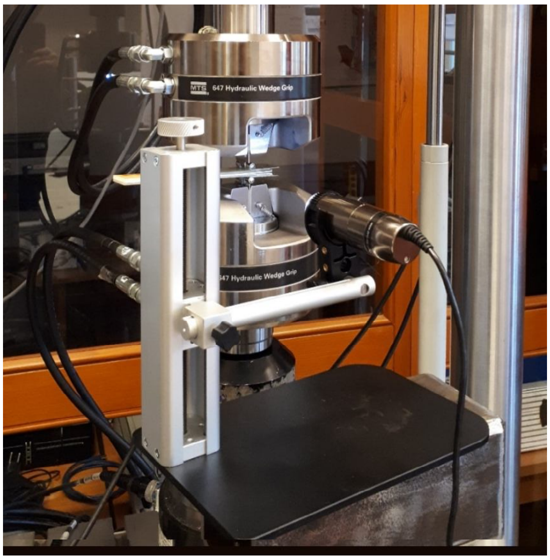

Fig. 1. Mode I fracture toughness test of the composite hybrid material

Acknowledgements

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DEPOSITION OF BRINE COMPONENTS ON MATERIALS IN GEOTHERMAL CONDITIONS

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Since geothermal wells are a feasible energy source to replace fossil fuel supply, many technologies have been developed to take advantage of geothermal energy. Nevertheless, service conditions in geothermal facilities are in many cases extreme in terms of corrosion due to the chemical composition of hydrothermal fluids and temperatures. Therefore, materials selection based on preliminary material qualification is essential to guarantee a secure and reliable operation of the facilities. During operation of a geothermal research facility in Groß Schönebeck copper and lead effects have been found downhole. Occurring mechanisms and measures to prevent precipitation or scaling needed to be investigated as well as potential influences of such precipitates on corrosion resistance of metallic materials used for equipment.

This contribution deals with the evaluation of the corrosion behavior of carbon steel and corrosion resistant alloys in copper and/or lead containing artificial geothermal water, simulating the conditions in the Northern German Basin.

The behavior of these materials in an artificial geothermal water obtained by electrochemical measurements and exposure tests are presented. While carbon steel exhibits precipitation and deposition, higher alloyed material shows different response to such species and a higher resistance in saline geothermal water.

Basing on these results the suitability of the investigated corrosion resistant alloy is given for use in such conditions, whereas carbon steel creates difficulties due to its susceptibility to Cu- and Pb-precipitation.

BARRIER PROPERTIES OF THE GRAPHENE LAYER IN CORROSIVE PROCESSES OF THE SYSTEM: ELECTROLYTIC LAYER (Zn, Mo) ON A STEEL SUBSTRATE

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The graphene layer can be a barrier layer limiting the corrosion rate of substrate, such as a steel substrate with a layer of zinc alloy with increased corrosion protection (Zn-Mo) [1, 2]. Such layers system can be competitive to currently produced in the industry ecological duplex layers (zinc coating on a steel substrate - organic polymer) not containing layers with chromium (VI).The workpresents the results of analysis of the corrosion process in Zn-Mo coatings electrolytically deposited on a steel substrate and covered with a graphene layer.

The alloy layers were deposited under steady hydrodynamic conditions in a system with a rotating disk electrode at a temperature of 20 ± 1°C. The chemical composition of molybdenum-containing samples was tested by X-ray fluorescence analysis with WD-XRF - Primini, Rigaku. X-ray structural studies of electrolytically deposited Zn-Mo layers were carried out using a Bruker D8 Discover diffractometer.The corrosion test was carried out in conditions of high humidity (constant partial steam pressure of RH = 82%) and elevated temperature (50°C).

The obtained results indicate that the graphene layer under the conditions of the corrosion test carried out significantly reduces the rate of the corrosion process in relation to samples not covered with the graphene layer.Corrosion occurs in areas where the graphene layer is defective in a localized manner.However, the increase in molybdenum content in the hexagonal phase to a content of approx. 0.4% wt. increases the corrosion rate even twice compared to the result obtained for the molybdenum-free zinc phase.This may indicate a lack of surfaces passivation of the(Zn, Mo) phase crystallites, which leads to an increase in corrosion rate resulting from a decrease in the crystallites size as well as from an increase in stress in these crystallites.

1. N.T. Kirkland, T. Schiller, N. Medhekar, N. Birbilis, Exploring graphene as a corrosion protection barrier // Corrosion Science. – 2012. – Vol. 56. – P. 1–4.
2. Karanveer S. Aneja, H.L. Mallika Böhm, A.S. Khanna, Siva Böhm, Functionalised graphene as a barrier against corrosion // FlatChem. –2017. –Vol. 1. – P. 11–19.

CORROSION MONITORING DURING COMMISSIONING OF HEATING AND COOLING SYSTEMSIN NEW REAL ESTATE

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Interior corrosion and fouling in closed water loop systems for heating and/or cooling, may have negative effects e.g. energy losses or defects of various components which are in contact with fill water (Fig. 1).Reports of non-optimum conditions and corrosion effects include several relatively new buildings and some which were not yet occupied. Often, the commissioning phase is decisive for the service life of a system. The service life depends on the early development of the metal surfaces and their (non-)protective properties. In alkaline surroundings, carbon steel forms compact films of oxides which passivate and protect the underlying metal as a barrier between the metal and the liquid environment. Non-protective properties result from surface impurities and roughness from continuous corrosion. The surface heterogeneity related to roughness facilitates the formation of microscopic corrosion cells and the local breakdown of thin oxide films. In this study, important processes for the durability of a system e.g.alkalization a remonitored online in four buildings with 2-3 loop systems (two hotels, one museum and one administrative building) using the field parameters redox potential, pH, dissolved oxygen, electrical conductivity and temperature. These field parameters are aggregated according to (Fig. 2) to give information about the ferrous iron concentration, ferric-mineral build-up kinetics as well as microbial processes. The sensor values are complemented with chemical analysis of fill water (e.g. Fig. 3). If the initially rapid corrosion rates do not decrease during commissioning, errors in planning or construction that hinder stabilization can be fixed to avoid further damage. Success of countermeasures can be monitored. The first results show that at least in one cooling system, total and ferrous iron values remain around 40 mg/L and the corrosion rate is elevated.

Fig. 1. Photograph of the inside of a cooling convector in a new building

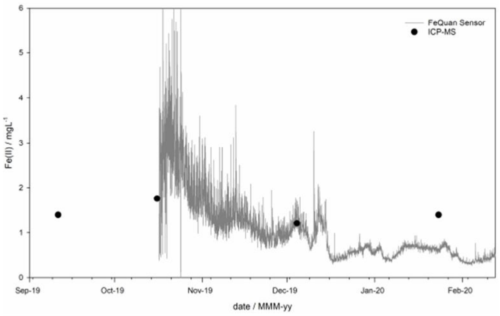

Fig. 2. Fe(II) determined by sensor values (line) and by ICP-MS (dots). Values are from a heating system in a high-rise building with hotel-business

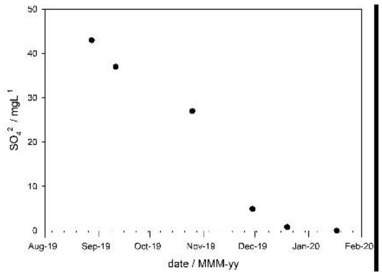

Fig. 3. Sulfate concentration is decreasing

1. Wiegand M, Opel O, Eggerichs T, Otte T, Zargari M, Plesser S. Corrosion monitoring of heating and cooling systems in buildings using pH, redox potential, dissolved oxygen, temperature and conductivity measurements. In: European Corrosion Congress (Eurocorr 2017) and 20th International Corrosion Congress and Process Safety Congress 2017 - Corrosion control for safer living. – 2017.
2. Opel O, Wiegand M, Neumann K, Zargari M, Plesser S. Corrosion in Heating and Cooling Water Circuits - A Field Study // Energy Procedia. – 2018. – Vol. 155. – P. 359–66.
3. Landolt D. Corrosion and surface chemistry of metals. 1. ed. Lausanne, Boca Raton, Fla.: EPFL Press; CRC Press. – 2007. (Engineering sciences Materials).
4. Opel O, Eggerichs T, Otte T, Ruck W. Monitoring of microbially mediated corrosion and scaling processes using redox potential measurements // Bioelectrochemistry. – 2014. – Vol. 97. – P. 137–44.

ASSESTMENT OF LOCALIZED CORROSION RESISTANCE OF DUPLEX STAINLESS STEEL 2205

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Duplex Stainless Steel 2205 it’s an alloy containing 22% of Cr and 5% of Ni. Its Microstructure it’s a matrix of d-ferrite BCC with g-austenite FCC grains islands in a 50/50 ratio. DSS is used in industry due its high mechanical strength and corrosion resistance, better than ferritic or austenitic stainless steels [1]. However, most structures or components contain welding joints, and this changes the d/g microstructural balance. Also, detrimental phases such as s or c, besides Cr Carbides or nitrides can precipitate. The formation of these phases weakens the passive film due to Cr depletion at the adjacent zones surrounding, this increases the localized corrosion susceptibility and it is said that the steel has been sensitized [2]. There are three main zones at welding joints: Base metal, Fusion Zone which is formed of filler metal, and Heat Affected Zone that is adjacent to Fusion Zone and is where most of the microstructural changes take place. Post welding heat treatments are common practice to minimize sensitization issues, this works for small components, however, for large structures it’s very expensive and it’s not feasible to do. This research work assesses the effect of the application of a 3 mT External Magnetic Field during Gas Metal Arc Welding process of Duplex Stainless Steel 2205 in terms of microstructural evolution associated to welding thermal cycles and localized corrosion resistance.

During the welding process, an Electromagnetic Interaction of Low Intensity was induced by applying axial External Electromagnetic Fields of 0, 3 and 12 mT. Microstructural characterization and the assessment of localized corrosion resistance in terms of pitting corrosion were conducted.

Resistance to nucleation and growth of fatigue cracks was also evaluated in the Low Cycle Fatigue regime was used to observe the short crack behaviour in a Fatigue Corrosion Test. The 3mT Electromagnetic Interaction of Low Intensity was found to improve the localized corrosion resistance but the 12mT one presented no improvement in this aspect, in comparison to 0 mT. The resistance to crack initiation and fracture toughness were also improved with the application of the 3 mTExternal Electromagnetic Fields due to the modification of the microstructural evolution during the thermal cycle involved in the welding process.

Based on experimental research criterial value of SIF for the stainless-steel duplex 2205 is determined. Applying analytical relations for SIF characteristics value of crack like defects length, that may take place in the considered frame construction are calculated. Engineering calculations for assessment of the given object durability are suggested and presented with modelled crack like defects of various form and geometry on the base of load cycles number.

1. R. Strubbia, S. Hereñú, M.C. Marinelli, I. AlvarezArmas. Short crack nucleation and growth in lean duplex stainless steels fatigue dat room temperatura // International Journal of Fatigue. –2012. –Vol. 41. – P. 90–94.
2. J.-O. Nilsson.Super Duplex Stainless Steel // Mater.Sci. and Tech.– 1992. –Vol. 8, Iss. 8. – P. 685–700.

ASSESTMENT OF FRACTURE BEHAVIOR OF DISSIMILAR WELDING OF INCONEL 600

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Inconel 600 is a nickel superalloy base, widely used in industry; mainly in applications such as processing plants natural gas, capacitors in the treatment of fatty acids in food storage tanks at elevated pressure, among others. As components are subjected to cyclic load fluctuations during its lifetime, where a crack can nuclear microscopic scale, followed by growth at a macroscopic level and finally causing material failure.

Fatigue may be defined as a deterioration under repeated cycles of stress or strain, leading to a progressive cracking until produces failure in the material. The number of load cycles that can be expected during the lifetime of a component may oscillate depending on the material and operating conditions [1].

Cracks, are generated are known discontinuities, defects in materials, therefore, in the period of crack initiation, fatigue phenomenon of surface material. [1]. The importance of the material surface is essential for the study of fatigue life, since most of the components in service have irregularities showing significant influence that affects the fatigue strength of the material.

The machining of the material, and integrity, such as cavities, microcracks, residual stresses; are known to play a key role in performance, particularly under high cycle fatigue [2]. Previous studies show that the onset of fatigue cracking occurs due to the accumulation of damage by plastic deformation. This damage is manifested in persistent slip bands (PSB), intrusions or extrusions in the external surface of fatigued samples. The start of fatigue cracks occurs to over the PSB or intrusions that are joined together and lead to material failure [2], because the slip is not a reversible process resulting from strain hardening or by the formation of an oxide layer.

The start of a process of crack growth is very important in the analysis of the fatigue life, covering much of the same to failure, although often this process is not very relevant, because it material already has type crack defects, which, interested growth thereof.

Although the start transition to crack growth is not well defined; because such change depends on microstructural barriers, which depend on each material. Know the start period is completed, when the growth of microcracks, longer depends on the surface condition, and passes the resistance to crack growth is controlled by the growth rate of material [3].

Fatigue occurs at a stress level below the elastic limit, by thus no plastic deformation is observed on the surface and is called high cycle.

The main objective of this study was to research and analyze the fatigue life of test pieces of dissimilar welding Inconel 600 in arrival condition and aged for a period of 100h and 300h with filler material ER-310, with dimensions of 6x6x100 mm, by a bending test at three points.

1. Z. Chen, J.J. Moverare, R. L. Peng, S. Johansson, D. Gustafsson,On the conjoint influence of broaching and heat treatment on bending fatigue behavior of Inconel 718 // Mater. Sci. and Eng. – 2016 –. Vol. 671 – P. 158–169.
2. M. Waqas Tofique, J. Bergström, C. Burman, Very high cycle fatigue crack initiation mechanisms in different engineering alloys // Procedia Structural Integrity. – 2016 – Vol. 2. – P. 1181–1190.
3. J. Schijve Fatigue crack growth under variable-amplitude loading. // Fatigue and fracture, – 1996. – Vol. 19. – P. 110–33.

INFLUENCE OF NANOSTRUCTURING ON CORROSION PROPERTIES OF Al-BASED AMORPHOUS METALLIC ALLOYS

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The aim of research: Investigation of electrochemical parameters of Al-based amorphous alloys doped by Y and Gd in alkaline solutions (1M KOH) and microhardness determination on the third step of the AMA crystallization.

Investigated materials: The Al-RE amorphous ribbons of 30 μm thickness were produced by melt spinning method *(Physics of Metals Institute, NAS Ukraine, Kyiv)* with the following compositions: $Al_{87}Y_5Ni_8$, $Al_{87}Gd_5Ni_8$.

Methods of investigation: Differential scanning calorimetry (DSC), scanning electron microscopy (SEM), voltammetric method in the potentiodynamic mode; microhardness by Vicker's method; X-ray energy-dispersive spectroscopy.

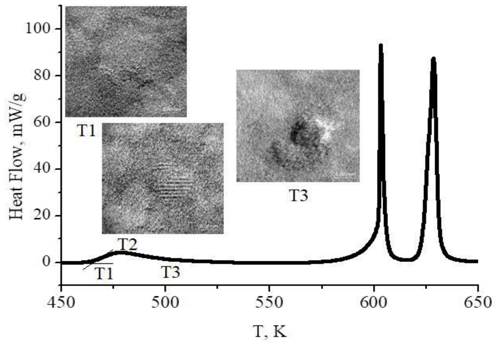


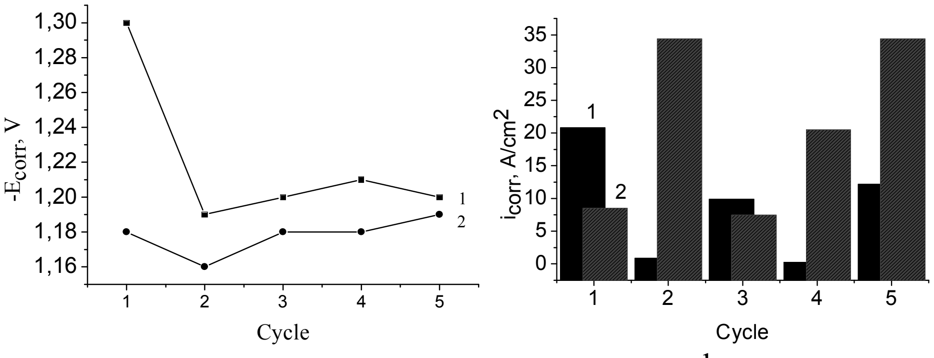
Fig. 1. DSC-curves of $Al_{87}Gd_5Ni_8$ with a heating rate of10 K/min .

Due to the anneling (T_3 = 532 K) of $Al_{87}Y_5Ni_8$ three-dimensional nanocrystals are formed in the amorphous matrix, when interecting to the alkaline environment they became centers of corrosion.

The AMA has been investigated using differential scanning calorimetry (DSC) with a heating rate of 10 K/min at the Silesian University Institute of Materials Science with the use of Perkin-Elmer Pyris 1. It is known that in the temperature range of the first DSC maximum, the nanoscale AMA is carried out. From the DSC [1] curves (fig.1), the temperature of origin (T_1), growth (T_2) and the formation of α-Al (T_3) nanocrystals were determined (Table 1).

Table 1. Temperatures (T ± 5K) of phase transitions of Al-based amorphous alloy AMA

AMA	β, K/min	T_1, К	T_2, К	T_3, К
$Al_{87}Y_5Ni_8$	10	491	501	532
$Al_{87}Gd_5Ni_8$		458	474	510



a b

Fig. 2. a – Dependence of corrosion potential on the polarization cycle of AMAs: *1- $Al_{87}Y_5Ni_8$, 2- $Al_{87}Gd_5Ni_8$;*
b – Dependence of corrosion currents on the polarization cycle of AMAs: *1- $Al_{87}Y_5Ni_8$, 2- $Al_{87}Gd_5Ni_8$*

Conclusions

Complete replacement of Y by Gd leads to the activation of electrochemical reactions, despite this, the AMA doped by Gd withstands a polarization load of -1,5 to +1,0 V.

1. Ahmadi S. Nanocrystallization of α– Fe crystals in $Fe_{52}Cr_{18}Mo_7B_{16}C_4Nb_3$ Bulk Amorphous Alloy // J. Mater. Sci. Technol. – 2011. – Vol. 27. № 6. – P. 497–502.

CORROSION RESISTANCE OF AMORPHOUS METAL ALLOYS $Co_{72}Si_{11}B_{12}$ AS ELECTRODES IN HYDROGEN EVOLUTION REACTIONS IN ALKALINE SOLUTION

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Due to close order of atoms amorphous metal alloys (AMA) have high corrosion resistance, which exceeds the resistance of stainless steels. Cobalt-based AMA have been used for cutting tools operating in aggressive chemical environments, in serial television production and instrumentation [1-2]. Expanding the use of AMA makes it necessary to evaluate the effect of the aggressive environment temperature on Cobalt-based alloys corrosion resistance.

The corrosion of the AMA samples was investigated electrochemically (Fig.1) in a 1 M solution of KOH relative to a chlorine-silver electrode at different range of temperatures (T_1 = 293 K, T_2 = 303 K, T_3 = 313 K, T_4 = 323 K, T_5 = 333 K). Electrode polarization occurred within -1.5 ... + 1.0 V at a potential sweep rate of 50 mV/s.

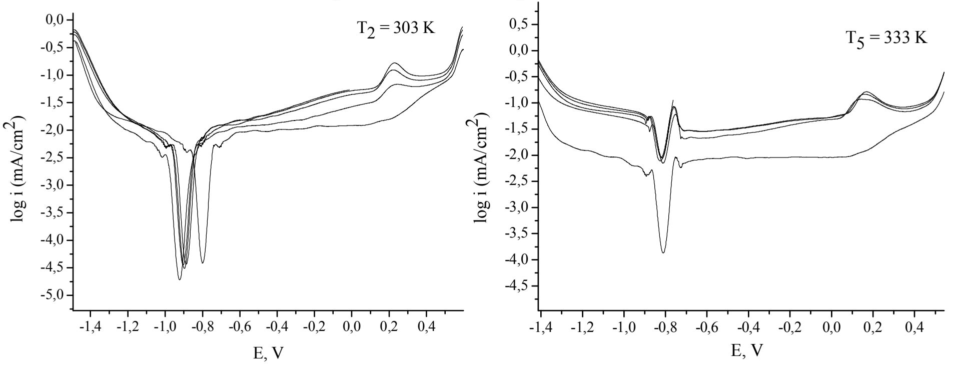

Fig. 1. Anodic polarization curves for $Co_{72}Si_{11}B_{12}$ in 1 M KOH at different temperature.

Results in Table 1 show that due to the polarization of the AMA electrode, the corrosion potential decreases from -1.35 to -0.79 V. Increasing the temperature of the solution from 293 to 333 K leads to a shift of the corrosion potential (E_{cor}) in the anode side, which indicates some difficulties in the oxidation processes, because of surface passivation. Corrosion currents (i_{cor}) throughout the temperature range of the solution remain constant.

At the electrode surface oxidation-reduction reactions occur at the same rate, indicating the reversibility of the processes confirmed by calculated coefficients *a* and *b* of the Tafel equation. The coefficient *a* indicates that the morphology of the surface of the AMA electrodes changes due to polarization.

Table 1. Corrosion characteristics of AMA in 1 M KOH at T = 293K

T,K	E_{cor}, V	i_{cor}, A/cm^2×10^8	a_{red}	b_{red}, V	a_{ox}	b_{ox}, V
293	-1.31	5.01	-1.31	-0.02	-1.25	0.03
303	-0.89	5.49	-7.31	-0.03	-1.02	0.02
313	-0.94	4.46	-0.95	-0.02	-0.92	0.03
323	-0.79	3.98	-0.80	-0.03	-0.78	0.02
333	-0.80	4.36	-0.81	-0.02	-0.80	0.01

1. Z. Zhou, Q. Wei, Q. Li, B. Jiang, Y. Chen, Y. Sun Development of Co-based bulk metallic glasses as potential biomaterials // Mater. Sci. Eng. – 2016. – 69. – P. 46–51.
2. Pardo, M. C. Merino, E. Otero, M. D. López, A. M'hich Influence of Cr additions on corrosion resistance of Fe- and Co-based metallic glasses and nanocrystals in H_2SO_4 // J. Non-Cryst. Solids. – 2006. – 352 (30–31). – 3179–3190.

THE INFLUENCE OF STRESS ON THE CORROSION PROCESSES OF Cr18Ni10Ti STEEL INTO LIQUID LEAD

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The heavy metals melts (Pb, Bi and its eutectic mixture) due to their properties are regarded as a cooling medium for fast reactors and subcritical hybrid systems managed by accelerator [1-2]. The austenitic steel due to their performance properties are candidate materials for cooling systems of nuclear reactors of new generation. The main problem of using heavy metal melts is their high corrosive aggressiveness to the structural materials of cooling systems. As materials are exposed to the simultaneous action of the medium and a certain level of loads during operation, the negative effect of the liquid metal environment is increasing [3]. Therefore, the purpose of the study was to evaluate the effect of different levels of applied load on the corrosion-mechanical properties of austenitic Cr18Ni10Ti steel.

The feature of corrosion behavior of austenitic Cr18Ni10Ti steel in liquid lead with oxygen concentration $C_{[O]Pb} \approx 5 \cdot 10^{-7}$ wt.% and applied loads of 35, 45 and 55 MPa at 550 °C at 1000 h exposure were investigated. It is established that the corrosive damages of the surface layers are inter-crystalline disposition (fig. 1), which is accompanied by the etching of the grain boundaries and the penetration of the melt into the matrix with the simultaneous dissolution of the main alloying elements Ni, Cr, Mn into the lead [4-5]. It is established that the applied load causes changes of the structure in the first place of the surface layer, that is, with increasing of the load level the grain size in the surface layer increases, which increases the damage of the surface layers.

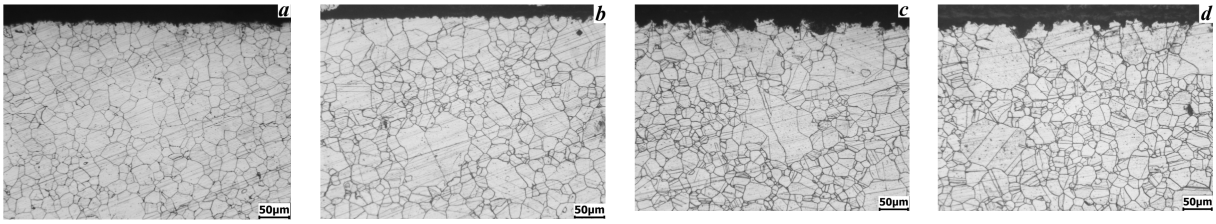

Fig. 1. The influence of the applied load on the change of the structure of the surface layer of austenitic steel Cr18Ni10Ti

Thus, the applied load changes the structure of both the surface layer and the matrix, and the impact on the surface layer is more intense.

1. Comparative assessment of thermophysical and thermohydraulic characteristics of lead, lead-bismuth and sodium coolants for fast reactors // IAEA-TECDOC-1289. – Vienna. – 2002.
2. Design of an Actinide Burning, Lead or Lead-Bismuth Cooled Reactor That Produces Low Cost Electricity // INEEL/EXT-01-01376. MIT-ANP-PR-083. FY-01. – Annual Report. – October, 2001. – P. 181–223.
3. Anna Hojná, Fosca Di Gabriele, Michal Chocholoušek, Lucia Rozumová, and Jan VítEffect of Applied Stress on T91 Steel Performance in Liquid Lead at 400 °C // Published online 2018 Dec 11. doi: 10.3390/ma11122512.
4. Fedirko, V.M., Kukhar, I.S., Pohrelyuk, I.M., Mel'nyk, K.R. Influence of Lead Melts on the Embrittlement of Chromium Steels of Ferritic and Austenitic Classes // Mater. Sci. – 2019. – Vol. 55. №3. – P. 430–434.
5. Fedirko, V.M., Kukhar, I.S., Mel'nyk, K.R. Influence of the Structural-Phase State of Chromium Steels on Their Corrosion in Lead Melts // Mater. Sci. – 2019. – Vol. 54. №4. – P. 551–555.

ELECTROCHEMICAL BEHAVIOUR OF SINTERED Ti-6Al-4V TITANIUM ALLOY OF DIFFERENT STRUCTURAL STATE IN 20% AQUEOUS SOLUTION OF HYDROCHLORIC ACID

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The machining of workpieces significantly complicates the manufacturing process of titanium products obtained by traditional technology. This allows us to simplify the production technology and reduce the cost of the finished product [1, 2]. Nowadays, it has been developed the scientific basis for the synthesis of sintered titanium alloys with density close to theoretical, and high complex of mechanical characteristics using the simplest technological scheme “pressing-sintering”. The proposed method is realised using titanium hydride powders instead of traditional titanium powder [3]. The samples of titanium alloy obtained by powder metallurgy were investigated. The raw materials were powder mixtures consisting of titanium hydride powder TiH_2 and alloying particles containing aluminum and vanadium. By varying synthesis parameters (sintering pressure and temperature) the sintered titanium alloy samples of different structural states were obtained. The density of the sintered materials was determined by hydrostatic weighing. The total porosity was determined by the ratio of the measured density to the theoretical density of Ti-6Al-4V alloy [4]. The metallographic studies were performed on an optical microscope "Epiquant". The microstructure of the polished surfaces was revealed by Kroll's etch: $1\div3$ ml HCl; $4\div5$ ml HNO_3; 95 ml H_2O. The electrochemical studies were performed on an IPC-Pro potentiostat. The potential sweep rate was 2 mV s^{-1}. The electrode potentials were measured relative to the saturated Ag/AgCl reference electrode.

It was determined that an uniform two-phase (α+β) lamellar structure is formed at sintering temperatures of 1200 ÷ 1350ºC. The pores are closed, have an almost spherical shape. The density of the material is (98 ÷ 99)% compared to theoretical density of the alloy. Therefore, the amount of residual pores in the material is (1 ÷ 2)%. Decreasing sintering temperature to 1050ºC causes a decrease of the theoretical density to 96% and forms an inhomogeneous structure. Such a structure includes undissolved ligature particles, light zones of α phase grains and (α+β) lamellar structure. An increase of the particle size of the powder to (100 ÷ 200) μm and decrease of the sintering pressure don't affect the chemical and microstructural homogeneity of the material. However, they affect the morphology and pore size. The elongated pores appear, and the material density decreases to 97%.

The potentiodynamic polarization curves of the sintered Ti-6Al-4V alloy in hydrochloric acid solution are typical for the alloys tendentious to passivation. The nature of the anode curves indicates the formation of stable oxide films. The passivation of the samples of all structural states begins at a potential of approximately 0 V.

The values of corrosion current density for samples with the theoretical density of 98 ÷ 99%, are 0.019 ÷ 0.044 $A\cdot m^{-2}$. At the same time, the samples with the theoretical density of 96–97% have chemical and microstructural inhomogeneities; the values of corrosion current density are by an order of magnitude higher of: 0.114÷0.471 $A\cdot m^{-2}$.

1. Moxson V.S., Senkov O.N., Froes F.H. Innovations in Titanium Powder Processing – JOM, (2000), P. 23–26.
2. Sekiguchi T., Ono K., Fujiwara H. and Ameyama K. New Microstructure Design for Commercially Pure Titanium with Outstanding Mechanical Properties by Mechanical Milling and Hot Roll Sintering – Materials Transactions – 2010. – Vol. 51, № 1 – P. 39–45.
3. Лобода П.І., Биба Є.Г., Сисоєв М.О., Гуцу О.С. Структура і властивості титану, отриманого спіканням порошків TiH_2 – Фізика і хімія твердого тіла – Т. 12, № 2 (2011) – P. 465–469
4. А.Т. Туманова, Авиационные материалы, Справочник, Москва. – 1975 – 520 с.

EFFECT OF TEMPERATURE OF NITRIDE OXIDATION ON CORROSION RESISTANCE OF Ti64 ALLOY IN 0.9% SODIUM CHLORIDE SOLUTION

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Ti-N-O films are promising coatings for medical devices (coronary and vascular stents) because of their ability to prevent thrombus formation and fibrinogen adhesion to the implant surface [1].

The corrosion resistance in an isotonic 0.9% sodium chloride solution, which simulates blood plasma, is one of the main criteria to choose a material as an implant. It is well known [2] that oxynitride coatings protect the metal base of the implant from the corrosive effects of body fluids (blood, lymph, interstitial fluid). Therefore, the purpose of this work is to study the effect of temperature of nitride oxidation on the corrosion resistance of Ti64 titanium alloy in an isotonic 0.9% NaCl solution at 36°C.

The oxynitride coatings were formed during oxidation of titanium nitride at cooling stage from temperatures of 950°C and 650°C to 500°C. It was determined that corrosion resistance of the oxynitrided alloy is improved compared to the untreated one (Fig. 1). These coatings provide lower corrosion current density and nobler corrosion potential (Table 1). It was shown that increasing oxidation temperature from 650°C to 950°C enhances the content of oxynitride phase on the surface layer of titanium alloy, which improves the anti-corrosion properties.

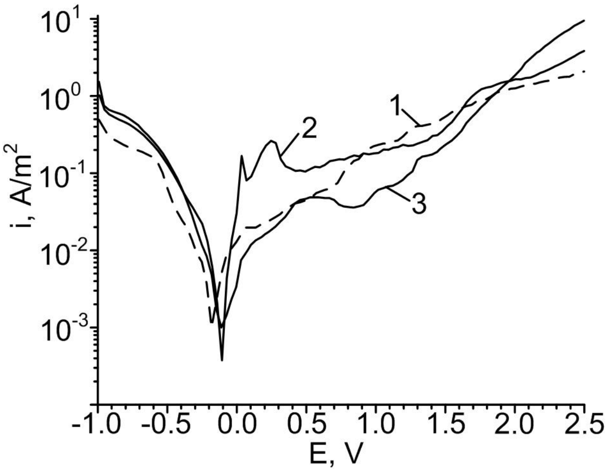

Fig. 1. Polarization curves of untreated (1), oxynitrided at 650°C (2) and 950°C (3) Ti64 alloy in 0.9% NaCl solution at 36°C

Table 1. Corrosion parameters of oxynitrided and untreated Ti64 alloy in 0.9% NaCl solution at 36°C

Ti64 alloy	E_{corr}, V	i_{corr}, A/m^2
oxynitrided (950°C)	-0.077	0.0013
oxynitrided (650°C)	-0.122	0.0021
untreated	-0.136	0.0030

1. N. Beshchasna, A. Y. K. Ho, M. Saqib, H. Kraśkiewicz, Ł. Wasyluk, O. Kuzmin, O. C. Duta, D. Ficai, R. D. Trusca, A. Ficai, V. F. Pichugin, J. Opitz, E. Andronescu. Surface evaluation of titanium oxynitride coatings used for developing layered cardiovascular stents // Mater. Sci. Eng. C. – 2019. –Vol. 99. – P. 405–416.
2. L. N. Huang, Y. X. Leng, P. Yang, J. Y. Chen, H. J. Sun, G. J. Wang, A. S. Zhao, P. D. Ding. Surface modification of coronary artery stent by Ti–O/Ti–N complex film coating prepared with plasma immersion ion implantation and deposition // Nucl. Instrum. Methods Phys. Res. – 2006. – Vol. 242. – P. 18–21.

RESEARCH OF CHEMICAL DISSOLUTION OF BERYLLIUM BRONZE AT PROPORTIONAL ETCHING IN VARIOUS ELECTROLYTES

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The dissolution rate of the Cu98Be alloy (beryllium bronze) electrode in acidic solutions based on $FeCl_3$ was studied by rotating disc electrode method at the rotation rate 74 rps. Determination of etching rate by gravimetry was based on rotating disk electrode, made from Cu98Be bronze. The quantity of Be^{2+} and Cu^{2+}ions was determined by atomic-absorption spectrometry method using atomic-absorption spectrometer MGA-915 MD.

On the base of our first investigations of determination of the ionization rate of Cu98Be alloy in various electrolytes, the solution of $FeCl_3$ was chosen as a basic component of etching solution. The series of five composition of etching solutions which provide high etching rate and uniform dissolution of beryllium bronze components was selected.

As the components of Cu98Be alloy dissolutions the composition of the etching solution and the rate of dissolution of the alloy components was changes. Therefore, it is very important to check the stability of the etching process of beryllium bronze.

In this regard, the change in the rate of dissolution of the alloy Cu98Be over time was investigated, and υ - τ– curved lines were constructed (Fig.1).

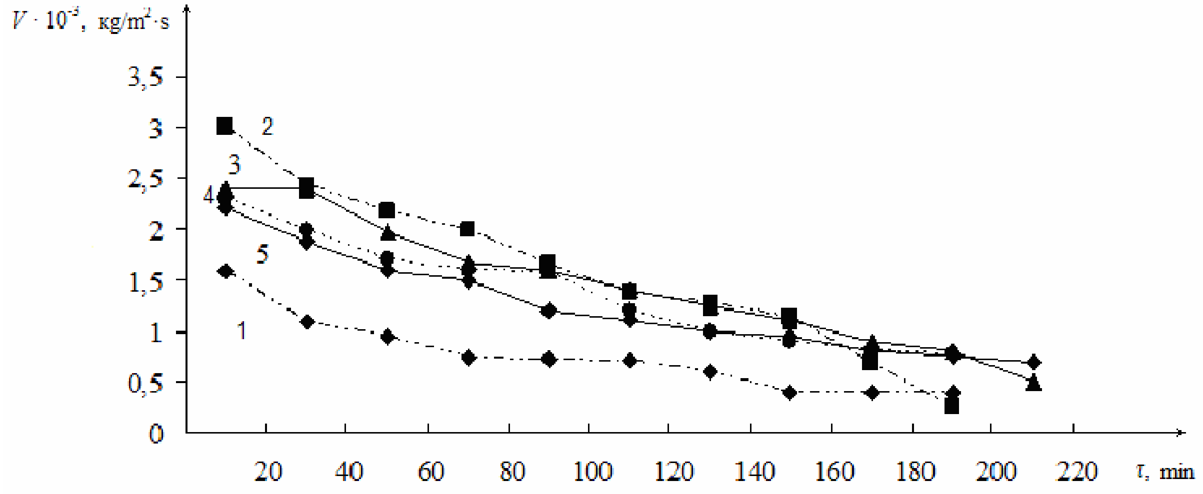

Fig. 1. Change in the etching rate of the alloy Cu98Be over time. In composition solutions mol/l: 1–0,5M $FeCl_3$, 2–1,0M $FeCl_3$, 3–0,5M $FeCl_3$ + 0,5M $Fe(NO_3)_2$ + 0,5M HCl, 4–0,5M $FeCl_3$ + 0,5M $Fe(NO_3)_2$ + 0,25M H_2SO_4, 5–0,5M $FeCl_3$ + 0,5M $Fe(NO_3)_2$

According to the experimental data fig.1, the quantitative indices of etching were calculated and the composition of the solutions, which provide a high speed was proposed (curves 2 and 3, fig. 1). The mineralogical composition of low-soluble compounds in exhausted etching solutions was determined by X-ray-phase analysis.

The process of chemical ionization of Cu98Be alloy in solutions of various composition based on $FeCl_3$ was studied. The optimal compositions of etching solutions, whit provide high-quality etching of beryllium bronze according to several criteria – high process speed, uniform dissolution of alloy components, high capacity for both components of beryllium bronze was proposed. The obtained results are of great importance in practical use because they allow selecting the composition of the etching solution, which in turn helps to optimize the technological etching process.

CORROSION-ELECTROCHEMICAL BEHAVIOR IN SOLUTION OF 3 % NaCl TITANIUM CARBIDE TICX AND THE EFFECT OF PRELIMINARY CATHODIC POLARIZATION ON IT

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Stoichiometric titanium carbide TiC is a synthetic superhard corrosion-resistant and wear-resistant chemically inert material that is in demand in the production of composites, protective coatings of metalworking tools and heat-resistant products. During exploitation in aggressive liquid natural environments, such products are subjected to corrosive attack, and can also be cathodically polarized upon contact with more electronegative materials [1–3].

In this work, the corrosion-electrochemical behavior of stoichiometric and non-stoichiometric titanium carbide TiC_x in the area of homogeneity ($x = 0.6; 0.7; 0.8; 0.9; 1.0$) and metallic iodide titanium was studied in a 3 % solution NaCl, imitating aggressive natural and biomedical liquid media.

The studies were carried out by the method of obtaining anodic and cathodic polarization curves in the potentiodynamic mode. Compact TiC_x samples were obtained from powders of the corresponding compositions by hot pressing with further annealing in a vacuum furnace. The structure and surface condition of the samples prepared for research were certified by X-ray phase analysis and Auger electron spectroscopy, as a result of which it was found that they are single-phase and have a polycrystalline structure.

It was shown that the rates of the anode processes of all the TiC_x materials under study are the limiting stages of the investigated corrosion processes occurring on their surfaces. It was found that the corrosion resistance of the studied materials decreases in the order $Ti \rightarrow TiC_{1.0} \rightarrow TiC_{0.9} \rightarrow TiC_{0.8} \rightarrow TiC_{0.6} \rightarrow TiC_{0.7}$, which is presumably explained by a change in the Ti – C bond strength [4].

It was also established that, after preliminary cathodic polarization, the $TiC_{0.8}$ and Ti iodide samples have the lowest anodic oxidation rate, while in all other cases this characteristic increases significantly.

1. L.S. Shiryaeva, A.K. Garbuzova, G.V. Galevskiy. Proizvodstvo i primenenie karbida titana (ozenka, tendenzii, prognozy). // Nauchno-technicheskie vedomosti SPbGPU. – 2014. – Vol. 21(195). – P. 100–108.
2. S.S. Kiparisov, Ju.V. Levinskiy, A.P. Petrov. Karbid titana: (poluchenie, svoistva, primenenie.– M.: Metallurgiya. – 1987. – P. 216.
3. Chukwuma C. Onuoha, Georges J. Kipouros, Zoheir N. Farhat, Kevin P. Plucknett. The effects of metal binder content and carbide grain size on the aqueous corrosion behaviour of TiC–316L stainless steel cermets // Int. Journal of Refractory Metals and Hard Materials. – 2014. – Vol. 44. – P. 129–141.
4. V.P. Pancheshnaya, V.M. Knyazheva, Zh.V. Klimenko, M.M Antonova. O vzaimodeystvii karbida titana razlichnogo stechiometricheskogo sostava s vodorodom pri katodnoy polyarisazii v kislych sredach // Zaschita metallov. – 1980. – Vol. 16. №6. – P. 684–891.

PROPENSITY TO THE CORROSIVE-FATIGUE FRACTURE OF THE LONG TERM OPERATED 34KHN3M STEEL

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Problems of the unpredictable fracture of steam turbine components are known for power engineers in the world [1–3]. First of all such feature is significant for steam turbine discs. From experience of the steam turbines operation well known that most cases of corrosion damage of this elements are caused by the steam ability as a technological environment to the metal hydrogenation. The corrosion-hydrogenation effect facilitates to the damage of the turbine disks, accelerates of the corrosion processes under the influence of corrosion-active impurities in the steam and intensifies the firm deposits formation, ulcers and cracks on their surface. Therefore, it is very important to take into account the effect of the corrosive environment when examining steel from an exploited disk [4].

It was investigated the high cycle fatigue in air and in the model corrosion environment of the 34KhN3M steel after operation during ~ 3×10^5 h in the disc of separately stage of a low-pressure cylinder of a steam turbine of a thermal power plant (Fig. 1). The obtained results were compared with the properties of steel in the initial state.

The fatigue limit σ_{-1} of the 34KhN3M steel in the initial state on air is significantly higher (almost 44%) than after its long-time exploitation. This difference is caused by the degradation of the steel during exploitation. The relative fatigue limit of the 34KhN3M steel in the initial state after testing in corrosive environment decreased by more than 4,5 times compared with testing on air (at test on the base near 5×10^7 cycles). In particular the relative fatigue limit of this steel in environment σ_{-1c} decreased to 103 MPa, relative of the obtained at air test the value σ_{-1} equals 429 MPa. A similar tendency was revealed on the exploited steel, but difference between the levels of σ_{-1} and σ_{-1c} was significantly less (the difference between them did not exceed 54%). This effect was explained by an influence of the long-term hydrogenation of the steel in service conditions. As a result the short-term impact of an additional embrittlement factor in the form of external corrosive environment was become less noticeable.

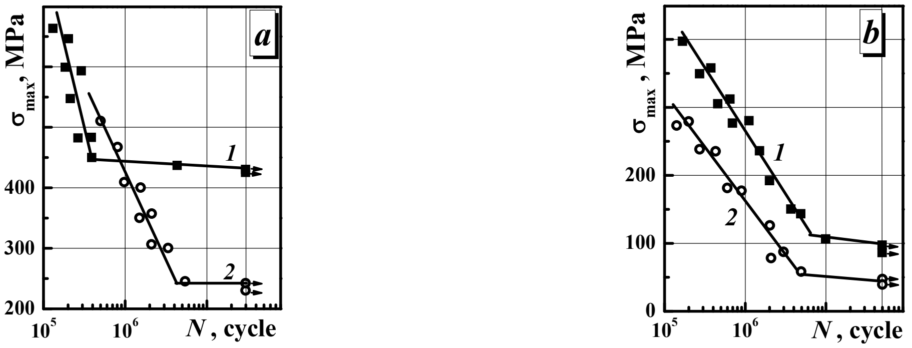

Fig. 1. Fatigue curves for the 34KhN3M in the initial state (*1*) and after operation during ~ 3×10^5 h in a rotor's disk of the steam turbine (*2*) which were obtained for testing in air (*a*) and in the model corrosive environment (*b*).

1. Naresh Kumar Doneti, Spoorthi Gopagoni, Tariku Achamyeleh. Analysis of steam turbine casing. // International Journal of Applied Research in Science and Engineering. – 2017. – Vol. 1, Iss. 10. – P. 474–477.
2. Shigeo Sakurai, Nobuhiro Isobe. Life assessment for creep and fatigue of steam turbine components. // Transactions of The Indian Institute of Metals. – 2010. – Vol. 63, Iss. 2–3. – P. 281–288.
3. Arun Kumar H D, Dr. S G Gopala Krishna. Life assessment for creep and fatigue of steam turbine. // Blisk International Journal of Advanced Engineering Research and Science. – 2016. – Vol. 3, Iss. 8. – P. 119–124.
4. Student O., Tkachuk Yu., Sydor P. Technical expertise of damaged structural elements of power plant steam turbine. // Proceeding 14th International Conference: Mechanika-2009, Kaunas, 2009. Kaunas: Technologija, 2009. – P. 396–400.

CONTACT FATIGUE OF STRUCTURAL STEELS WITH SURFACE NANOCRYSTALLINE STRUCTURE IN CORROSIVE MEDIA

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The important characteristic of the bearing capacity of machine elements is their fracture strength at the contact loads. It is very important for rolling bearings, gears, drilling bits, elements of metallurgical equipment, e.g. rollers of rolling mills, agricultural machineries, etc. The fracture strength of steels with surface nanostructure at the high contact loads has not been widely studied.

In this paper, developing the researches [1-3], the contact fatigue of 20XH3A and 55CMΦA steels after thermal or chemicothermal treatment and with additional surface nanostucturization by mechanical-pulse treatment were studied in corrosive and corrosive-abrasive media; the contact fatigue of 60X2M roller steel after quenching and tempering at the temperature of 450°C and with surface nanocrystalline structure was also studied in corrosive medium. 20XH3A and 55CMΦA steels are used for production of drilling bit legs, balls and rollers exploited under high contact loads; 60X2M steel are used for production of hot rolling forming rollers exploited under simultaneous action of abrasive, high alternating contact and thermal loads (rollers are cooled by water during rolling). Hence, the contact fatigue studies were carried out at high contact loads in different working media for maximal approach to real working conditions and was established that mechanical-pulse treatment significantly improved contact fatigue of studied structural steels.

The contact fatigue was studied for 20XH3A steel after carburizing, quenching and tempering at the temperature of 150°C, 55CMΦA steel after quenching and tempering at the temperature of 100°C and with additional mechanical-pulse treatment for both steels. It was showed, that surface nanostructurization of 20XH3A and 55CMΦA steels increased their contact fatigue in 3 and 2.2 times in corrosive medium and in 2 and 1.3 times in corrosive-abrasive medium, respectively. The surface layer with nanocrystalline structure of 60X2M steel increased its contact fatigue in corrosive medium: quenching and tempering at the temperature of 450 °C provided the contact fatigue $1.14 \cdot 10^6$ cycles and the additional mechanical-pulse treatment improved it almost in 4 times ($4.08 \cdot 10^6$ cycles).

Based on the research results obtained in this paper, it was concluded that combination of thermal or chemicothermal treatment with surface nanostucturization by mechanical-pulse treatment significantly increased contact fatigue of low-alloyed structural steels in corrosive and corrosive-abrasive media.

1. Kyryliv V. I., Chaikovs'kyi B. P., Maksymiv O. V., Shal'ko A. V. Contact fatigue of 20KhN3A steel with surface nanostructure // Materials Science. – 2016. – Vol. 51. №6. – P. 833–838.
2. Kyryliv V. I., Chaikovs'ky B. P., Maksymiv O. V., Shal'ko A. V. Contact fatigue of 20KhN3A and 55SMFA steels with surface nanostructured layer in corrosive-abrasive media // Materials Science. – 2018. – Vol. 53. № 4. – P. 508–513.
3. Kyryliv V. I., Chaikovs'kyi B. P., Maksymiv O. V., Shal'ko A. V., Sydor P. Ya. Serviceability of 60Kh2M roll steel with surface nanostructure // Materials Science. – 2017. – Vol. 52. № 6. – P. 848–853.

STRESS-CORROSION OF WELDED JOINTS OF PIPE STEEL, OBTAINED BY DIFFERENT METHODS OF WELDING

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Welded pipes of low-alloy steel have low cost and stable dimensions. Welding provides the possibility of making pipes of different size in comparison with the whole ones. However, the resistance to corrosion and mechanical failure of welded joints of such pipes may be impaired due to structural, mechanical and electrochemical heterogeneity. This is influence on the life of the pipeline in general. Under providing good welding, the corrosion, which is the most often appear in the weld area, may result in to failure [1, 2].

The peculiarities of stress corrosion in the neutral environment of welded joints of low carbon 17G1S steel, which are differ by their welding technology, namely: high frequency welding (HFW) and arc welding (AW), were investigated. Such joints are used in manufacture of pipes including pipes for oil pipelines. The influence of such factors as the duration of exposing in solution and the load level on the corrosion resistance of these welded joints was studied. The type of corrosion damages of the surface was determined and the corrosion resistance of welded joints was evaluated according to the current regulations. It was shown that the rate of uniform corrosion of welded joints of 17G1S steel, made using different welding technologies, in the unstressed state during the whole time of exposure in 3% NaCl solution has not practically differ from the corrosion rate of base metal, fig.1.

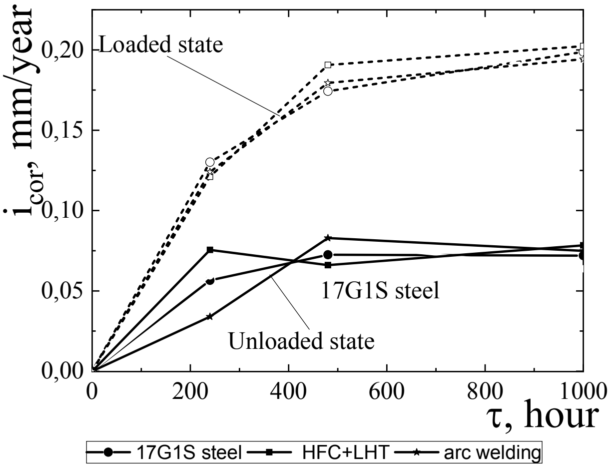

Fig. 1. Corrosion resistance of base metal of 17G1S steel and welded joints, received by high frequency welding (HFW) and arc welding (AW) after corrosion-mechanical investigations in unloaded and loaded states during 1000 hours of exposing to 3 % NaCl solution

Under the maximum stress of the samples to the level of 0.95 from the yield strength of the base metal, the rate of solid corrosion is about 30-40% higher than that of the base metal. It was concluded that corrosion resistance of welded joints of low carbon steel 17G1S, welded by high-frequency currents is not worse than welded joints obtained by arc welding.

1. Vyboyshchik L.M., Luchkin R.S., Ioffe A.V. Ensuring of corrosion resistance of welded joints of oil pipelines at the level of the metal being welded / TSU Science Vector. –2010. – № 4 (14). – P. 60–64.
2. Luchkin R.S. Improving of uniformity of the structure and properties of welded joint of oil pipes / R.S. Luchkin, L.M., Vyboyshchik L.M. // Proceedings of the All-Russian scientific and technical conference with international participation «Modern problems of increasing the efficiency of welding production», Togliatti: TSU. – 2006. – Part I. – P. 134–140.

CORROSION RESISTANCE OF WELDED JOINTS MADE BY UNDERWATER WET WELDING

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One of the reasons for the failure of metal constructions, especially welded joints, which working in the water environment, including marine conditions, is corrosion. For example, the rate of welds' destruction exceeds the rate of corrosion of the base metal and in some cases may reach (1-3) mm/year [1, 2].

Wet underwater welding is used to repair the corroded welds of the pipelines operated under water. In E.O. Paton Electric Welding Institute has developed specialized flux-cored wires for welding low-carbon and low-alloy steels. In the latter case, to provide resistance to the formation of cold cracks in the heat affected zone, electrode materials of austenitic type is used [3].

To study the corrosion resistance of such types of welded joints corrosion tests were carried out in a running flow of 3% NaCl solution during 250 hours. After corrosion tests the region in the vicinity of deposited layer was examined by the optical microscopy method.

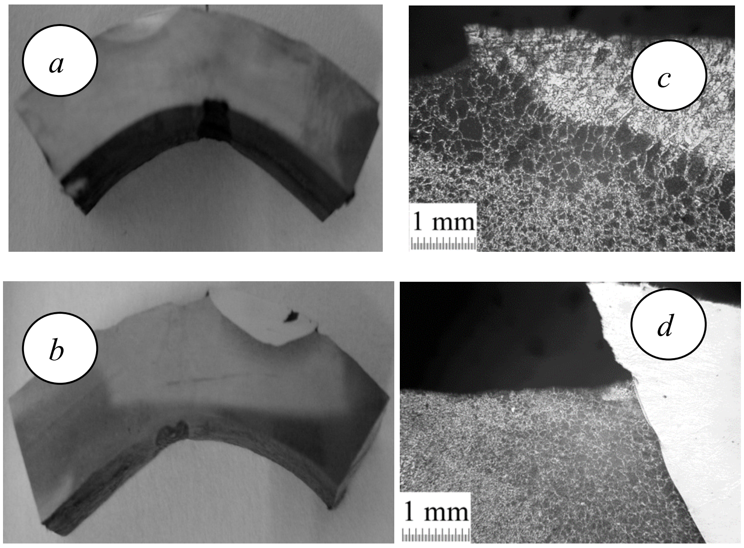

Fig. 1. Appearance of a fragment of a central part of welded joints of steel St3 (a, b) and microstructure of near-surface layers (c, d), with a ferrite deposited metal made by wire PPS AN-2 (a, c) and austenite deposited metal, made by wire of Ni strip (b, d), after study of resistance against corrosion cracking in a running flow during 250 h and bending up to initiation of the first crack

As is seen from the analysis of experimental data, after investigations in the conditions of varying wetting, the cracks were not observed along the fusion line of both types of welded joints, which proves their resistance under the conditions of effect of tensile stresses.

1. Kolomijtsev E.V. Corrosion resistance of welded joints of ship hull materials // Avtomatich. Svarka. – 2012. No.4. – P. 59 – 64.
2. Sirotyuk A.M., Dmitrakh I.M. Assessment of corrosion-mechanical defects of underwater pipeline steels // Visnyk of admiral Makarov NYK. – 2014. No.2. – P. 66–72.
3. Maksimov S.Yu., Savich I.M., Zakharov S.M. Structure and properties of metal, deposited under water by flux-cored wire with Ni sheath // Avtomatich. Svarka. – 2003. No.4. – P. 19–22.
4. OST 5.9255–76. Metals and coatings for ship building. Methods of express corrosion tests.

THE INFLUENCE OF HEAT TREATMENT ON THE CORROSION RESISTANCE OF THE WELDED JOINTS OF ALUMINUM ALLOY OF THE SYSTEM Al-Mg-Si-Cu

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The results of complex studies of influence of complete cycle heat treatment, HT, (quenching and artificial aging) of aluminum alloy of alloying system Al-Mg-Si-Cu welded joints [1] on durability against local corrosion and resistance against corrosion cracking were presented. The welded joints obtained by a non-fused electrode free arc in the environment of a protective gas argon.

Potentiometric studies have shown that HT promotes the reduction of electrochemical heterogeneity between the base metal and the weld: the potential difference is halved – from 18 to 9 mV. Such potential difference is acceptable in welded joints according to GOST 9.005 and will not practically promote of preferential destruction of weld metal [2].

It has been experimentally shown that the TO does not impair the resistance to exfoliation corrosion of the welded joint of the alloy of the Al-Mg-Si-Cu alloying system and slightly impairs the resistance against intergranular corrosion, fig. 1a, but the depth of intergranular breaking of the grain boundaries does not exceed the value (0.350 mm) installed in the documentation [3].

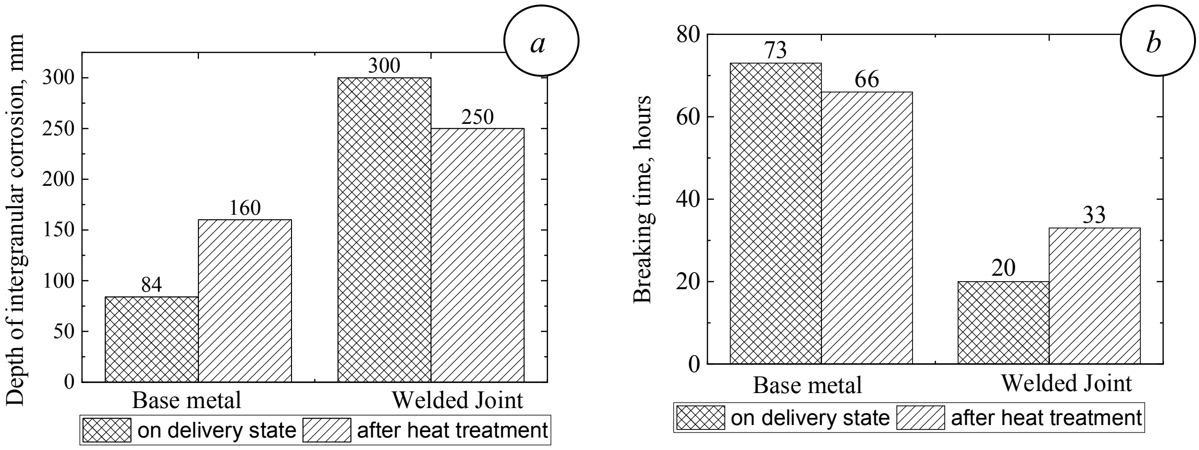

Fig.1. Influence of full heat treatment cycle on intergranular corrosion resistance (a) and résistance against corrosion-mechanical breaking (b)

The effect of HT on the corrosion-mechanical durability of the base metal and welded joint under conditions of combined long-acting continuous loading under fully immersion into the corrosive medium is ambiguous. An insignificant reduction in breaking time was observed for the base metal after up to 66 hours on average (compare to 73 hours in the initial state), but the welded joint showed a some greater resistance to corrosion-mechanical fracture after HT, as evidenced by an 35% increase in fracture time (up to 33 hours), fig. 1*b*.

1. A. Ischenko, T. Labur. Welding of modern aluminum alloy structures. // Kiev, Nauk. Dumka. – 2013. – Vol. 416.
2. L. Nyrkova, T. Labur, O. Riabyko, Yu. Borysenko. Correlation between electrochemical properties of the welded joint of aluminum alloy of the Al-Mg-Cu-Si system and its resistance to local corrosion // Bulletin of KNUTD. – 2018. – №6 (128). – P. 71–77.
3. Influence of the state of the B1341T aluminium alloy of the Al-Mg-Cu-Si system on resistance against intergranular corrosion Nuriachmetova M.M., Nyrkova L.I., Labur T.M., Borysenko Yu.V. Promising Materials and Processes in Technical Electrochemistry: Monograph / V.Z. Barsukov, Yu.V. Borysenko, O.I. Buket, V.G. Khomenko. – Kyiv.: KNUTD. – 2016. – P. 152–155.

FATIGUE LIFE OF WELDED JOINTS WITH THE COMBINED EFFECTS OF HIGH-FREQUENCY PEENING AND CORROSION ENVIRONMENT

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Present paper shows effectiveness of high frequency mechanical impact (HFMI) treatment technology to improve corrosion resistance and corrosion fatigue behaviour of butt and T-welded joints of low-alloy steel 15KhSND. Corrosion tests of welded joints were carried out at their exposure in high humidity and neutral salt fog. The conditions of high humidity were simulated by exposing the specimens in a moisture chamber of G4 at a temperature of 40^{0}C and air humidity of 98%. The conditions of neutral salt fog were simulated by exposing the specimens in a salt spray chamber KST-1 at the temperature of (35±2)^{0}C with spraying of sodium chloride solution. The duration of the corrosion test of the welded joints before fatigue tests was 1200 h. The microstructure of as-welded and HFMI treated joints both before and after corrosion environments influence was investigated. Corrosion-mechanical fracture of the hardened surface layer of the base metal, weld zone and HAZ after 1200 h of exposure is observed. The fatigue tests were carried out on six series of the welded T-joints and six series of the butt welded joints: as-welded and treated by HFMI on air; as-welded and treated by HFMI states after corrosion tests; after accumulation $2\cdot10^6$ cycles and corrosion tests; after accumulation $2\cdot10^6$ cycles, corrosion tests and subsequent treated by HFMI. It was established by the experiment that the use of HFMI technology can significantly increase the fatigue life of the welded T-joints of steel structures. It is found that HFMI is an effective method to increase the fatigue strength of welded joints at all stages of operation of the metal structure [1, 2]. The results of fatigue testing of the six series welded T-joints with combined effects of HFMI and high humidity is shown in Fig. 1.

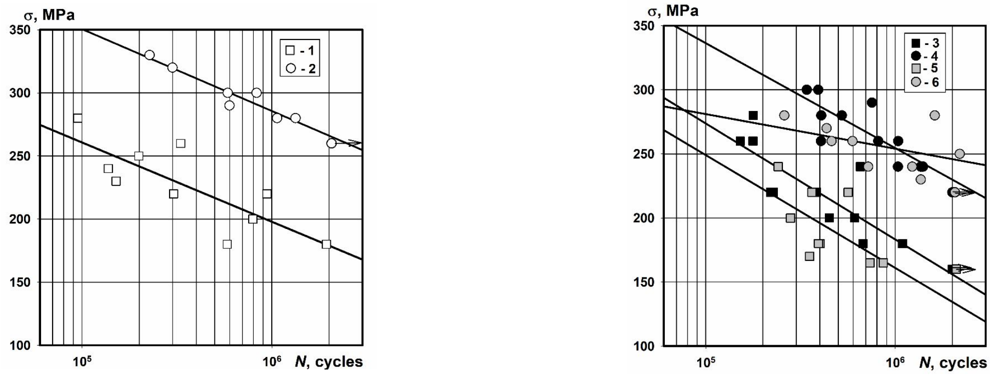

Fig.1 *S-N* curves of welded T-joints of 15KhSND steel as-welded (1) and treated by HFMI (2) in air; as-welded (3) and treated by HFMI (4) after corrosion tests; after pre-loading $2\cdot10^6$ cycles and corrosion testing without HFMI treatment (5) and with further HFMI treatment (6)

It is found that peening by HFMI of the T-welded joints of 15KhSND steel before exposure to high humidity during 1200 hours leads to increasing of their fatigue life in 5…7 times (Fig. 1, curves 3,4); peening by HFMI of the T-welded joints with fatigue and corrosion damages (pre-loading $2\cdot10^6$ cycles and corrosion test during 1200 hours) leads to 10 times increase of their fatigue life (Fig.1, curves 5, 6).

1. V. Knysh, S. Solovei, L. Nyrkova, I. Klochkov, S. Motrunich. Influence of the atmosphere corrosion on the fatigue life of welded T-joints treated by high frequency mechanical impact// Procedia Structural Integrity. – 2019. – Vol. 16. L – P. 73-80.
2. V.V. Knysh, S.O. Solovei, L.I. Nyrkova, S.O. Osadchuk. Influence of Hardening by High-Frequency Mechanical Impacts of Butt Welded Joints Made of 15KhSND Steel on Their Atmospheric Corrosion and Fatigue Fracture Resistance// Mater. Sci. – Vol. 54. Iss. 3. – P. 421 –429.

MECHANISM OF THE OXIDATIVE AND SALT PASSIVATORS COACTION WITHIN BINARY INHIBITIVE MIXTURES

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The mechanism of joint action of oxidative and salt passivators within binary inhibitive mixtures for protection of steel in aqueous saline solutions has been investigated. Preconditions for achieving synergistic effects in relation to the electron structure of the mixture components, pH of the medium and the metal potential have been identified.

The inhibitive performance of the VO_4^{3-}, CrO_4^{2-}, and:NO_2^- paired with PO_4^{3-}, SiO_3^{2-} has been studied both individually and within their binary mixtures. The protective efficiency has been investigated using gravimetric and electrochemical methods, while the obtained protective films morphology have been analyzed using SEM. The optimal concentration and concentration ratio for studying synergistic and antagonistic phenomena within binary mixtures have been determined using isomolar series method (Fig. 1).

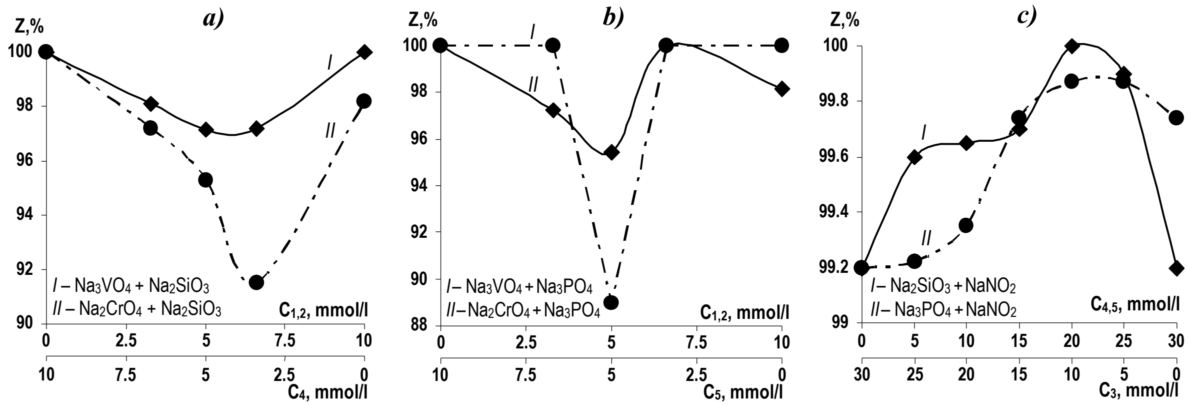

Fig. 1. Inhibitive efficiency vs concentration ratio of the binary mixture components.
Key: 1– Na_3VO_4; 2– Na_2CrO_4; 3– $NaNO_2$; 4– Na_2SiO_3; 5– Na_3PO_4

The presence of the mixture components that are characterized by different mechanism of action while retaining structural similarities may result in antagonistic effects that may be attributed to a concurrent specific action. On the other hand, components with different mechanism of action where one of the components possesses active unshared electron pair on hybrid orbital of the central atom tend to provide reliable synergistic behaviour in binary mixtures.

On the basis of obtained results, the theoretical model that predicts joint action of the additives of different nature within binary inhibitive mixtures [1, 2] has been further refined in regard of the electron structure of their components.

1. V. Ledovskykh, Yu. Vyshnevska, I. Brazhnyk, S. Levchenko Metal Surface Modification for Obtaining Nano- and Sub-Nanostructured Protective Layers // Nanoscale Research Letters. – 2017. – Iss. 12. – P. 186–191
2. V.M. Ledovskykh, Yu.P. Vyshnevska, I.V. Brazhnyk, S.V. Levchenko Thermodynamic Approach to the Purposeful Design of Synergistic Inhibiting Compositions for the Corrosion Protection in Aqueous Saline Media // Materials Science – 2019. – Vol. 54. – №4. – P. 485 – 495.

CORROSION RESISTANCE OF C.P. TITANIUM AND Ti-6Al-4V ALLOY PREPARED BY POWDER METALLURGY IN AQUA SOLUTIONS OF HYDROCHLORIC ACID

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In general, titanium metal products (sheets, tubes and various profiles) are fabricated by vacuum arc melting of the titanium sponge and subsequent deformation. Powder metallurgy allows to increase the use-effectiveness of metal in production of titanium products [1].

The corrosion resistance of material in corrosive media is a criteria of exploitation suitability evaluation under conditions of the effect of corrosion factor. If it is well studied for materials obtained by traditional technology, then an information on the corrosion properties of titanium and its alloys synthesized by powder metallurgy technique in various corrosive media is limited.

Samples of c.p.titanium and Ti-6Al-4V alloy, obtained by cold pressing and vacuum sintering of titanium hydride powder TiH_2, were investigated at G.V. Kurdyumov Institute for Metal Physics of the National Academy of Sciences of Ukraine. The residual porosity of the samples varied from 1 to 4%. Before testing, the surface of the samples was ground and polished. The corrosion rate was determined by gravimetric method by varying weight of the samples in 10, 20 and 30% aqua solutions of hydrochloric acid at 504 h exposure.

The corrosion resistance decreases by increasing concentration of the corrosive medium and residual porosity of the test samples. The corrosion rate of c.p. titanium and Ti-6Al-4V alloy increases at 20% acid concentration and 4% residual porosity, 30% concentration and 3% porosity significantly, but the most at 30% concentration and 4% porosity (up to 11,503 g / (m^2 × h) for c.p. titanium and 4,848 g/(m^2×h) for Ti-6Al-4V). Compared to the corresponding material obtained by traditional technology, it increases by 9 and 4 times, respectively.

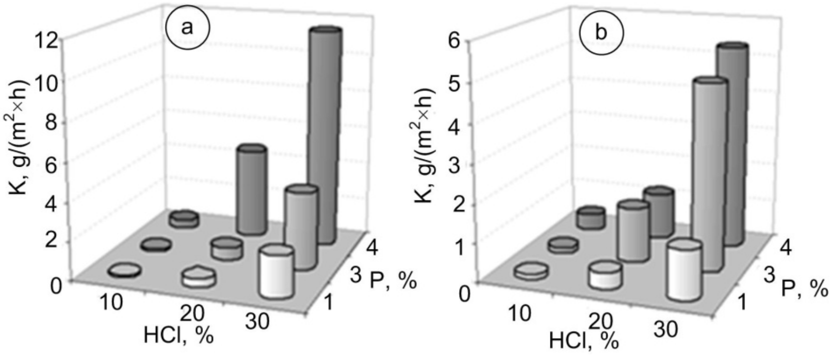

Fig. 1. Dependence of corrosion rate of sintered powder materials on their residual porosity in 10, 20 and 30% aqua solutions of hydrochloric acid: a – c.p. titanium; b – Ti-6Al-4V alloy

The corrosion rate of Ti-6Al-4V alloy in 10 and 20% aqua hydrochloric acid solutions exceeds a little the one for c.p.titanium obtained by traditional technology. These rates are comparable in 30% aqua acid solution. The corrosion rate of sintered Ti-6Al-4V is lower than the c.p. titanium regardless of the residual porosity for different acid concentrations, and with the increasing of the porosity this difference is increased significantly.

1. F. H. Froes, S. J. Mashl, V. S. Moxson, J. C. Hebeisen, V. A. Duz. The technologies of titanium powder metallurgy // The J. of the Minerals. Metals & Mat. Soc. – 2004. – Vol. 56. № 11. – P. 46–48.

STRUCTURE, MECHANICAL PROPERTIES, OXIDATION AND CORROSION RESISTANCE OF Fe-Cr-Al BASED ALLOYS

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FeCrAl-based alloys are considered within the ATFC concept as one of the possible materials for replacing traditional zirconium alloys for fuel claddings after the Fukushima nuclear power plant accident (March 11, 2011) [1,2]. A specific feature of FeCrAl-based alloys is the formation of a thin alumina protective film during the high-temperature tests in water vapor and high corrosion resistance under the test conditions close to normal operation due to the formation of spinel film from chromium and iron oxides [3]. Microalloying of these alloys can significantly improve their properties.

The aim of this work is to study the influence of alloying elements (Y, Mo, and Zr) on the structure, mechanical properties, oxidation and corrosion resistance of the model FeCrAl-based alloys.

Six samples were selected as materials for the study (No1-6), two of them (No1 и No2) were commercial Kanthal-type alloys Kanthal A1. Sample No.1 was in delivery state, sample No.2 was the same rod, remelted by the argon-arc method and casted into a cylindrical copper mold. Experimental alloys No.3-6 were melted at the same conditions. High purity metals were used as the raw materials (iron, aluminum, chromium, molybdenum and zirconium). At least five meltings with turning over at each remelting were performed to improve the chemical homogeneity of the ingots. The final solidified ingots were cylindrical bars with a diameter of 10 mm and height of 30 mm. Microstructure characterization was performed using scanning electron microscope JSM-7001F equipped with Oxford Link ISIS 300 EDX attachment. The crystalline structure and phase composition were studied using X-ray diffractometer DRON-2.0 with Co-Kα radiation and Fe selective filter. The effect of alloys composition on their high-temperature oxidation resistance was studied by annealing in furnace in air at atmospheric pressure and a temperature of $T = 1300$ °C for 3 hours. The microhardness of the alloys was measured using Leco LM700AT microhardness tester with a Vickers indenter. Nanohardness and Young's modulus of the alloys were measured on a Nano Indenter G200 instrument (Agilent Technologies) with a Berkovich indenter. The average corrosion rate in the water simulator of the primary circuit of a nuclear power plant was determined using the potentiostat IPC-Pro in a standard electrochemical cell of NPP-2 at temperature of 20 °C.

The main phase in all studied alloys is the BCC phase. Alloying with ~ 2% zirconium leads to the formation of microstructure, which consists of the matrix phase grains and intergranular eutectic - BCC matrix phase + FCC Laves phase $ZrFe_2$.

The highest corrosion and oxidation resistance has an alloy doped with yttrium and molybdenum. Microhardness and nanohardness have close values for all alloys except Zr-doped alloy, which have significantly higher values.

1. K. A. Terrani. Accident tolerant fuel cladding development: Promise, status, and challenges // J. Nucl. Mater. – 2018. – 501. – P. 13–30.
2. Z. Duan, H. Yang, Y. Satoh, K. Murakami, S. Kano, Z. Zhao, J. Shen, H. Abe. Current status of materials development of nuclear fuel cladding tubes for light water reactors // Nucl. Eng. and Des. – 2017. – 316. – P. 131–150.
3. B. A. Pint, K. A. Terrani, M. P. Brady, T. Cheng, J. R. Keiser. High temperature oxidation of fuel cladding candidate materials in steam–hydrogen environments // J. Nucl. Mater. – 2013. – 440. – P. 420–427.

INFLUENCE OF THERMOCHEMICAL TREATMENT MODES ON THE OXIDATION PROCESS OF FUEL CLADDING TUBES FROM Zr-1%Nb ALLOY

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For zirconium materials and their products, which are widely used in atomic reactors of nuclear power plants, the processes of interaction with the environment significantly affect the degradation of mechanical properties and reduce the service life [1]. These processes include hydrogenation and corrosion. In order to reduce their negative impact, intensive studies are currently underway to develop methods for applying protective coatings to the surface of zirconium materials and for modification of near-surface layers. A promising method for the targeted formation of the phase-structural state of the surface layer of a metal is chemical thermal treatment (CTT), in particular, the method of thermal diffusion saturation with oxygen and nitrogen of the surface layers developed at the H.V. Karpenko (L’viv). This method has proven to be very effective for improving the properties of titanium and its alloys [2]. Zirconium alloys are very similar in structure and properties to titanium alloys, and the first experiments carried out on zirconium alloy tubes showed a significant increase in the hardness of the surface layers and a decrease in the amount of hydrides formed [3]. In this paper, we studied the effect of CTT regimes on the oxidation rate, mechanical and acoustic characteristics of samples from fuel cladding of Ukrainian-made Zr-1%Nb alloy.

Ring samples of a width of 2.8 mm outer diameter of 9.13 mm and a wall thickness of 0.68 mm were cut from a fuel tube. Some of the samples were set aside in the initial state of P7, while the rest passed CTT in a nitrogen medium in three modes: P4 (pressure 1 atm., temperature 580°C), P5 (pressure 0.1 atm, temperature 580°C) and P6 (pressure 1 atm., temperature 680°C). All samples were oxidized in air at 550°C for 5...100 hours with registration of the weight gain. After oxidation, the samples were tensile tested to determine the mechanical characteristics and acoustic emission parameters. The figure shows the dependences of the weight gain of the samples of the Zr-1%Nb alloy after CTT in different modes on the oxidation time. It is seen that CTT noticeably changes the character of the dependence of the change in overweight on time and increases the oxidation resistance.

So, after holding for 100 h (Fig. 1), CTT according to P5 mode reduces weight gain by 2.5 times, by P4 mode by 2 times and by P6 mode by 1.5 times compared to untreated samples. It is shown that CTT reduces the degree of degradation of the mechanical characteristics of fuel cladding, that is, it is a promising method for reducing the corrosion rate and increasing the life of zirconium products.

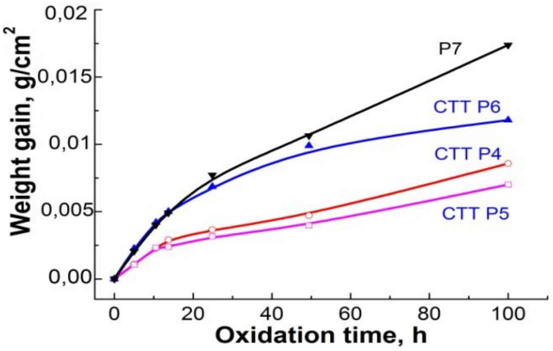

Fig. 1. The kinetics of oxidation of fuel cladding tubes from Zr-1%Nb alloy

1. Никулин С.А. Коррозионное растрескивание циркониевых оболочечных труб. С.А. Никулин, А.Б. Рожнов // МиТОМ. – 2005. – №2. – С. 31–39.
2. Федирко В.Н. Твердорастворное упрочнение поверхностного слоя титановых сплавов. Часть 1. Механические свойства / В.Н. Федирко, А.Г. Лукьяненко, В.С. Труш // МИТОМ. – 2014. – №7. – С. 18–24.
3. Trush V.S. Influence of thermochemical treatment on properties of tubes from Zr1%Nb alloy / V.S. Trush , V.N. Fedirko , A.G. Luk’yanenko , M.A. Tikhonovsky , P.I. Stoev // VANT – 2018. – 21(114). – P. 70–75.

QUANTUM CHEMICAL MODELLING OF DEGRADATION OF CORROSION PROTECTIVE POLYSILOXANE COATINGS

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Polysiloxane coatings due to unique physicochemical properties are used for ambient temperature and high-temperature corrosion protection [1]. Their synthesis to produce the barrier corrosion protection coatings can be easily realised by sol-gel nanotechnology [2].

The work is devoted to quantum chemical modelling of oxidative degradation of polysiloxane sol-gel corrosion protective coatings containing methyl $-CH_3$ or phenyl $-C_6H_5$ functional groups. Two cases have to be separately considered: (i) partial oxidation of functional methyl or phenyl groups related to polysiloxane coating degradation at ambient temperature and sun exposure (atmospheric corrosion), and (ii) complete oxidation of functional methyl or phenyl groups related to polysiloxane coating degradation at elevated temperature in oxidative environment (high-temperature corrosion).

Quantum chemical calculations were performed using the DFT method with B3LYP hybrid functional approximation and 6-31G** basis set. In Fig. 1 the model siloxane cluster $(HO)_7Si_8O_{12}$–R where R = OH, CH_3, C_6H_5, CH_2OH or C_6H_4OH is shown.

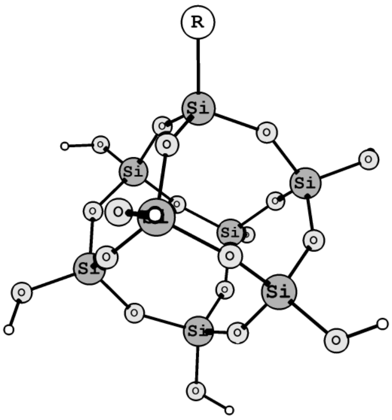

Fig. 1. Model siloxane cluster

Degradation reaction related to the case of ambient temperature partial oxidation of $-CH_3$ group

$$(HO)_7Si_8O_{12}–CH_3 + 0.5\ O_2 \rightarrow (HO)_7Si_8O_{12}–CH_2OH$$

is accompanied by the energy effect of -97.0 kJ/mol.

Similar process of partial oxidation of $-C_6H_5$ group with the formation of hydroxyl group in para position to the silicon atom

$$(HO)_7Si_8O_{12}–C_6H_5 + 0.5\ O_2 \rightarrow (HO)_7Si_8O_{12}–C_6H_4OH$$

has the energy effect of -162.5 kJ/mol.

This means that partial oxidation of $-C_6H_5$ group is characterized by a lower energy effect than the partial oxidation of $-CH_3$ group of the corresponding clusters to form the hydroxyl group. The calculation of Gibbs free energy also indicates that $-C_6H_5$ group of polysiloxane is more sensitive to partial oxidation than $-CH_3$ group.

The high-temperature complete oxidation of $-CH_3$ group in $(HO)_7Si_8O_{12}–CH_3$ cluster

$$(HO)_7Si_8O_{12}–CH_3 + 2\ O_2 \rightarrow (HO)_7Si_8O_{12}–OH + CO_2 + H_2O$$

is accompanied by the energy effect of -792.3 kJ/mol.

The energy effect of complete oxidation of $-C_6H_5$ group in $(HO)_7Si_8O_{12}–C_6H_5$ cluster

$$(HO)_7Si_8O_{12}–C_6H_5 + 7.5\ O_2 \rightarrow (HO)_7Si_8O_{12}–OH + 6\ CO_2 + 2\ H_2O$$

reaches -2966.9 kJ/mol.

Meanwhile, the energy effects of complete oxidation of $-CH_3$ group in the $(HO)_7Si_8O_{12}–CH_3$ cluster and $-C_6H_5$ group in $(HO)_7Si_8O_{12}–C_6H_5$ cluster per 1 mol of O_2 almost coincide and are -396.1 kJ/mol and -395.6 kJ/mol respectively. This means the almost similar sensitivity of $-CH_3$ and $-C_6H_5$ group to high-temperature degradation that is confirmed by calculation of the Gibbs free energy.

1. O. Knudsen, A. Forsgren. Corrosion Control Through Organic Coatings, 2nd. ed. – CRC Press – 2017. – P. 256.
2. S. Pehkonen, S. Yuan. Tailored Thin Coatings for Corrosion Inhibition Using a Molecular Approach. – Academic Press – 2018. – P. 414.

STUDY OF THE STRUCTURE, MECHANICAL AND CORROSIVE CHARACTERISTICS OF THE ALUMINUM INTERMETALLIC

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Significant successes in improving of the mechanical properties of aluminum alloys due to microalloying with scandium, zirconium, titanium and other components have been achieved in the last decade. This allowed not only to increase the strength and plasticity characteristics of same alloys, but also to significantly improve their weldability and corrosion properties. Alloying with scandium was the most effective for Al-Mg alloys.

The aim of this work was to study the structure, mechanical characteristics, and behavior of the intermetallics compounds (INC) strengthening phases on aluminum base with various alloying components (Sc, Ti, Zr, Hf, V) under conditions of corrosion and anodic dissolution in a 3% NaCl solution.

The intermetallics compounds (INC) Al_3Sc, Ti_3Al, Al_3Zr, Al_3Hf, Al_3V, that are used for strengthening of aluminum alloys were selected for the study. The technology of rapid crystallization from the liquid state developed by the authors for producing amorphous alloys by the spinning method was used for intermetallics production. Using the technology of rapid crystallization from a liquid state made it possible to obtain sufficiently fine grain for the as-cast material in a molten state with a size of 15...20 μm. X-ray analysis showed that the Ti_3Al, Al_3Zr intermetallics are a single-phase material, and the Al_3Sc, Al_3Hf, Al_3V intermetallics contain several phases, but the content of the secondary phases did not exceed 3 vol. %.

Studies of the mechanical characteristics showed that the maximum hardness HV of 6.75 GPa had the IMC Al_3Hf and the minimal (2.0 GPa) had the IMC Al_3Sc and this phase is the most plastic.

It was found that in a 3% NaCl solution, the corrosion potentials (E_{cor}) of Al_3Sc, Al_3Hf, and Al_3V have close values (-0.52 -0.57V), and E_{cor} IMC Ti_3Al is significantly shifted to the region of more positive potentials (-0.30V). In the field of potentials close to E_{cor} the dissolution rate of intermetallic phases in a 3% NaCl solution increase in the sequence: $AlTi_3 < Al_3Sc < Al_3Hf < Al_3V$.

The role of the IMC phase in the process of corrosion dissolution of an aluminum alloy depends on its composition, which determines the value of $E_{cor.}$ in this aggressive environment. It was shown that the anodic dissolution of the Al-3 wt% Mg alloy alloyed with 0.3 wt. % Sc in a 3% NaCl solution proceeds in the potential region more negative than the dissolution of the IMC Al_3Sc. Thus, the IMC phases are cathodic inclusions relative to the Al-Mg alloy matrix and will not selectively dissolve from the alloy under corrosion conditions.

OBTAINING OF POROUS SILICON AND SILICON NANOWIRES BY CONTACT CORROSION ETCHING OF NANOSTRUCTURES Si/MNPs

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Metal-assisted chemical etching (MACE) of n-type silicon, which by the mechanism is the contact corrosion of the surface of Si/M nanostructures [1], is an effective method of obtaining nanoporous semiconductors and nanowires (SiNWs) [2, 3]. The pore diameter, their depth and the geometry of SiNWs depend on the nature of the metal and the morphology of its nanostructures, in particular the geometry of metal nanoparticles (MNPs). However, such a pattern is not sufficiently elucidated in the literature that constrains the controlled synthesis of silicon nanostructures. The purpose of the work is to determine the influence of the geometry of MNPs (M = Ag, Pd, Au) of Si/MNPs on the formation of 3D silicon nanostructures by the method (MACE).

According to the electrochemical mechanism (1-4), the contact corrosion of silicon is directed (Fig. *a*) by anode (2, 3) and chemical (4) reactions. It is shown that the formation of Si nanoporous mainly occurs by etching in a solution of H_2O_2 + HF nanostructures of Si/AgNPs and Si/PdNPs (Fig. *b*), the formation of SiNWs (Fig. *c*) – Si/AuNPs. This difference is due to the significant difference in the values of standard electrode potentials Ag, Pd, Au. This results in different values of ΔE in the etching process and, accordingly, in different geometries of pores and nanowires.

Cathode region (M): $2H^+ + 2e \rightarrow H_2$ (1)
Anode region (Si): $Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e$ (2)
$3Si + 6HF \rightarrow H_2[SiF_6] + 4H^+ + 4e$ (3)
$SiO_2 + 6HF \rightarrow H_2[SiF_6] + 2H_2O$. (4)

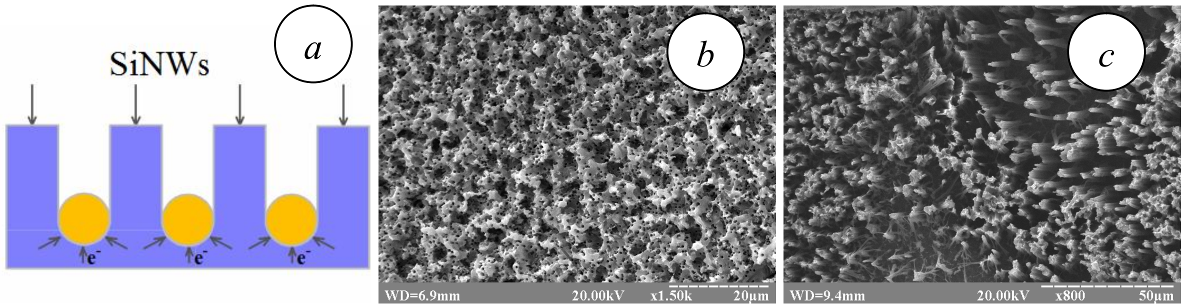

Fig. Scheme of contact metal activated silicon system Si/MNPs (*a*) and SEM images product of MACE – Si nanoporous (*b*) and SiNWs (*c*)

The correlation between the sizes of MNPs, the morphology of the Si/MNPs metal deposit and the geometry of silicon nanostructures (Si nanoporous, SiNWs) obtained by the MACE method was established. The directions of application of the latter are given.

1. General corrosion during metal-assisted etching of n-type silicon using different metal catalysts of silver, gold, and platinum / A. Matsumoto, H. Son, M. Eguchi, K. Iwamoto, Y. Shimada, K. Furukawa, S. Yae // RSC Adv. – 2020. – Vol. 10. – P. 253–259.
2. Deposition of nanostructured metals on the surface of silicon by galvanic replacement: a mini-review / O.Î. Kuntyi, G.I. Zozulya, M.V. Shepida, S.I. Nichkalo // Voprosy khimii i khimicheskoi tekhnologii. – 2019. – No. 3. – P. 74–82.
3. Deposition of Gold Nanoparticles via Galvanic Replacement in DMSO and Their Influence on Formation of Silicon Nanostructures / M. Shepida, O. Kuntyi, S. Nichkalo, G. Zozulya, S. Korniy // Adv. Mater. Sci. Engineer. – 2019. – Article ID 2629464. – P. 7.

OBTAINING OF POROUS-Cu/Ag-NANO SURFACES BY DEALLOING AND GALVANIC REPLACEMENT PROCESYS

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Modern research in the field of electrochemical catalysis is aimed at the formation of a highly developed active surface. Porous and rough nanomaterials are characterized by a large electrocatalytic surface area and high density of active sites, especially at the edges, vertices, and defects. Modification of such a metastable surface by metallic nanostructures is a promising method of obtaining electrocatalysts with high activity and selectivity [1, 2]. The proposed work presents the results of studies on obtaining bimetal surface Cu-porous/Ag-nano for CO_2 reduction on catalytic active cathode.

The following scheme of obtaining of Cu-porous/Ag-nan is proposed for using такі послідовні processes: 1) formation of Cu-porous surface by anode dealloing of Cu-Zn system in H_2SO_4 solution; 2) deposition of silver nanostructures by galvanic replacement (GR). It is shown that when using electrochemical dissolution of zinc using a brass foil is formed well to develop an average surface with a pore size of 100-300 nm. Electroplating of silver to the last in the $AgNO_3$ outlet in the ultrasonic mode used nanosized dendritic structures (70…100 nm) with good adhesion to the level and uniform distribution (Fig. 1a). It is established that the main factors of this galvanic substitution are the morphological sediment of silver, which is the concentration of dissolved reducing metal and the deposition time. With long-term processing of the process, the sediment fluid and the strength of filling the average force are reached (Fig. 1b).

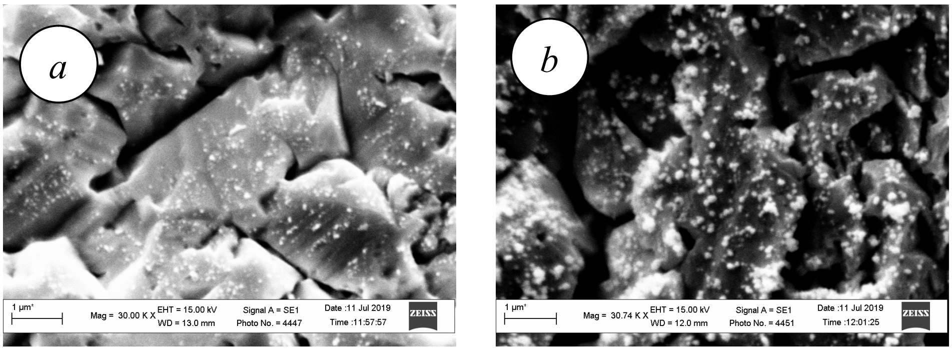

Fig. SEM images of Cu-porous/Ag-nano obtained by galvanic replacement of silver on dealloyed Cu-Zn system in $AgNO_3$ during 15 (*a*) and 45 s (*b*)

Bimetal surface Cu-porous/Ag-nano was investigated as cathodes for the reduction of carbon (IV) oxide in a 0.1 M solution of $KHCO_3$, saturated with CO_2. It is shown that porous copper electrodes modified with nanoscale silver are characterized by significantly higher catalytic activity compared to brass foil and porous copper surface formed by electrochemical dissolution of zinc from the brass foil surface.

1. J.-H. Zhou, Y.-W. Zhang. Metal-based heterogeneous electrocatalysts for reduction of carbon dioxide and nitrogen: mechanisms, recent advances and perspective // React. Chem. Eng. – 2018. – 3. – P. 591–625.
2. Electrochemical synthesis of metal nanoparticles and nanocomposites / O. Kuntyi, M. Yatsyshyn, G. Zozula O. Dodrovetska, O. Reshetnyak. Monograph. – Lviv: Lviv Polytechnic Publishing House. – 2019. – P. 288.

INSTRUMENTS FOR IMPROVING THE MANAGEMENT OF CORROSION PROTECTABILITY OF INDUSTRIAL FACILITIES

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The present paper deals with a study of the theoretical bases for forming and developing the innovative potential of corrosion protectability as an important element of the state technical and economic policy in the field of quality and safety of industrial production. Significant features are viewed of disturbances of an operable state linked with a critical corrosion state, increase in losses due to early failures and shutdown of industrial facilities. Relationship is determined between the research of the of risk essence as an economic category and technical and economic parameters of wear of industrial facilities, which causes emergence of threats to quality, reliability and safety in the long-term operation of production assets of enterprises. It has been found that formation of economic mechanisms for corrosion protectability assuring under the limited financial and material resources is linked with justification of technical and economic threats criteria. It is shown that contemporary market of materials and services formed under lack of requirements for quality and reliability of system of corrosion protection of structural steel carries a high level of risks.

Mechanism is determined for transforming the source information on threat factors into information on possibilities of realization conditions and corresponding intervals of variation in efficiency indices of technical and economic protection. Procedural requirements are developed for economic safety concerned with confirmation of compliance of quality and reliability indices of primary and secondary protection. Considering the design provisions of the limit state concept, the classification features of a generalized reliability matrix for corrosion protection of structural steel have been developed. A risk-based approach is proposed to overcome the uncertainty of parameters of corrosion protectability of structures and installations according to the requirements of the quality function deployment *QFD*. Established are the nomenclature, indices and methods of the *off-line* and *on-line* monitoring (conformity assessment) of the determinative parameters of the corrosion state of structures and their protective coatings. The classified risk level scale was developed based on the degree of corrosion hazard (protectability) to assure serviceability and durability of structures with account for the requirements of the process safety of industrial facilities.

The mechanism of controlling the cycle of economic development of corrosion protection systems is justified. Determined are advantages of reengineering of obsolete regulatory requirements for developing the entrepreneurial risk management programs on the basis of preventive measures to prevent corrosion losses. The procedure is implemented of making and controlling acceptable solutions on the principles of «lean production» of the *Lean Six Sigma* concept. It is proved that the use of the balanced indices of technical and economic protectability promotes to ensure reliability at an acceptable risk, as well as to switch from the costly to innovative management of resource saving and technological safety of industrial enterprises.

DIFFERENTIAL EQUATIONS OF THE EFFECT OF STRESSES ONTO ELECTRIC POTENTIALS IN A FILLED WITH A SUBSTANCE CRACK-TYPE DEFECT

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A model of a filled crack cavity whose shape is a thin elongated ellipse is analyzed. The electrochemical state near a tip of a filled crack in a metal body was estimated. The relation between stress-strain state and the electric potential of the medium in such a defect was established. The corresponding electrode potential at the interface between the medium and the deformed metal was estimated. The distributions of electrical potentials in stress-strained metal, in a double electric layer arising at the contact of the metal with the medium, as well as in the metal-contacting medium, obtained on the basis of an analytical solution of the equations [1,2].

$$\begin{cases} \dfrac{1}{\chi_m^2}\nabla^2\varphi_m(x,y)-\varphi_m(x,y)=\dfrac{\beta K\varepsilon_\sigma(x,y)}{\chi_m^2\varepsilon_0}, \quad \chi_m^2=\dfrac{\rho_m C_m}{\varepsilon_0}; \\ \dfrac{1}{\chi_{mc}^2}\nabla^2\varphi_{mc}(x,y)-\varphi_{mc}(x,y)=0, \quad \chi_{mc}^2=\dfrac{2F^2 I}{\varepsilon\varepsilon_0 RT}; \\ \dfrac{1}{\chi_c^2}\nabla^2\varphi_c(x,y)-\varphi_c(x,y)=0, \quad \chi_c^2=\dfrac{e^2}{kT\varepsilon\varepsilon_0}\sum z_i^2 n_i. \end{cases} \qquad (1)$$

Here, ∇^2 is the Laplacian operator; $\varphi_m(x,y)$, $\varphi_m(x,y)$, $\varphi_c(x,y)$ are the electric potentials in metal, in double electric layer, and in medium, respectively; ρ_m, C_m are the density and electrical capacitance of the metal, respectively; ε_0 is the dielectric constant; β is the coefficient of the volumetric electrical expansion; K is the bulk modulus; ε_σ is the volumetric expansion of the body element, $I=0{,}5\sum c_{0i}z_i^2$ is the ionic force of the solution determined according to the Debye-Huckel theory of solutions; z_i is the charge of the i-th kind ions; n_i is the number of ions of i-th kind; c_{0i} is the concentration of the i-th kind ions; ε is the relative permittivity of the medium; T is the absolute temperature; k is the Boltzmann constant; R is the universal gas constant; F is the Faraday constant. On the basis of the aforesaid equations, a solution for the electric potential in the metal is analyzed. An analytical solution concerning the change in electrical potential in the medium that fills an elliptical crack type defect is obtained. The electric potential φ_{mc} is estimated in a double electric layer. The calculations had indicated that the maximum shift of the electrode potential at the crack tip with a length of 14 mm is achieved at the ratio b / a = 0,01 of the ellipse axes (0,2 % strain) in the case of different activity of interacting of the mediums. The greatest shift is the electrode potential $\Delta\varphi \approx 20$ mV is experienced in case of metal contact with 3% NaCl solution. On the basis of the dependence of the electrode potential shift at the tip of the "elongated" ellipse (b / a = 0.01, a = 7 mm, p = 1.8 MPa, $\varepsilon_\sigma = 0{,}2\%$) on the concentration of c_{NaCl} medium, it was found that with increasing of the content of NaCl ions, the maximum possible shifts of the electrode potential reach a certain asymptotic value. The results obtained allow us to conduct studies of the interaction of hydrogen-containing media with metals [1,2].

1. M. H. Stashchuk Analysis of the influence of elastic deformation on the electrode potential of a metal cylinder in a mediumin // Mater. Sci. – 2000. – Vol. 36. No 1. – P. 54–59.
2. Stashchuk M. H. Influence of Hydrogen Concentration on the Stresses in a Solid Metallic Cylinder // Mater. Sci. – 2018. – Vol. 53, No 6. –P. 823–831.

IMPACT OF CORROSIVE MEDIUM ON FATIGUE STRENGTH OF BASALT REINFORCEMENT

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At the present stage of the construction industry development in the reinforced concrete structural elements, along with the traditional steel reinforcement, composite basalt reinforcement is used, which is made from continuous basalt fiber and a polymer matrix. Such a replacement significantly reduces their cost and leads to significant metal savings. Basalt fibers are obtained from one-component cheap raw materials using single-stage technology. Basalt rocks are used as raw materials for the production of basalt fibers. Basalt reinforcement is characterized by high tensile strength ($\sigma_B \approx 1100$ MPa), corrosion resistance and low thermal conductivity.

However, the properties of basalt reinforcement has not been adequately studied yet. Therefore, the purpose of this work is to determine the fatigue strength of samples made of basalt reinforcement with a nominal diameter of 10 mm considering cyclic stretching and the influence of corrosive medium. To determine the corrosion resistance, one batch of experimental samples was kept in distilled water and the other one in alkaline medium (5% potassium hydroxide solution). Weller curves are built and endurance limits (σN) are set on a given test database (N). The test database (N) equals to 2 · 106 cycles. To determine the fatigue strength of basalt reinforcement experimental studies were carried out in the laboratory at T = 20°C, with the hydraulic certified pulsator EUS-20 at cycle asymmetry R = 0,33 and load frequency f = 10 Hz [1].

According to the results of experimental studies fatigue curves of basalt reinforcement for various corrosive media (fig. 1) are built and the endurance limits (σ_N) are established.

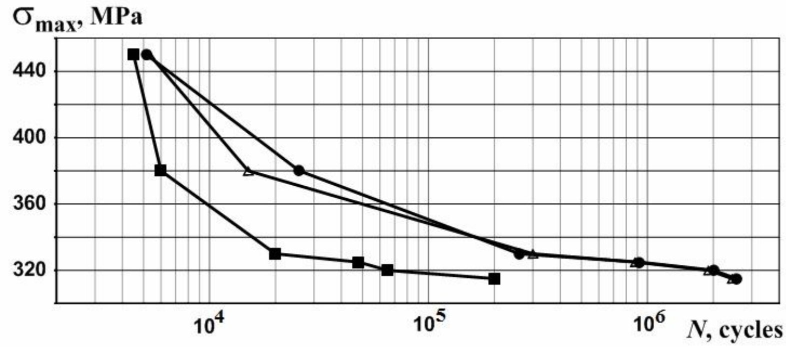

Fig. 1. Weller curve for basalt reinforcement:
● – air; ∆ – distilled water; ■ – KON.

The diagram shows that distilled water slightly affects the fatigue endurance of basalt reinforcement compared with the strength in air, and an alkaline medium abruptly reduces it in time.

1. Hvozdyuk, M.M., Babyak, I.P., Hembara, T.V., Kostiv, R.B. Static and fatigue strength of basalt reinforcements // Mater. Sci.. – 2015. – Vol. 49. Iss.5. – P. 644–649.

EFFECT OF CORROSION ENVIRONMENT ON METAL CREEP

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Creep and corrosion cracking is characteristic of thermal and nuclear power plant equipment components, which are operated at high mechanical loads and temperatures and interact with chloride-containing work environments. The substantiation of the operability of such structural elements with regard to creep is greatly complicated by the dependence of the creep rate of structural materials on many factors - temperature, mechanical stresses and working environments. In the report, have based on the previously developed by the authors of the energy approach [1], is constructed calculated model for determining the durability of structural elements by high-temperature creep in metallic materials under the action of long-term loads and corrosive environment.

To take into account the effect of the chloride medium on the creep of the metal, we have obtained the relation of the creep rate:

$$\frac{\partial \varepsilon_{ij}^{cr}}{\partial t} = A\sigma_{eq}^{m} 10^{n\sigma + m_1 \chi},$$

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

The developed model was tested on the example of the study of heat exchange tubes manufactured with an inner radius r_1 = 17 mm and an outer radius r_2 = 21 mm (Fig. 1.a) made of stainless steel 12X18H12T, convection surfaces of an intermediate superheater of a steam boiler. It was believed that the temperature of the metal of the heat exchange tubes corresponds to T = 500 °C and the working medium, which causes corrosion cracking, acts on the inner surface of the pipes. Boiling solutions of magnesium chloride were taken as the equivalent of the steam-water working medium.

The results of calculations of the deformation and fracture of heat transfer tubes of steam superheaters of steam boilers under creep and corrosion cracking conditions of structural materials are presented in Fig. 1.b.

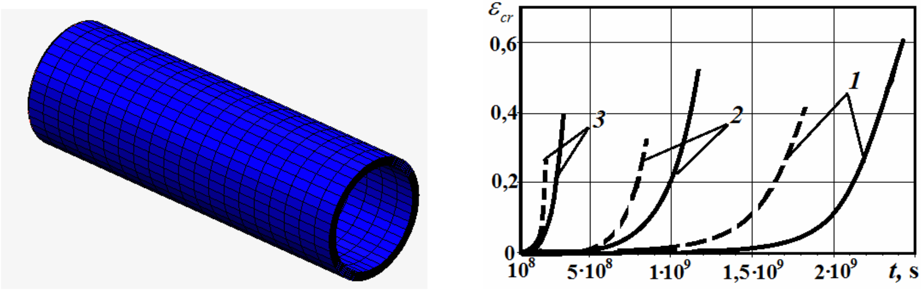

Fig. 1. Heat exchanger pipe fragment (*a*) and accumulation of creep strain over time in place of the highest strain energy on the outer wall of the pipe (solid lines), on the inner wall (dashed lines); without considering the environment (1), in 5% (2) and in 10 % solutions $MgCl_2$ (3) (b)

The results obtained are the basis for assessing the strength and reliability of structural elements, taking into account the mutual influence on the resource of various damage mechanisms of structural materials. This is illustrated by the example of heat transfer pipes from operation under creep and corrosion cracking conditions.

1. Ivanytskyi Ya., Kharchenko Ye., Hembara O., Chepil O., Sapuzhak Ya., Hembara N. The energy approach to the evaluation of hydrogen effect on the damage accumulation // Procedia Structural Integrity. – 2019. – 16. – P. 126–133.

TRIBOCORROSION PROPERTIES OF Fe-Ni BASED PLASMA-POWDER COATINGS

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Corrosion and tribocorrosion of Fe-Ni-based alloy, obtained by plasma-powder surfacing, have been investigated in a solution 3% NaCl+NH_3, 3% NaCl+H_2S and 3% NaCl. The corrosion rate of alloy in 3% NaCl, 3% NaCl+H_2S and 3% NaCl+ NH_3 environments is determined by cathode reactions. The lowest cathode currents are found in a solution 3% NaCl+ NH_3, in 3% NaCl+H_2S they are ~ 2 times higher, in 3% NaCl - three times (table 1). The character of the anode curves illustrates the formation of incompact passive films, which provide partial inhibition of the anode processes.

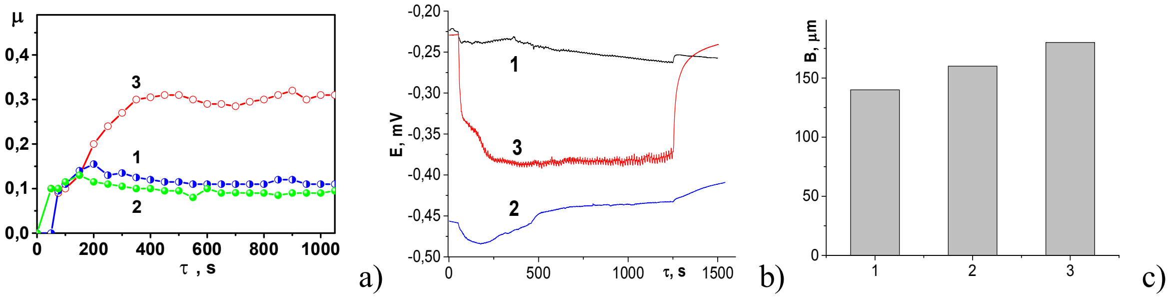
Table 1. Electrochemical parameters of deposited alloy in corrosive environments

Environment	i_{anode}; mA/cm^2	$i_{cathode}$; mA/cm^2
3% NaCl	$1{,}9\cdot10^{-3}$	$1{,}5\cdot10^{-3}$
3% NaCl+H_2S	$1{,}6\cdot10^{-3}$	$1{,}1\cdot10^{-3}$
3% NaCl+NH_3	$4{,}5\cdot10^{-4}$	$4{,}7\cdot10^{-4}$

Correlation between coefficients of friction and tribocorrosion potentials of alloy was found. Significant shift of electrode potential at the beginning of the friction and further its oscillations indicate fast formation of secondary surface structures in the corrosion environment. In this case destruction of the metal is determined mainly by the corrosion factor.

Slight difference between the potentials of corrosion and tribocorrosion and its stability during friction illustrates the low rate of chemical processes. Therefore, wear of metal mostly depends on mechanical factors.

The corrosion factor dominates at the friction in a 3% NaCl + NH_3 solution. Fluctuations of electrode potentials indicate a high rate of secondary structures formation after activation of surface by friction (fig.1). Instability of the structure at the friction surface contributes to increasing the friction factor and wear increase. Persistent growth of electrode potentials was observed at the friction in 3% NaCl + H_2S. It indicates a formation of secondary structures on the surface, which decrease the friction factor. Probably, these are sulfide phases, which act as a solid lubrication.



a) b) c)

Fig. 1. Changes of friction factor (a), electrode potential on the friction surface (b), and friction track width (c) in solutions 3% NaCl (1), 3% NaCl + H_2S (2), 3% NaCl + NH_3 (3)

COMPARATIVE STUDIES OF CALCIUM PHOSPHATE COATINGS FORMED ON Mg-RE AND Mg-Ca MAGNESIUM ALLOYS

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Mg and its alloys are the lightest structural metals. Their low mass density and elastic modulus present similar properties to those of human bones, hence one of the most promising candidate osteogenic metals materials for the production of bioresorbable implants [1]. Magnesium alloys dissolve readily in aqueous solution especially in the presence of chloride ion. Such corrosion process leads to a fast evolution of hydrogen gas and strong local alkalinisation, which becomes a serious problem especially for the surrounding bone tissue. Therefore it is a strong demand for elaboration of an effective surface protective layer slowing down the corrosion process in physiological solution and simultaneously facilitate formation of hydroxyapatite which is called bone mineral. At Łukasiewicz - Institute of Precision Mechanics the plasma electrolytic oxidation process in phosphate ions containing solution was elaborated which provided a coating of improved corrosion resistance, as well as, adequate biocompatibility in comparison to uncoated substrate. Electrochemical deposition of conversion coating can be an alternative method of surface modification of magnesium alloys. This study aims to prepare calcium phosphate coatings on RZ5 and Mg–1.0 Ca alloys by cathodic deposition and compare their different biodegradation behaviour by means of electrochemical impedance spectroscopy (EIS) and hydrogen evolution test in SBF (simulated body fluids) solutions. XRD results show that the deposited coatings mainly consist of brushite (DCPD, $CaHPO_4 \cdot 2H_2O$) crystallites. The increase of impedance of the coated samples indicate an improvement of corrosion resistance of the substrates. The hydrogen evolution rates of the coated samples were much lower than that of uncoated alloys exposed to SBF solution at 37°C.

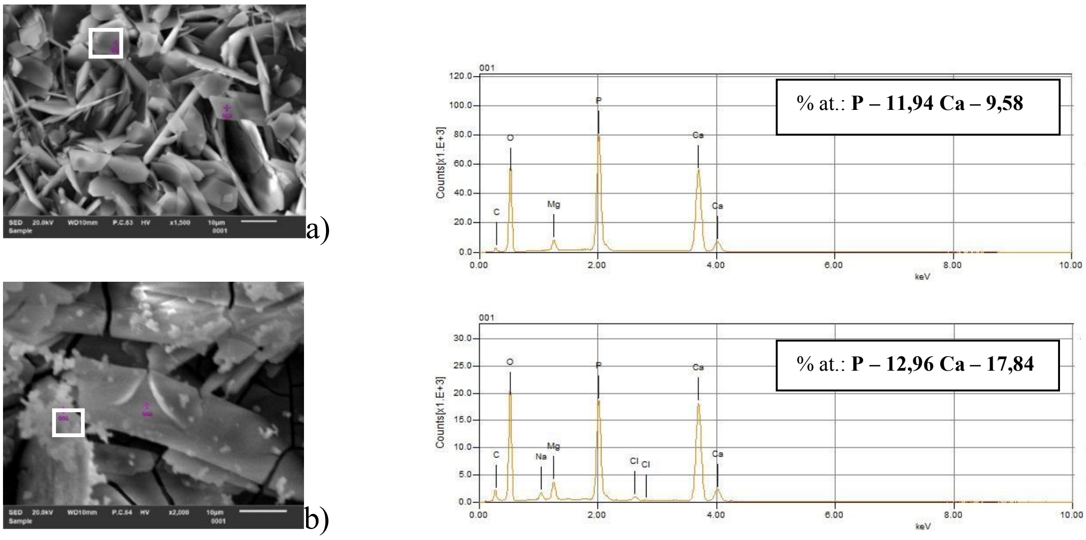

Fig. 1 SEM images and EDS analysis of calcium phosphate coating on RZ5 mangesium alloy before (a) and after (b) 9 days of immersion in SBF solution.

1. MP Staigera, AM. Pietaka, J. Huadmaia, G. Dias, Magnesium and its alloys as orthopedic biomaterials: a review. // Biomaterials – 2006 – Vol. 27 – P. 1728 – 1734.

CORROSION PROPERTIES OF COMPOSITE COATINGS Ni /DIAMOND

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The paper presents the results of research of Ni/diamond nanocomposite coatings produced by electrochemical reduction on carbon steel substrate. The performed study concerned nanocrystalline composite coatings and for comparative purposes nanocrystalline nickel coating. The coatings Ni/diamond were deposited in the Watts bath containing nanometric particles of diamond. The research included: chemical and phase composition analysis, surface roughness and microhardness measurements using the Vickers method. Corrosion resistances of Ni/diamond and nickel nanocomposite coatings were tested by electrochemical potentiodynamic method.

The results of performed research have shown that the produced composite coatings exhibit compact structures and good adhesions to the steel substrate. Moreover, Ni/diamond composite coatings are characterized by an increased surface development.

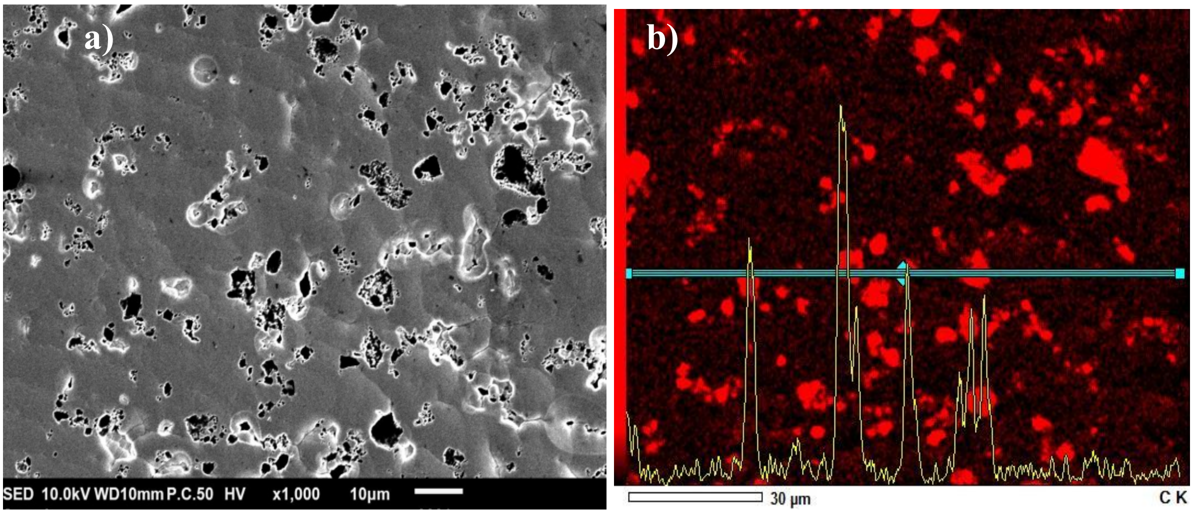

Fig. SEM image of surface topography (a) and carbon distribution (b) in a composite Ni/diamond coating

Embedding nanometric diamond particles into the nanocrystalline nickel matrix increases the hardness of the coating material. Moreover, despite of the higher degree of development, composite coatings Ni/diamond produced by electrocrystallization exhibited greater corrosion resistance than Ni nanocrystalline coating.

ELECTRODEPOSITION AND CHARACTERIZATION OF Ni/Si_3N_4 COMPOSITE COATINGS

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Nickel matrix composite coatings are widely used, especially in the automotive and aerospace industries because of their very good mechanical properties and suitable corrosion resistance.

Electrochemical nickel coatings with a built-in dispersed phase are characterized by enhanced properties, in comparison with regular nickel coatings. Inclusions at the surface affect both the layer's corrosion behaviour, as well as its mechanical and physical properties. The brush plating technique can be used in the production of many composite coatings. In the literature can be found the data on the application of nickel matrix composite coatings and Al particles [1], carbon nanotubes [2], C or Cu particles [3], with a Ni-P matrix and WC particles [4] produced by this method. Co-deposited electrobrush plating is widely used to produce particle-reinforced metal matrix composite coatings due to its simplicity, low cost and versatility [4].

The paper presents the results of research on Ni/Si_3N_4 composite coatings produced by selective brush plating method on a copper substrate. The surface topography and morphology, structure, microhardness and the corrosion resistance of the Ni and Ni/Si_3N_4 coatings were investigated. Analysis of the chemical composition by the energy dispersive spectroscopy (EDS) showed that the particles of the dispersion phase were embedded into the nickel matrix. The produced composite coatings exhibit a finer Ni grains, higher microhardness and corrosion resistance than coatings of pure nickel.

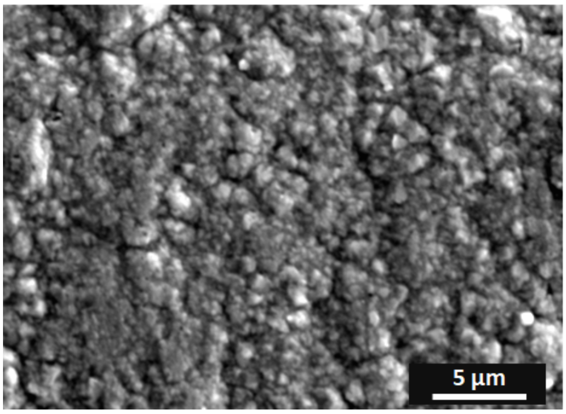

Fig. 1. SEM image of surface topography and morphology of Ni/Si_3N_4(15) composite coating

1. L. Isern, S. Impey, H. Almond, S.J. Clouser, J.L. Endrino Structure zone diagram and particle incorporation of nickel brush plated composite coatings // Sci. Rep-UK – 2017. – 7,44561 – P. 1–12.
2. J. Tan, T. Yu, B. Xu, Q. Yao Microstructure and wear resistance of nickel-carbon nanotube composite coating from brush plating technique // Tribol. Lett. – 2006. – 21 – P. 107–111.
3. H. Liu, X. Wang, H. Ji Fabrication of lotus-leaf-like superhydrophobic surfaces via Ni-based nano-composite electro-brush plating // Appl. Surf. Sci. – 2014. – 288 – P. 341 – 348.
4. M. Xu, S. Zhu, H. Ding, X. Qi Influence of electric contact strengthening on the microstructure and properties of electro brush plating Ni-P/nano-WC composite coatings // Int. J. Refract. Met. H. – 2017. – 62 – P. 70 – 77.

THE CORROSION RESISTANCE OF GALVANIC Fe-Co-Mo COATINGS

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The influence of the quantitative and phase composition and coatings surface relief on the corrosion resistance of ternary Fe-Co-Mo alloys is investigated.

The Fe-Co-Mo coatings were formed onto a copper and mild steel substrates from the Fe (III) based citrate electrolyte at (*i*) direct current (dc) with density *i* of 2–4 A/dm^2 and (ii) pulse current (pc) with amplitude *i* of 3–5 A/dm^2 in the on/off time range of 2–50 msec [1].

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. The structure of the deposits was examined by X-ray diffraction analysis using a diffractometer (DRON-2.0) in the emission of cobalt anode and CuKα radiation. Coatings surface relief was determined by contact method using atomic force microscope probe (AFM) NT-206. The analysis of AFM images was performed using Explorer software.

The polarization resistance method, the electrode impedance spectroscopy and gravimetric measurements were used for the investigation of Fe-Co-Mo coatings corrosion behavior in the media of a different acidity. It was established that the corrosion resistance of the sample coated with Fe-Co-Mo exceeds that of the substrate, i.e. mild steel by the two orders of magnitude. The corrosion rate is decreased with an increase in pH of the solutions and with the enrichment of the alloys with refractory components. The corrosion resistance of Fe-Co-Mo system is equal to 3400 Ohm·cm^2 and it is conditioned by the formation of the layer film consisting of molybdenum oxides [2].

Table 1. The corrosion indicators of mild steel, and Fe-Co-Mo coatings

Electrode materials, ω, at. %	pH 3		pH 5		pH 9,5	
	E_{cor}, V	lg i_{cor}, A/dm^2	E_{cor}, V	lg i_{cor}, A/dm^2	E_{cor}, V	lg i_{cor}, A/dm^2
mild steel	–0.34	–2.8	–0.35	–3.0	–0.32	–2.8
Fe78Mo22	–0.26	–3.3	–0.49	–3.2	–0.67	–3.3
Fe51Co36Mo13	–0.25	–3.7	–0.3	–4.9	–0.46	–5.5
Fe31Co31Mo38	–0.16	–4.5	–0.31	–4.8	–0.32	–5.1

Triangular diagrams "the corrosion depth index k_h, mm/year – the alloys composition" for the electrolytic system Fe–Co–Mo were designed on the basis of experimental data. The diagrams allow us to define the range of the metals content in the binary Fe-Mo, Co-Mo and ternary Fe-Co-Mo alloys in order to obtain the coatings with appropriate corrosion resistance depending on service conditions [3].

1. M.V. Ved', I.Yu. Ermolenko, N.D. Sakhnenko, S.I. Zyubanova, Yu.I. Sachanova Methods for controlling the composition and morphology of electrodeposited Fe–Mo and Fe-Co-Mo coatings // Surf. Eng. Appl. Electrochem. – 2017. – Vol. 53. No. 6. – P. 525–532.
2. M. Ved', N. Sakhnenko, T. Nenastina, I. Yermolenko, V. Proskurina, & M. Volobuyev Corrosion behavior of the electrolytic ternary cobalt alloys with Mo(W) and Zr in alkaline solution // Ukrainian Chemistry Journal. – 2019. – Vol. 85. No. 12. – P. 96–109.
3. I.Yu. Yermolenko, M.V. Ved', N.D. Sakhnenko Galvanichny pokryttya ternarnymy splavamy zaliza: formuvannya, vlastyvosti [Galvanic coatings of iron ternary alloys: formation, properties]: monography. – Kharkov: Харьков: FOP Brovin O.V., 2019. – P. 248. (in Ukrainian).

FUNCTIONAL PEO-COATINGS ON VALVE METALS IN CORROSION PROTECTION TECHNOLOGIES AND ENVIRONMENTAL CATALYSIS

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The widespread use of valve metals and alloys based on them in the aerospace industry, shipbuilding and engineering, medicine, electronics and many other fields of science and technology is due to the complex of important physicochemical characteristics such as high corrosion resistance, specific strength, heat resistance and processing technology. To improve the operational characteristics and expand the range of functional properties of structural materials, various methods of surface treatment are used. One of the most promising of them is plasma electrolytic oxidizing (PEO). The use of PEO allows in one technological process to combine surface homogenization of the processed material with the formation of coatings with enhanced functional properties [1].

Oxide coatings were formed from alkaline electrolytes with the addition of transition metal salts (Co, Mn) on aluminum (A99, D16, AMn, AK12M2MgN) and titanium (VT1-0, OT-4) alloys by the PEO method under galvanostatic mode using the direct current source B5-50. Current density of treatment was of 1–20 A/dm^2, voltage – up to 240 V. PEO was carried out at constant agitation of working electrolytes for 30–60 minutes. Study of the surface morphology of the oxide systems was carried out using the scanning electron microscope ZEISS EVO 40XVP. Topography of the surface was studied applying the atomic force microscope NT-206. The energy dispersion spectrometer Oxford INCA Energy 350 was used to determine chemical composition of the surface oxide layers. The structure of the coatings was examined by X-ray diffraction analysis using a diffractometer DRON-2.0 in monochromatic Co-Kα radiation. The corrosion resistance of mixed oxide coatings was determined by the methods of polarization resistance and electrode impedance spectroscopy (EIS).

It was found that the coatings surface morphology depends on the nature of both processed material and used dopants. Management of the chemical and phase composition of such coatings, as well as the surface topography and grain size can be carried out by varying the composition of the electrolytes, the concentration and ratio of components, as well as the energy and time parameters of the electrolysis [2].

The composition, morphology, and topography of the surface of the oxide systems doped with Co and Mn formed on the titanium and aluminum alloys are a prerequisite for the high corrosion resistance. The results of EIS measurements reflect the high chemical resistance of the synthesized materials in media of different acidity. Calculated parameters namely deep corrosion index of k_h of the PEO-coatings is several times lower than for coatings formed by classical oxidizing. The obtained oxide coatings also are characterized by high catalytic activity [3]. The complex of functional properties makes it possible to use mixed oxide systems in the technologies for neutralizing toxicants in the liquid and gas phases, including elevated temperatures.

1. V. S. Rudnev, I. V. Lukiyanchuk, M. S. Vasilyeva, M. A. Medkov, M. V. Adigamova, V. I. Sergienko Aluminum- and titanium-supported plasma electrolytic multicomponent coatings with magnetic, catalytic, biocide or biocompatible properties // Surf. Coat. Technol. – 2016. – Vol. 307(Part C). – P. 1219–1235.
2. Karakurkchi, M. Sakhnenko, M. Ved' Study of the influence of oxidizing parameters on the composition and morphology of $Al_2O_3{\cdot}CoO_x$ coatings on AL25 alloy // East.-Europ. J. Enterpr. Technol. – 2018. – Vol. 2/12. Iss. 92. – P. 11–19.
3. V. Parsadanov, M. D. Sakhnenko, V. O. Khyzhnyak, H. V. Karakurkchi Improving the environmental performance of engines by intra-cylinder neutralization of toxic exhaust gases // Intern. Combust. Engin. – 2016. – Iss. 2. – P. 63–67.

CORROSION RESISTANCE OF COMPOSITE ALLOY COATINGS OF COBALT WITH REFRACTORY METALS

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The development of cheap catalysts based on multi-component systems is an urgent scientific and technological challenge. This is due to milder corrosion conditions, accelerated cathodic oxygen reduction and anodic oxidation of simple alcohols in alkaline electrolytes. Nanocrystalline composite coatings of tungsten, molybdenum, and zirconium alloys with metals of the iron group can replace platinum electrocatalysts. Therefore, the purpose of the study was to determine the corrosion resistance of functional composite coatings of cobalt alloys with refractory metals deposited from poly-ligand electrolytes.

For coatings of tungsten and molybdenum alloys containing zirconium oxide, corrosion behavior depends not only on the material composition and surface morphology, but also on the pH of the test solutions. It should be noted that corrosion occurs mainly with oxygen depolarization, especially at pH> 3. Therefore, corrosion tests were carried out in 1M Na2SO4 solution with addition of sulfuric acid for pH 3 or sodium hydroxide for pH 11, and 3% solution of NaCl and at room temperature. To determine the polarization resistance (Rp), cathode and anode voltammograms were recorded near the corrosion potential. The corrosion resistance of the materials was evaluated using a deep corrosion rate indicator.

It was found that the corrosion rate in acidic medium decreases with increasing zirconium content (Table). Despite its rather negative potential, zirconium is an extremely corrosion-resistant metal due to the formation on its surface of a thin film of very stable zirconium oxide (IV), which reliably protects it from oxidation and destruction.

Cobalt, on the contrary, forms oxides of the basic character, and therefore exhibits its chemical resistance in alkaline and neutral media.

The results show that in alkaline and neutral environments, the corrosion potentials shift in the negative direction relative to those measured in the acidic ьувшгь, and the corrosion resistance does not change significantly. This can be explained by the fact that the tungsten and molybdenum acid oxides formed on the surface are not stable in an alkaline environment. Considering the fact that in the neutral there is the local alkalinity of the surface layer due to the reduction of oxygen, and chlorides provoke the local destruction of the protective film, it is possible to state the synergistic effect of alloying metals on the corrosion rate of coatings.

Table 1. Corrosion characteristics of cobalt-based composite alloys

Alloy coating	pH 3		pH 7		pH 11	
	E_{cor}, V	k_{h}, mm/year	E_{cor}, V	k_{h}, mm/year	E_{cor}, V	k_{h}, mm/year
Co70.9Mo20.4W8.7	–0.04	$3.05\cdot10^{-4}$	–0.14	$1.53\cdot10^{-4}$	–0.28	$3.2\cdot10^{-4}$
Co80.8Mo18.6Zr0.6	0.09	$2.8\cdot10^{-4}$	–0.14	$1.65\cdot10^{-4}$	–0.22	$3.12\cdot10^{-4}$
Co64.3Mo32.3Zr3.1	–0.2	$1.3\cdot10^{-4}$	–0.36	$3.0\cdot10^{-3}$	–0.23	$1.6\cdot10^{-3}$
Co85.5W13.9Zr0.6	0.06	$3.3\cdot10^{-4}$	0.03	$1.69\cdot10^{-4}$	–0.13	$2.4\cdot0^{-4}$
Co83.0W16.6Zr0.4	–0.04	$6.1\cdot10^{-4}$	–0.11	$1.56\cdot10^{-4}$	–0.23	$1.8\cdot0^{-4}$

The calculated values of the depth index of the corrosion rate make it possible to attribute the considered coatings to the group of very stable, and the alloy Co64.3Mo32.3Zr3.1 in the neutral and alkaline environment refers to very resistant materials, which allows their further use in aggressive environments.

ELECTROCHEMICAL PARAMETERS OF TIN FILMS AS LITHIUM-ION BATTERY ANODE MATERIALS

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The development of new anode materials for lithium-ion batteries (LIB) that provide high values of specific capacitance and charge-current density is an urgent task. A possible alternative to carbon materials is the use in the LIB of electrolytic tin films [1, 2], tin based composite coatings, and nickel, copper, cobalt alloys with tin [3, 4].

We have developed a technology for electrolytic deposition of functional tin films from pyrophosphate electrolyte. By the methods of potentodynamic and galvanostatic cycling in a 1M solution of *bis*-(trifluoromethane) lithium sulfonimide (LiTFSI) in a mixture of fluoroethylene carbonate and dimethyl carbonate solvents taken in a ratio of 1:3 (wt.%) the influence of electrolysis parameters, coating mass on the electrochemical characteristics of tin films as anode materials for LIB was investigated. It is established that the density of the deposition current, the duration of the electrolysis affect not only the thickness of the tin films, but also significantly increase their specific capacity. Processes of intercalation/deintercalation of lithium do not occur on the surface of the electrode, but over the entire thickness of the film, due to the optimum porosity of the obtained electrolytic films of tin. Long-term cycling of tin films results in the stabilization of their specific capacity within 470–710 $mA \cdot h \cdot g^{-1}$. The Coulomb efficiency of tin films on the first cycle is practically independent of the weight of the tin film and is 70%, further increasing to 90%. The obtained tin films are capable of providing a high charge-to-discharge current density without mechanical destruction, which will allow them to be used as anode materials in the LIB

The highest and most stable electrochemical characteristics (specific capacitance, stability and ability to reverse cycling in LIB) are common to tin films with a minimum mass obtained from pyrophosphate electrolyte at a current density of 1.0 $mA \cdot cm^{-2}$, including discharge with different current densities. Higher specific characteristics of these tin films during prolonged introduction and extraction of lithium compared to the characteristics of tin films obtained from tartrate, citrate, citrate-trilonate electrolytes, are conditioned by their production. The process of deposition of tin (II) from pyrophosphate electrolyte depending on the pH of the solution is limited by the previous chemical dissociation reaction of protonated $[Sn(HP_2O_7)(P_2O_7)]^{5-}$ (pH 4,5) or non-protonated $[Sn(P_2O_7)_2]^{6-}$ (pH 7,2) complexes. This allows controlling the morphology, structure and functional properties of the obtained tin films, namely, determines the size of the tin particles and the density of their packaging.

This work was carried out in the framework of the target research program of the National Academy of Sciences of Ukraine "New Functional Substances and Materials of Chemical Engineering", project №.7–19, 2019.

1. V. S. Kublanovsky, V. N. Nikitenko, N. I. Globa Effect of the nature of a ligand on electrochemical characteristic of tin films in cycling in lithium-ion batteries // Russian Journal of Applied Chemistry. – 2015. – Vol. 88. Iss. 3. – P. 407–412.
2. Yu.V. Shmatok, N.I. Globa, V.M. Nikitenko, E.A. Babenkov, V.S. Kublanovsky Electrochemical characteristic of tin films in cycling in lithium-ion batteries // Ukr. Khim. Zh., – 2019. – Vol. 85. Iss. 10. – P. 67–77.
3. N.I. Globa, V.D. Prisyazhnyi, V.S. Kublanovsky, V.N. Nikitenko Investigation of electrolytic tin-nickel alloys as anode materials for lithium-ion batteries // Surface Engineering and Applied Electrochemistry. – 2014. – Vol. 50. Iss. 3. – P. 280–284.
4. V. S. Kublanovsky, V. N. Nikitenko, N.I. Globa Electrochemical Deposition of Corrosion-Resistant Coatings from Tin-Nickel Alloys // Material Science – 2017.– Vol. 52. Iss. 5. – P. 687–693.

CORROSION PROPERTIES OF ELECTROLYTIC COATINGS OF CoW, CoRe AND CoWRe ALLOYS

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Alloys with refractory metals such as tungsten and rhenium are of great importance in modern technology, due to their unique mechanical and physico-chemical properties: high corrosion resistance, as well as abrasion and heat resistance. The method of electrodeposition from aqueous solutions provides the ability to control the chemical composition and thickness of the precipitated alloys, and therefore, the properties of ones. Modern studies pay much attention to tungsten alloys due to their high durability, while the deposition of rhenium alloys has been poorly studied and is currently developing. A new area of research is the electrodeposition of ternary alloys of refractory metals with metals of the iron subgroup containing either two refractory metals or two metals of the iron subgroup depending on the functional purpose of the coatings [1, 2].

We investigated the electrodeposition processes and corrosion properties of CoW, CoRe binary alloys, and CoWRe ternary alloys obtained from two types of electrolytes: monoligand citrate and polyligand citrate-pyrophosphate. It was found that among alloys, which were deposited at the same deposition current density (10·mA cm^{-2}) from the (1) citrate electrolyte as well as from the (2) citrate-pyrophosphate electrolyte, the first one contained significantly more refractory metals (51.0 at.% Re and 46.2 at.% (W + Re)) than the second one (13.5 at.% Re and 23.9 at.% W + Re). The main advantage of using the polyligand electrolyte in comparison with the citrate one is the high current efficiency of electrodeposition process (up to 85.7%).

Corrosion studies of these coatings performed in solution of 3.5% NaCl have shown that the corrosion resistance of CoWRe alloys is higher than that of CoRe and is 12.5 and 6.5 kOhm for the deposition from citrate electrolyte and 21.6 and 15.1 kOhm for the polyligand electrolyte, respectively.

When comparing coatings were electrodeposited from different electrolytes, no direct correlation was found between the chemical composition of the alloys and their protective properties. Therefore, at the analysis of experimental data it is necessary to take into account structure, morphology and phase composition of the alloys, in particular, the possibility of formation of intermetallic compounds. Based on the studies, it can be concluded that the use of polyligand citrate-pyrophosphate electrolyte allows obtaining more corrosion-resistant coatings with high current efficiency, despite the low content of refractory metals.

Acknowledgments

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1. M.V. Ved', N.D. Sakhnenko, A.V. Karakurkchi, K.D. Pershina, I.Yu. Yermolenko Corrosion properties of galvanic Fe-Mo(W), Fe-Mo-W coatings // Functional Materials – 2019. – 26. – P. 534–540.
2. Yu. S. Yapontseva, T.V. Maltseva, V.S. Kublanovsky, O.A. Vyshnevskyi Electrodeposition of CoWRe alloys from polyligand citrate-pyrophosphate electrolyte // J. of All. and Comp. – 2019. – Vol. 803. – P. 1–8.

ELECTRODEPOSITION AND CORROSION PROPERTIES OF NANOCRYSTALLINE Ni-Re ALLOY COATINGS

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Electrodeposition is one of the most promising methods for producing nanostructure materials owing to its low cost compared to the other techniques. Electrodeposition produces nanocrystalline materials when the deposition parameters (bath composition, pH, electrolysis mode, current density, temperature) are optimized such that electrocrystallization results in massive nucleation and reduced grain growth [1 - 5]. Due to high corrosive and mechanical stability characteristics of Ni-Re alloys, the electrodeposition of these alloys plays an important role [6 - 7].

Ni-Re nanocrystalline deposits (5 – 35 nm) were obtained from sulfamate and citrate electrolytes for current densities varying within the range 0.3–5.0 $A \cdot dm^{-2}$ at temperatures of 15 and 40°C. The quantitative composition of the coatings and the structure and morphology of the obtained deposits depending on the bath composition and the modes of electrolysis were determined. The Ni–Re alloys contain 20–60 wt% Re if they are deposited from a simple sulfamate electrolyte, 5–30 wt% Re if they are obtained from a complex citrate bath [for a low concentration (0.01 M) of potassium perrhenate $KReO_4$], and 90–92 wt% Re in the presence of 0.02 M of $KReO_4$. As temperature increases in the course of codeposition from a sulfamate electrolyte, the rhenium content of the alloy decreases. However, for the codeposition from a citrate electrolyte, the temperature only slightly affects the composition of deposits.

Nanocrystalline metals and alloys usually experience deterioration while being used for catalytic activities as cathodes for hydrogen production from water electrolysis. Electrodeposited Ni-Re alloys were proved to be of more corrosion resistance in NaOH solution than that of steel substrate. The corrosion behavior for Ni-Re nanocrystalline alloys was dependent on two contradicting factors: the rhenium content, and the grain size. The corrosion resistance is higher for coatings with lower content of rhenium in the deposit. The increase in the Re content in the Ni-Re alloys increases the corrosion resistance, but it leads to grain size refining. The best anticorrosive properties are exhibited by the alloys with about 8–10 wt% of rhenium.

This work was carried out in the framework of the target research program of the National Academy of Sciences of Ukraine ‘‘New Functional Substances and Materials of Chemical Engineering”, project No. 7–20, 2020.

1. Electrodeposition and Characterization of Nanocrystalline Ni-Mo Catalysts for Hydrogen Production / J. Halim, R. Abdel-Karim, S. El-Raghy, et. all. // Journal of Nanomaterials. –2012 – Article ID 845673.
2. Corrosion and anodic behavior of electrodeposited Ni-Mo alloys / Bersirova O., Cesiulis H., Donten M., Krolikowski A., Stoek Z., and Baltrunas G. // Physicochemical Mechanics of Materials. – 2004. – No. 4. – P.620–625.
3. Cesiulis, H.; Sinkeviciute, J.; Bersirova, O.; et al. Tribocorrosion testing of self-passivation molybdenum and tungsten alloys containing cobalt and iron // V International Scientific Conference BALTTRIB 2009 (19-21 November 2009): Proceedings. – Kaunas, Lithuania. – P. 25–258.
4. Bersirova O., Kublanovskii V., Crystalline Roughness as a Morphological Characteristic of the Surface of Electroplated Silver Coatings // Russian Journal of Applied Chemistry. – 2009 – Vol.82, №11. – P. 1944–1948.
5. Bersirova O., Kublanovsky V., Corrosion properties of electrodeposited thin coatings of polycrystalline silver // Mater. Sci. – 2012 – Vol. 48, Iss. 2. – P. 197–202.
6. Berkh O., Burstein L., Gladkikh A., Eliaz N., Gileadi E., Characterization of Re–Ni films after the initial stages of electrodeposition. J. Electrochem. Soc – 2016 – Vol. 163, №.7. – P. 295–299.
7. Bersirova O., Nickel–Rhenium Electrolytic Alloys: Synthesis, Structure, and Corrosion Properties / O.L. Bersirova, V.S. Kublanovs'kyi // Mater. Sci. – 2019 – Vol. 54, №4. – P. 506 – 511.

THE EFFECT OF CHITOSAN COATINGS ON THE CORROSION RESISTANCE OF TI-ZR ALLOY WITH PEO-COATED SURFACE

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Currently, the Ti-Zr alloys are used to create dental and bone implants. Such alloys are distinguished by mechanical strength and bioinertness, high corrosion resistance. At the same time, some studies indicate an adverse effect of chlorine ions on Zr, while titanium corrodes in the sodium chloride/lactic acid medium [1]. PEO (plasma electrolytic oxidation) process is widely used to obtain protective oxide layer on the surface, however, adverse physicochemical reactions may occur. In this regard, there is a need for further surface treatment in order to give it both biocompatibility and increased corrosion resistance, e.g. surface modification with polymers. Chitosan is a biocompatible non-toxic polysaccharide, employed also as a corrosion inhibitor for metals and alloys.

In this work, samples of Ti-Zr alloy with a PEO treated surface were obtained from *NanoPrime* (Dębica, Poland). To obtain polymeric coatings, dip-coating, spin-coating (1000 rpm) and electric deposition methods were applied. 2% and 0.5% solutions of chitosan (300 kDa, 87% deacetylation) in 1% acetic acid were used. The resulting coatings were treated with 1% NaOH for crosslinking. To determine biocompatibility and corrosion resistance, the immersion in model solutions (2SBF, 3% H_2SO_4/0.9% NaCl) for 5 days was used. Scanning electron microscopy was used to control the changes in the state of the surface; the phase composition of the surfaces was studied with the X-ray diffraction.

When using 2SBF, calcium salts are deposited both on the PEO surface of the samples and the surface with a chitosan coating deposited by electrophoresis and spin-coating. After the incubation of the samples in a model H_2SO_4/NaCl solution for 5 days, the deep cracks form on the PEO treated surface. In the case of dip-coated and spin-coated samples, a smooth film is formed on the surface, which in the first case is peeled off from the implant surface, and in the second it is more firmly fixed and prevents the appearance of cracks on the surface in aggressive acidic medium. Electrodeposited films protect the PEO surface preserving structure of the polymeric coating itself. The dip-coating method can also be used to form asymmetric chitosan membranes with a structured surface. This work was partially supported by H2020 MSCA, grant NanoSurf 777926.

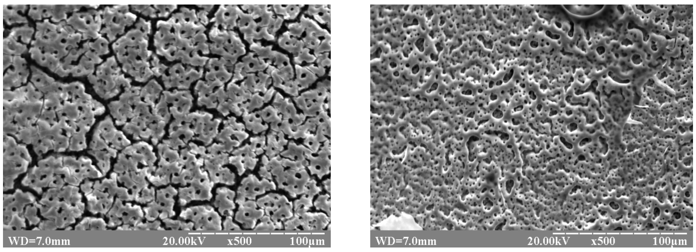

Fig. 1. Ti-Zr PEO treated surface without (left image) and with (right image) chitosan coating after incubation in H_2SO_4/NaCl solution

1. T. Akimoto, T. Ueno, Y. Tsutsumi, H. Doi, T. Hanawa, N. Wakabayashi N. Evaluation of corrosion resistance of implant-use Ti-Zr binary alloys with a range of compositions // J. Biomed. Mater. Res. Part B: Appl. Biomater. – 2018. – 106B. – P. 73–79.

COMPLEX ANTI-CORROSION COATING FOR THE PROTECTION OF METAL PRODUCTS

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Varnish coatings account for 60% of all existing methods of protecting metals from corrosion. However, the production and use of varnish materials often requires the use of chemicals that are unhealthy. Therefore, improving the environmental friendliness of varnishes is an important direction for the development of this industry [1,2]. The purpose of this study is the development of new compositions of water-dispersion primers and finish epoxy varnishes, as well as the creation of a complex decorative and protective coating of metal products based on them.

Regularities were found in the changes in the physicochemical properties of the studied compositions and coatings obtained on their basis on the qualitative and quantitative composition of the ingredients were esteblishert and the effect interfacial acid-base interactions. The obtained dependencies allowed scientifically based selection of components for new environmentally friendly fireproof primer and varnish compositions coatings on their basis whit operational parameters (Table.1).

Table. 1. Properties of complex decorative-protective coating

Measured properties	Weight
Adhesion of the coating to the base, points	0-1
Hardness according to tml, not less	0.6
Impact strength at 20c, not less	70
Gloss at an angle of 45, %	60
Resistance to engine oil, hours, not less	1000
Resistance to 3% NaCl solution, hours, not less	400
Resistance to salt fog, hours, not less	500
Resistance to oil, hours, not less	300

The new varnishes are recommended for application in mechanical engineering, petrochemical and construction industries.

1. L.L.Bezukladnikova, S. G. Mityashina. Development of high-quality anticorrosive water-dispersion materials for protective and decorative painting of metals // practice of anticorrosive protection. – 2011. – Vol. 62. Iss. 4. – P.12–21.
2. V.P. Lobkovsky. New construction water-based paints and varnishes // paints and varnishes and their application. – 2001. – Iss. 2-3. – P. 56–58.

POLYMER-MAGNETITE THERMOSETTING COMPOSITES WITH PROTECTIVE AND ANTIRADAR FUNCTIONS

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Composite materials containing dielectric or semiconductor nanoparticles of a particular shape as well as periodical micro- and nanostructures capable of spatial redistribution of scattered electromagnetic radiation in desired directions are perspective for that task. The goal of our present work is fabrication of hybrid polymer-inorganic composite coating with antiradar and anticorrosive properties. Iron oxides, magnetite or Fe_3O_4 in particular are especially interesting among other components due to their ability to absorb electromagnetic waves of near IR and microwaves ranges [1]. Carbon threads or carbon nanotubes inclusions in magnetite-based composites may provide a synergetic effect, i.e. enhance electromagnetic energy absorption and improve anticorrosive properties on metal surface. We suggest exploring organic compounds based on conductive conjugated polymers along with magnetite immersed into epoxy resin matrix as an effective coating [2]. Dispersed magnetite Fe_3O_4 in a form of spherical particles with the diameter of 1.2 -2 μm capable of not only absorb but also scatter electromagnetic radiation served as magnetic filler for composites. The magnetite colloidal dispersion was stabilized via surfactants that results in the formation of self-assembled molecular aggregates and provides overall stability of the system [3]. Prepared polymer composites were characterized by X-ray and EDAX-analysis, Raman spectroscopy, thermogravimetric, mechanical and thermo-mechanical techniques. Variation in the size of Fe_3O_4 particles and their concentration in the composites does not affect the period of elementary cell of magnetite and has a complex effect on the magnetic susceptibility, microhardness and thermomechanical properties of magnetite–polymer composite. It was found that composite containing magnetic microparticles and particles of polyaniline doped with sulfuric acid in 1:1 ratio exhibits the strongest microwave absorption. At the same time this optimal composition provides high microhardness and anticorrosive properties of the coating on the surface of steel. The value of the relative water absorption of the composite coatings during 30 days of exposure in a moist chamber with a humidity of 95% turned out to be half as much compared to an unfilled epoxy composition. The electrochemical potential of the coated steel surface based on the developed thermosetting composition showed a significant anode shift (by 0.3-0.4 V), while the surface state of the coatings remained unchanged. The obtained results confirmed the sufficient corrosion resistance of the coatings in comparison with the known analogues [4]. On the basis of obtained results method of composite formation with special purpose would be developed.

1. Yu.I. Borisov. Dynamics of Radioelectronics-3. - Moscow, Technosphereю – 2009. – P. 276 – 279 (in Russian).
2. R. Filipsonov, S.Malynych, O.Aksimentyeva, G. Martynyuk. Composite polymer coatings for special purpose //VII International scientific-technical conference «The modern technologies of polymer materials obtaining and processing» Book of abstracts, Lviv, November 06–08, 2019. – P. 42.
3. O.I. Aksimentyeva, V.P. Savchyn, V.P. Dyakonov et al. Modification of polymer-magnetic nanoparticles by luminescent and conducting substances// Mol. Cryst. Liq. Cryst. – 2014. – Vol. 590. – P. 35–42.
4. Zhanhu Guo, Huige Wei, Hongbo Gu et al. Epoxy/Magnetite/Carbon Nanofibers Nanohybrid Coatings for Anticorrosion / // 2014 ECS-The Electrochemical Society. Abstract MA2014-02 709.

CORROSION-ELECTROCHEMICAL BEHAVIOUR OF SiC LASER MODIFIED 7075 ALUMINIUM ALLOY IN NEUTRAL WATER SOLUTIONS

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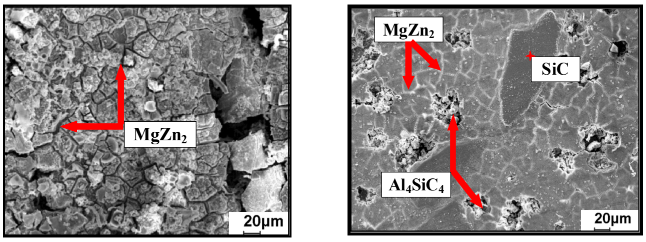
The work is devoted to establishing the influence of the structure of the aluminum alloy surface layers by laser modification with silicon carbide fractions as alternative strengthening method for replacing galvanic chrome plating, and evaluating their corrosion-electrochemical properties in neutral aqueous media.

The process of modification of surfaces of aluminium alloys by means of powders of silicide across, oxides, carbides, and other compounds entails considerable technological difficulties because of great difference of their physical properties, that obstruct uniform distribution of powder grains in a pool of melted metal. Besides, it is necessary to take into account the turbulent streams of melted metal, non-uniform distribution of temperature, which causes a gradient of viscosity of the melt, and rapid progress of the process of melting-crystallization of the alloy. Taking this into consideration, the modification-reinforcement of surfaces of alloys was conducted both at room temperature and under heating the specimens to 100 or 250 ºC. The surface was strengthened by the laser melting of the surface layers of the alloy with the introduction of SiC disperse powders. For laser surface reinforcement of the 7075 alloy, a SiC powder of 80 μm dispersion, a hardness of 2600 HV and a melting point of 2760 °C was used. The preliminary heating of an alloy reduces the temperature gradient in the melted metal and ensures slow crystallization rate, that would increase the depth of modified layer and improve the uniformity of the distribution of solid particles in it.

It has been established that several technological factors affect the properties of the modified layers. The determining ones are the energy of the laser beam, the particle size of SiC, the temperature of heating of the samples immediately before surface modification by laser. By metallographic analysis (fig. 1) of the corroded surface, it was found that, unlike an unmodified alloy, in which, under the corrosive medium influence, sections enriched in $MgZn_2$ ($Al/MgZn_2$ galvanic couple) are dissolved, the modification by SiC particles of B95 alloy inhibits their dissolution, slowing down corrosion processes, and the size and depth of local defects significantly reduced. Obviously, after the modification, another Al/Al_4SiC_4 galvanic pair appears and the corrosion failure proceeds localized with the formation of a pitting in places where Al_4SiC_4 inclusions are present.



a *b*

Fig. 1. The surface of unmodified (*a*) and SiC laser-modified (*b*) alloy 7075 particles after corrosion of a 3% NaCl solution for 192 h

By potentiodynamic studies, it was found that heating the substrate to 250°C is less efficient than 100°C, due to the higher volume content of Al_4SiC_4 inclusions, which are the cause of the corrosion destruction of the modified layer. It was revealed that, although the modified layer is heterogeneous, its corrosion resistance increases by 2-6 times depending on the medium.

INFLUENCE OF PARAMETERS OF PLASMA-ELECTROLYTE OXIDATION OF D16 ALLOY ON CORROSION RESISTANCE OF SYNTHESIZED COATINGS

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Aluminum alloys are characterized by ulcerative corrosion, which eventually becomes intergranular. The Plasma Electrolyte Oxidation (PEO) method allows to form corrosion and wear resistant coatings on the surface of aluminum alloys. Formed PEO coatings are chemically inert to most corrosive media. However, the discharge channels leave pores in them, which can be either melted or reach the metal base. Due to the penetration of corrosive media through the pores, the metal base – aluminum alloy – is exposed to corrosion destruction. The aim of this study is to investigate the choice of synthesis modes that allow to obtain corrosion-resistant coatings on the surface of aluminum alloys.

To achieve this goal, studies were conducted of PEO coatings synthesized on samples of aluminum alloy D16 in an alkaline-silicate electrolyte, for 1 hour. The ratio of cathodic to anodic current density j_c/j_a, varied in the range of 10/15, 10/10, 15/10 A/dm^2. Potassium hydroxide (KOH) and liquid glass (PC) ($nNa_2O \cdot mSiO_2$) in the amount of 3 g/l and 2 g/l, respectively, were used as components of the base electrolyte.

The phase composition of the coatings was determined by the X-ray method. The major phases are Al, α-Al_2O_3 (*R-3C*) and γ-Al_2O_3 (*Fd3m*). The decrease of density of the cathodic current relatively to the anodic one leads to the formation of an oxide ceramic coating of greater thickness, which way show the decrease in the intensity of Al reflexes.

The porosity of the oxide ceramic coatings was investigated by analysis of surface micrographs obtained with a Zeiss EVO-40XVP electron microscope using the INCA Energy 350 X-ray microanalysis system according to the method described in [1].

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 oxide ceramic coating on the D16 alloy on its corrosion electrochemical behavior in 3% aqueous NaCl solution. Exposure of specimens coated in the medium lasted from 3 h to 24 h.

It was found that oxide ceramic coatings significantly reduce corrosion currents in comparison with the original alloy. The lowest corrosion currents are observed in coatings synthesized by the density ratios j_c/j_a – 15/10, 10/10 A/dm^2. Analysis of the porosity of the coatings shows the change in the number of pores from the mode of formation. Although the oxide ceramic coatings formed by the ratio of current densities j_c/j_a – 10/15 A/dm^2 have the smallest number of pores, their average size is larger. This contributes to the penetration of the corrosive medium through the through pores to the base and as a result the dissolution of aluminum intensifies.

Therefore, PEO coatings obtained j_c/j_a – 15/10, 10/10 A/dm^2 with minimal number and size of pores and cracks have the highest corrosion resistance. It is established that regardless of the properties and structure of PEO coatings and their modes of production, the mechanism of corrosion destruction remains unchanged.

1. Ivasenko I. B., Posuvailo V. M., Klapkiv M. D., Vynar V. A., Ostap'yuk S. I. Express method for determining the presence of defects of the surface of oxide-ceramic coatings.// Materials Science. – 2009. – Vol. 45, Iss. 3. – P. 460–464.

CORROSION AND OXIDATION RESISTANCE OF VACUUM ARC CHROMIUM COATINGS ON Zr1Nb ALLOY

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Zirconium alloys are used as a base material of fuel claddings in the LWR-type thermal neutron reactors. The Zr-based alloys, possessing a high chemical stability provided by the zirconium oxide film, 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 Station 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]. The Zr-based alloys with Cr coatings, obtained by different methods of physical deposition, demonstrate protective properties in different test conditions [2-6].

The report presents the results of own research on the development of vacuum arc chromium coatings for the protection of zirconium claddings of the fuel rods in the case of LOCA (high temperature oxidation in air and steam flow) and under normal operating conditions (autoclave tests at different temperatures and pressures). Information review on the international experience of development of such coatings is also given.

Chromium coatings were deposited by the vacuum arc method from the two counter flows of metallic plasma with planetary rotation of samples on the system axis [3]. Chromium (99.9%) was used as cathodes. The temperature of samples during deposition did not exceed 500 °C. The coating thickness was 10-12 μm. For autoclave and steam flow tests 80 mm long welded on both sides samples made from the Zr1Nb alloy cladding tube (outer diameter 9.1 mm, wall thickness 0.7 mm). The samples after the tests were investigated by the gravimetric method, optical and electron microscopy.

Autoclave tests (6000 hours) of fuel rod models in the water simulator of the coolant of the first reactor circuit (T=350 °C, P=15 MPa) showed that the kinetics of oxidation of uncoated zirconium tubes proceeds according to parabolic law, the weight gain is 78 mg/dm^2, and with protective coatings Cr and Cr/CrN increases very slow and is 5-10 mg/dm^2. Autoclave tests (500 hours) of fuel rod models in water vapor simulator of overheating of the coolant (T=400 °C, P=10.3 MPa) showed that the kinetics of oxidation of zirconium tubes without coatings proceeds according to a parabolic law, weight gain is 58 mg/dm^2, and with protective coatings is only 3-4 mg/dm^2.

The present results indicate that chromium coatings are a good candidate for providing corrosion protection of zirconium alloy claddings for LWR-type reactors.

1. S. J. Zinkle, K. A. Terrani, J. C. Gehin, L. J. Ott, L. L. Snead. Accident tolerant fuels for LWRs: a perspective // J. Nucl. Mater. – 2014. – Vol. 448. Iss. 1. – P. 374–379.
2. J. H. Park, H. G. Kim, J. Y. Park, et al. High temperature steam-oxidation behavior of arc ion plated Cr coatings for accident tolerant fuel claddings // Surf. Coat. Technol. – 2015. – 280. – P. 256–259.
3. S. Kuprin, V. A. Belous, V. V. Bryk et al. Vacuum-arc chromium coatings for Zr-1Nb alloy protection against high-temperature oxidation in air // Prob. At. Sci. Tech. – 2015. – Vol. 96. Iss 2. –P. 111–118.
4. S. Kuprin, V. A. Belous, V. N. Voyevodin, et al. Vacuum-arc chromium-based coatings for protection of zirconium alloys from the high-temperature oxidation in air // J. Nucl. Mater. – 2015. – 465. – P. 400–406.
5. S. Kuprin, V. A. Belous, V. N. Voyevodin, R. L. Vasilenko, V. D. Ovcharenko. Irradiation resistance of vacuum arc chromium coatings for zirconium alloy fuel claddings // J. Nucl. Mater. -2018. – 510. – P. 163–167.
6. K. A. Terrani. Accident tolerant fuel cladding development: Promise, status, and challenges // J. Nucl. Mater. – 2018. – 501. – P. 13–30.

CORROSION RESISTANCE OF SiC (Cr) CERAMICS COMPOSITE IN HYDROTHERMAL CONDITIONS

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The accident at the Fukushima-1 nuclear power plant showed a particular danger of the steam-zirconium reaction that occurs when the temperature of the fuel cladding increases, i.e. under the loss-of-coolant accident (LOCA) conditions. A steam-zirconium reaction starting at temperatures above 950°C is the main factor that destroys fuel elements.

The term Accident Tolerant Fuel (ATF) appeared after the Fukushima-1 nuclear disaster. In the IAEA wording, this fuel should be able to work both under normal operating conditions, and which is most important under LOCA conditions.

For existing nuclear power plants there are two solutions to prevent the steam-zirconium reaction – the use of protective coatings or complete replacement of the zirconium alloy with new materials. Such materials include SiC/SiC composites, which are resistant to oxidation in air up to 1600°C. One of the main methods for producing SiC/SiC composites is based on the impregnation of SiC fibers by SiC nanopowder with subsequent formation of the SiC matrix by hot pressing (HP) [1].

But with the subsequent use of such composites, the problem occurs that, despite the corrosion resistance in high-temperature vapor (LOCA condition), the SiC matrix dissolves under non-emergency operation in water-cooled reactors.

The possibility of improvement the corrosion resistance of SiC-based ceramics in the environment, similar to the VVER-1000 reactor coolant conditions, by Cr doping in an amount of 0.5%wt was studied in this work. SiC sintered samples with/without Cr additives were produced using High-Speed Hot Pressing Method (HSHP). Corrosion tests of samples were carried out in the aqueous environment which is similar to PWR coolant conditions. Microstructure and composition of the SiC-based ceramics before/after tests were investigated using SEM and EDX analysis. The results of studies of the structure and elemental composition of the SiC surface with/without Cr additives before/after corrosion tests in hydrothermal conditions are presented. It is shown that the alloying by Cr additives leads to changes in the corrosion mechanism of SiC ceramics and increases its corrosion resistance. After 100 hours of exposure an average mass gain of 3.27 mg/dm^2 is observed, while the mass gain of SiC samples without Cr additives decreases to -4.01 mg/dm^2. Corrosion of the SiC(0.5%Cr) composite under hydrothermal conditions leads to the formation of corrosion resistant Cr_2O_3 products, which significantly affect the ability of SiO_2 films to passivate the surface of the samples, which in turn leads to increase in corrosion resistance [2].

The obtained results confirmed that Cr doping of the SiC-based ceramics leads to the increasing of the corrosion resistance in high-temperature water conditions. This conclusion allows to propose SiC-based composite as a perspective material for the fuel claddings manufacturing.

1. Hyun-Woo Yu, Pipit Fitriani, Sungho Lee, Ji-Yeon Park, Dang-Hyok Yoon Fabrication of the tube-shaped SiC_f/SiC by hot pressing // Ceram. Int. – 2015 – Vol. 41. – P. 7890–7896.
2. K.V. Lobach, S.Yu. Sayenko, V.A. Shkuropatenko, V.M. Voyevodin, A.V. Zykova, V.A. Zuyok, A.A. Bykov, L.L. Tovazhnyanskyy, O.M. Chunyayev Corrosion stability of SiC-based ceramics in hydrothermal conditions // Fizyko-khimichna mekhanika materialiv. – 2019. – Vol. 55. Iss. 5. – P. 56–66.

CORROSION RESISTANCE OF CEMENT MATRIX MODIFIED BY CELLULOSE ETHER

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At this stage of human development, Portlandcement is the main construction material. Its corrosion resistance in harsh environments had been studying and various methods of improving this indicator are developed [1]. But in the recent years dry building mixes are gaining significant usage. Due to the expansion of usage field for mixes, despite the presence of main compounds of mixes, becomes necessity in adding different additives that provides the necessary modifications for establishing parameters of setting time, slurry, compression and adhesive strength and etc. One of these additives is cellulose ethers – water retention additive that provides the required plasticity of slurry [2]. Methyl hydroxyethyl cellulose is most commonly used. The injection of this additive leads to a dramatic change in the rheological properties of the mixture and certain changes in the processes of hydratation of the binder. Due to the usage of mortars in abodes with different environment, the effect of the addition of cellulose ether on the strength and corrosion resistance of the cement matrix were studied. The samples were stored in water and corrosive media for 180 days (Table 1).

Table 1. Samples strength at 180 days in aggressive solutions

Mixes composition, mass.%		Samples strength, MPa, after 180 days of curing in solutions			
Cement	Additive	Water	Na_2SO_4	$MgSO_4$	$CaSO_4$
100,00	0,00	52,9	45,9	38,8	41,1
99,75	0,25	46,3	40,0	37,5	37,3
99,50	0,50	45,8	38,3	36,3	33,8
99,25	0,75	40,0	19,0	28,3	27,3

Corrosion resistance coefficient are calculated as ratio of the strength of samples that was held in aggressive solutions to the strength of samples that was held in water (Table 2).

Table 2. Corrosion resistance coefficient of samples

Mixes composition, mass.%		Corrosion resistance coefficient after 180 days of curing in solutions		
Cement	Additive	Na_2SO_4	$MgSO_4$	$CaSO_4$
100,00	0,00	0,87	0,73	0,78
99,75	0,25	0,86	0,81	0,81
99,50	0,50	0,85	0,79	0,73
99,25	0,75	0,48	0,71	0,68

Achieved results allow to made such conclusions:

1. Injection of cellulose ether leads to monotone decrease of samples strength with increasing of additive amount;
2. At low amount of cellulose ether (up to 0.25 mass %) corrosion resistance of samples is the same to the cement or slightly exceeds it;
3. With increasing of concentration of cellulose ether in cement matrix there are significant decrease of corrosion resistance of samples occurs.

Thus, the manufacturing and using of dry building mixes with low concentration of water retention additives are better for conditions of contact with aggressive environment

1. F. Pacheco-Torgal, J. A. Labrincha The future of construction materials research and the seventh UN Millennium Development Goal: A few insights // Constr. and Build. Mat. – 2013. – Vol. 40. – P. 729–737.
2. D. Bülichen, J. Kainz, J. Plank Working mechanism of methyl hydroxyethyl cellulose (MHEC) as water retention agent // Cem. and Con. Res. – 2012. – Vol. 42. Iss. 7 – P. 953–959.

DEVELOPMENT AND APPLICATION OF MnO_x-BASED COMPOSITE FILMS

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Alternative energy devices have recently become particularly popular. Thus, electrode boilers for direct conversion of electric energy into heat can be installed in any type of premises, they allow to use previously installed pipes and radiators and achieve significant energy savings.

To ensure durability and reliability in operation, the working electrodes of such installations must have high thermal and corrosion resistance under the influence of strong electric fields. In addition, the decomposition of heat carriers, especially water, should not occur on the electrode surface during the operation of the heater, since the result of water splitting is an explosive mixture (H_2+O_2).

The use of titanium, lead, nickel, and various steel marks as electrode materials in electrolyzers with the industrial voltage of 220 V is accompanied by their destruction and gas release. Considering the capability of Mn^{3+} / Mn^{4+} redox system to provide high-speed cycling of electric charge at potentials significantly lower than the water splitting potential, we have developed composite MnO_x coated electrodes on metal oxidized substrate. Simple carbon steel was used as the substrate. The MnO_x film was deposited electrochemically from an electrolyte containing monobasic carboxylic acids. Mixed electroneutral complexes $[Mn(L)_2(H_2O)_4]$ formation ensured the deposition of MnO_x-based composite at low potentials. The corrosion resistance of the obtained composite films was very high. The industrial tests of the developed Fe, FeO_y/MnO_x electrodes showed their ability to work for at least 10000 hours.

The potential of $Mn^{3+} \leftrightarrow Mn^{4+}$ reaction that ensures electric charge cycling is quite high. If 1 mg MnO_x is placed on an electrode with the geometric surface of 1 sm^2, such a system will be able to pass an alternating current of 50 Hz with the Faraday component of the reaction $Mn^{3+} \leftrightarrow Mn^{4+}$ $\overline{i_f}$ = 77,8 A/cm^2.

The developed electrodes were introduced into the industrial production of electric boilers "Energy" with direct heat carrier heating of various capacities, which are used in residential premises and other facilities. Their long-term operation confirmed their high performance characteristics.

CORROSION RESISTANCE OF AISI 304 STEEL FROM COMPOSITIONAL OXIDE COATINGS

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One of the most dangerous types of corrosion destruction of high-alloy steels is the appearance of pits and ulcers on the surface of materials in certain industrial conditions. The most common cause of pits and ulcers is solutions containing chloride, bromide or hypochlorite ions, which, under favorable conditions, locally activate the surface. This form of corrosion is often more detrimental than general corrosion due to local dissolution, which can cause rapid penetration of metal thickness [1]. In many cases, such corrosion is not manifested until serious damage, such as through perforation of the material, in particular, the walls of tanks, plates of heat exchangers, pipelines, and can lead to production accidents, which will result in large material losses [2]. The solution to this problem is the formation of composite oxide coatings on metals and alloys [1, 2]. Modification of coatings by valve metals such as titanium, aluminum and others is known to provide materials with protective properties in harsh environments [1, 2]. Therefore, the development of oxide systems on the surface of AISI 304 steel with high corrosion characteristics, which would ensure the reliable operation of the equipment, is of great practical importance [2].

The purpose of this work is the electrochemical study of the resistance of stainless steel with oxide systems $Cr \cdot CrO_x$; $Cr \cdot CrO_x \cdot TiO_y$; $Cr \cdot CrO_x \cdot Al_xO_y$ in chloride medium.

The formation of composite oxide coatings was carried out in galvanostatic mode in a two-electrode cell with a system of continuous stirring at a current density of 50 A / dm^2 for 60 minutes in titanium, aluminum-containing electrolytes [2].

Tests for resistance to pitting corrosion of the obtained coatings were performed by the electrochemical method according to [3], which consists in the measurement of the free corrosion potential (E_{cor}) and the potentiodynamic polarization of the samples, followed by the determination of the pitting potentials (E_b - the potential of ping formation, the potential of base formation, pitting resistance (ΔE_b, ΔE_{rp}).

E_{cor} for AISI 304 steel is more electropositive than for composite materials, which indicates a significant change in the control of the corrosion process.The calculated electrochemical parameters ΔE_b and ΔE_{rp} indicate that the composite oxide coatings significantly increase the resistance to stainless steel. Studies on the surface morphology of samples after polarization using a ZEISSAxio metallographic microscope (×1000) digital video camera have shown that the composite materials have no defects, which is consistent with the results of electrochemical studies.

Composite oxide coatings significantly increase the alloy's resisting strength and thus provide reliable protection. The results of the study suggest that AISI 304 steel with $Cr \cdot CrO_x \cdot TiO_y$ oxide system has the highest pitting resistance.

1. V. Shtefan, N. Kanunnikova, A. Pilipenko, H. Pancheva. Corrosion Behavior of AISI 304 Steel in Acid Solutions // Materials Today: Proceedings. – 2019. – Vol. 6. No.P2. – P. 149–156.
2. V. Shtefan, N. Kanunnikova, N. Balamut. Anodic oxidation of AISI 304 steel in acidic solutions // Proceedings of Odessa Polytechnic University. – 2018. – 56. № 3. – P. 89–94.
3. H.S. Khatak, B. Raj (Eds.). Corrosion of Austenitic Stainless Steel: Mechanism, Mitigation and Monitoring // Woodhcad Publishing. – 2002. – P. 385.

INFLUENCE OF PLASMA ELECTROLYTIC COATINGS ON ELECTROCHEMICAL CORROSION ACTIVITY OF ALUMINUM ALLOYS IN TECHNOLOGICAL ENVIRONMENT OF GRINDING PROCESSES

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Practical implementation of plasma electrolytic coatings is far from being exhausted. Its further extension can be carried out both by improving the plasma electrolytic oxidation (PEO) method and by identifying new objects for the rational use of certain properties of the PEO layers.

In particular, the corrosion protection function of the coatings can be realized on diamond grinding wheels, the bodies of which are made of aluminum alloys. Operation of the wheels in the grinding process involves the contact of their surface with a coolant or electrolyte, which is supplied under pressure into the treatment area. In this case the corrosive effect of the technological media is enhanced by the temperature factor, mechanical activation of the surface by solid particles of wear and the influence of the electrode potential when electrophysicochemical grinding [1].

The corrosion protection properties of plasma electrolytic oxidation coatings (PEO-coatings) formed by the galvanostatic method in alkali-silicate electrolytes on aluminum alloys D16T and AK6 were investigated. The corrosion activity was evaluated by electrochemical method in model media – 5 % sodium nitrate solution ($NaNO_3$) and 1.5 % sodium carbonate solution (Na_2CO_3), and sodium triphosphate (Na_3PO_4).

It was established that PEO coatings with a thickness of 30…45 micrometers in 2…10 times reduce the electrochemical corrosion activity of both aluminum alloys in all the technological environments. The effectiveness of the substrate (base) protection depends on the grade of the structural alloy, the aggressiveness of the corrosion solution, and the composition of the electrolyte in which the coatings were formed. The best performance of the protective properties was obtained when forming the layers in a liquid glass solution with a concentration of 12 g/l [2].

1. L. Zhu, J. Oiu, J. Chen, W. Zhang, Z. Chen, F. Wang Microstructure and corrosion resistance of the PEO coating on extruded Al6Cu alloy // Surface and Coating Technology. – 2019. – Vol. 369. No. 15. – P. 116–126.
2. Yu. Gutsalenko, E. Sevidova, I. Stepanova Evalution of technological capability to from dielectric on AK6 alloy, using a method of microarc oxidation // Surface engineering and applied electrochemistry. – 2019. – Vol. 55. Iss. 5. – P. 602–606.

CORROSION AND CATALYTICAL PROPERTIES OF Ni-Cu ALLOYS DEPOSITED FROM CITRATE ELECTROLYTE

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The study of electrodeposited nickel alloys is motivated from the prediction of a synergistic effect from the combined properties of the component metals of alloys. So, nickel-copper alloys were characterized high corrosion resistance and electrocatalytical activity towards many reactions. Ni-Cu coatings were electrodeposited from citrate electrolyte in the absence and in the presence of brighteners under current density 2 A/dm^2 and temperature 35 – 40 and 50 – 55 °C. Chemical and phase composition, morphology of Ni-Cu coatings were characterized by X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), scanning electron spectroscopy (SEM). The corrosion performance of Ni-Cu alloys was determined by using potentiostatic polarization in 3,5% NaCl. The alcohol oxidation was investigated by using cyclic voltammetry in 1M NaOH.

It was found that Ni-Cu coatings had a more positive corrosion potentials and 1,2 – 2 times smaller corrosion currents than matte and bright nickel. It can be attributed to smoothness and very low porosity of Ni-Cu coatings (Fig. 1a) and formation of single-phase solid-solution alloys. XRD patterns showed that Ni-Cu alloys are solid solutions with structure similar to crystalline nickel (lattice parameter a = 3,529 Å). The results of chemical composition analysis obtained by XRF showed that content of copper in the alloys didn't exceed 5 wt.%.

Fig. 1 b and c show cyclic voltammograms of Ni-Cu coatings in 1M NaOH in the presence and in the presence of CH_3OH and C_2H_5OH at potential sweep rate 10 mV/s.

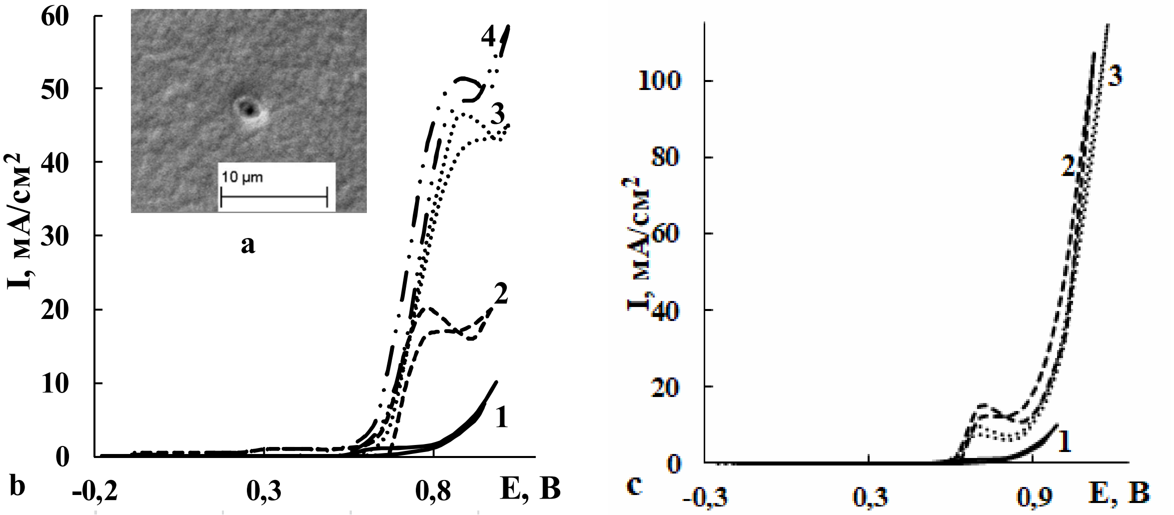

Fig. 1. a) SEM micrograph and voltammograms of the Ni-Cu coatings in 1M NaOH in the absence (1) and presence of b) 0,3M (2), 1M (3), 2M CH_3OH (4); c) 1M (2), 2M C_2H_5OH (3)

A gradual increase in the oxidation current at the anodic sweep starts at 0,6 V when the active sites with $NiOOH/Ni(OH)_2$ mediator have been formed on the alloy surface. The anodic peak of methanol oxidation appeared at 0,87 V and ethanol oxidation – at 0,7 V. An increase in the concentration of methanol caused an enhancement of the anodic currents (Fig. 1 b). It is seems probable that methanol oxidation on Ni-Cu alloys is diffusion controlled process. A notable peak near 0,8 V at reverse scan show that methanol or intermediates can be oxidized again.

RESEARCH OF CORROSION RESISTANCE HIGH-STRENGTH DIAMOND GRINDING POWDERS

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Expansion of a scope of new kinds of the diamond tool has resulted in use of high-strength synthetic diamonds of marks AC200 and is higher than the increased quality with controllable characteristics on strength and thermostability (under the normative documentation of Ukraine).

As a rule, work of the diamond tool is carried out on air at temperatures not less 1000°C. In this connection, research corrosion resistance of diamonds the air environment at high-temperature processing is rather considers revising. Usually thermostability of powders of superhard materials including powders of synthetic diamond, it is determined by ability of grains of these powders to keep strength characteristics in result to thermal processing at the certain temperatures. For development of ways of manufacturing of tools use of thermally strong grains diamond grinding powders is necessary. Thermal strength of grains of diamonds which we do not identify thermostability (temperature constancy) to concept, is closely connected with graphitization and oxidation, i.e. the processes proceeded on surface of diamond grinding powder grains at heating.

The purpose of the present work was research kinetics of oxidation process of the high-strength diamond powders synthesized with application of ferroalloys, in the air environment at temperature operating modes of the diamond tool.

Researches of influence gas phase oxidations carried out in air and inert environments on powders of diamond of the different dispersion, synthesized in systems iron-nickel-carbon, iron-cobalt-carbon. For research samples have been made of high-strength diamonds of mark AC200 of grain size 250/200, 315/250 and 400/315. Preliminary before the beginning of oxidation process grinding powder diamond have been divided in a magnetic field of different intensity into the groups of powders differing among themselves on a specific magnetic susceptibility and accordingly under the contents in them of intracrystalline metal inclusions. Samples of diamonds different grain size were exposed to oxidation at temperature 900°C and 950°C during various times from 10 minutes till 6 o'clock.

Results of oxidation of grains of diamond it was estimated on a loss of their weight before oxidation. Comparison of results of experiments on gas phase oxidation diamond grinding powder different grain size estimated on changes of rate oxidation of diamonds at them of 10 % of loss of weight.

It is shown, that with increase in time of oxidation grows loss of weight of samples of high-strength diamonds researched grain sizes both in air, and in inert environments as a result of the executed researches. With increase in time of oxidation loss of weight of samples of all grain sizes grows, but loss of weight of diamonds of 250/200 grain size is more than diamonds of 400/315 grain size. The rate of oxidation of diamonds increases at rise in temperature gas phase oxidations. With growth of grain sizes of rate oxidation diamond grinding powder decreases as at gas phase oxidation at 900°C, and at 950°C. It is established, that for the diamonds synthesized with application of ferroalloys, with growth of concentration in them of intracrystalline metal inclusions, speed of oxidation grows. To increase corrosion resistance of diamond in tools have been developed the method of production of diamond powders with minimum of metal impurities. It allows to greatly increase resistance of diamond to oxidation in the atmosphere and to improve operation characteristics of diamond tools.

IMPROVING THE CORROSION RESISTANCE OF WEAR-RESISTANT CAST IRONS

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Products from wear-resistant high-chromium cast irons (parts of soil, slurry and sand pumps, hammer crushers, ball mills, flotation machines) are operated in conditions of intensive hydroabrasive wear. Under such conditions of use, simultaneous mechanical action of abrasive particles and a liquid medium occurs. The cutting of surface with abrasive particles contributes to the activation of corrosion processes. The presence of a liquid causes the appearance of the Rebinder's effect, which accelerates the process of mechanical destruction of details.

As our studies have shown, structure formation processes significantly affect the exploitative resistance of details from high-chromium cast irons. Chromium as the main component of the alloy provides corrosion resistance of these materials. In the process of crystallization and cooling of castings in the form, structures with significant chemical heterogeneity by chromium are formed, which leads to the appearance of zones with different electrochemical potential, which accelerates the processes destruction of parts by corrosion. An analysis of the alloying of high-chromium cast irons by manganese and nickel showed that an increase in the concentration by manganese enhances the chemical heterogeneity of the metal base by chromium. The amount of nickel in the range of 0.5 ... 3.0% increases the wear-resistant properties and corrosion resistance of high-chromium cast irons.

It has been established that the effect of manganese on the distribution and redistribution of chromium between phases lies in the fact that manganese is a carbide-forming element that has an affinity for carbon between iron and chromium. With a sufficiently fast crystallization of the eutectic, primary carbides are formed with a significant content of manganese and chromium. In the process of cooling castings in the mold, redistribution of manganese and chromium between carbides and the metal base occurs. The amount of chromium in carbides increases, and manganese decreases. As a result, in the metal base near the carbides, zones with a reduced chromium concentration and an increased concentration of manganese arise. Thus, in a cast iron with a content of 3.0% C, 2.0% Mn, 2.0% Ni, and 25% Cr, a metal base is formed containing about 15% chromium in the center of grains and less than 11% chromium in zones near carbides. With such a difference in chromium concentrations microgalvanic pairs are formed that accelerates the processes destruction of parts by electrochemical corrosion.

Using the methods of mathematical statistics, laboratory and industrial tests of parts, a wear-resistant cast iron with increased corrosion resistance 180X24H2 was developed (patent of Ukraine for the invention No. 119284).

ELECTROCHEMICAL AND CORROSION PROPERTIES OF THE MULTI-COMPONENT COMPOSITE OF THE TiH_2-FeSiMn-B_4C SYSTEM

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In recent time composite materials based on titanium have a widely used in the aggressive industrial environments, due to their high corrosion resistance, which can be enhanced by alloying. The feasibility of choosing an alloying element is determined by technical and economic factors. The introduce to the powder mixture up to 3-5% of iron, silicon or manganese significantly increases strength of the sintered alloy. In addition, in the process of the synthesis of TiH_2 with FeSiMn is active interaction with the formation of solid and wear-resistant silicidal phases of titanium, which favorably affect the corrosion resistance in seawater and sulfuric acid. The addition of boron carbide also significantly improves the corrosion resistant and tribotechnical characteristics of the material. The composite of TiH_2-FeSiMn-B_4C system was pressed and sintered in vacuum at the 1250°C [1, 2].

Corrosion properties were carried out in a 3% NaCl solution simulating seawater by the method of obtaining potentiodynamic polarization curves with use PI-50-1 potentiostat. The results of the researches are shown in Fig. 1.

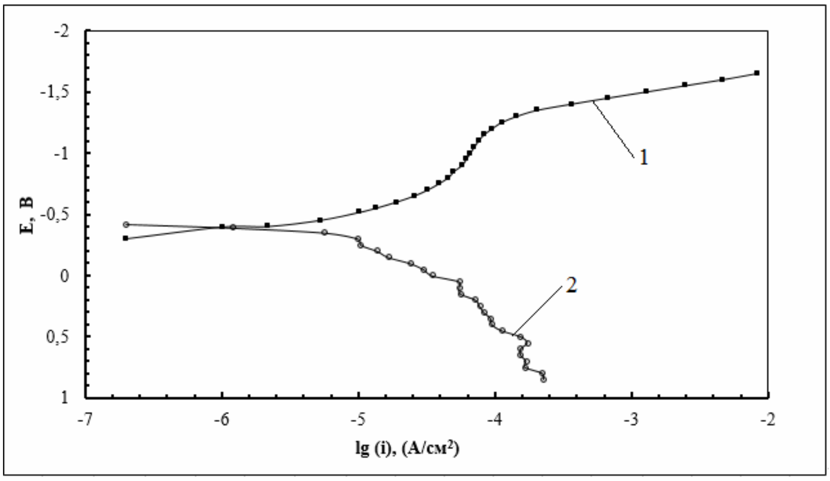

Fig. 1. Cathodic (1) and anodic (2) polarization curves of 65TiH_2-30FeSiMn-5B_4C composite in 3% NaCl solution

It is shown that near the stationary potential ($\varphi_{stat.}$), the velocities of the anode and cathode processes are -0.42 V and -0.3 V, respectively. The corrosion rate is controlled by the formation on the surface passivating layers at both anode and cathode processes in the initial stage. Given the lack of electrical conductivity of the sample, a passivating film formed on the surface probably consists mainly of a mixture of titanium oxides.

Thus, it was found that the formation of silicon and boride phases of titanium in the synthesis process leads to an increase in corrosion resistance due to the inhibition of the velocities of both the anode and cathode processes.

1. O. V. Suprun, G. A. Baglyuk, A. A. Mamonova Features of Structure Formation in TiH_2 - FeSiMn - C/B_4C Titanium Matrix Composite after Thermal Synthesis // XIII International Conference «Strategy of Quality in Industry and Education» (June 5-8, 2017) Varna, Bulgaria. P. 157–162.
2. Патент України на корисну модель UA 129662, C22C 33/02, C22C 14/00, C22C 38/54. Зносостійкий композиційний матеріал / О.В. Супрун, Г.А. Баглюк. – № u 2018 04189; заявл. 17.04.2018; опубл. 12.11.2018. – Бюл. № 21.

CORROSION BEHAVIOUR OF ALUMINIUM-BASED COMPOSITES PREPARED BY HOT FORGING

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Hot forging of porous performs is the alternative method for the manufacturing of composite materials that ensure the possibility for the production of materials with fine-grained structure and advanced mechanical and service characteristics. The aim of the present investigation is to characterize the corrosion resistance of aluminum-based composites reinforced with TiC and synthesized Al-Ti-C master alloy (MA), with additions of Cu and brass, as well, to analyzes the effect of hot forging on structure and properties of materials prepared using powder metallurgy techniques. Three types of master alloys with different amounts of carbon were used as alloying additions to compare properties of composites after hot forging. Various compacts based on aluminum and previously prepared Al-TiC, Al-Al_xTi_y-TiC master alloys powder with different dispersion ratios have been studied. The corrosion resistance of composites has been evaluated in 3,5 % NaCl and 3,5 % NaCl + 10 % HCl. The pitting corrosion was observed only in samples reinforced with TiC particles and alloyed with Cu and brass.

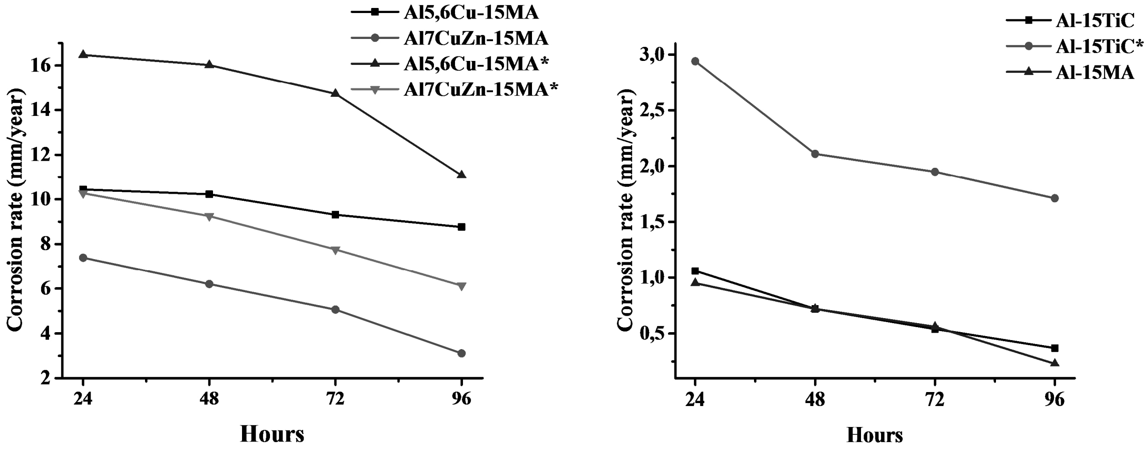

Fig. 1. Variation in the corrosion rate with the exposure duration in 3.5 wt.% NaCl and in 3,5 % NaCl + 10 % HCl (*) solutions

Fig. 1 shows the variation in the corrosion rate of composites with the exposure duration in 3,5 % NaCl and 3,5 % NaCl + 10 % HCl solution at room temperature. Experimental results showed that the corrosion rate of the composites decreases with exposure time which indicates some passivation of the matrix material. The Al-15MA exhibits excellent corrosion resistance in 3,5 % NaCl solution, presumably due to the beneficial effect of titanium aluminides, which formed as a result of the reaction between Al and Ti particles during master alloy fabrication. The weight loss for Al-15MA was so low, that it was hard to evaluate the corrosion rate and whiles Cu and brass addition enhance wear properties of the composite materials reinforced with Al-Ti-C master alloy, the corrosion resistance decreased significantly.

EFFECT OF ULTRASONIC IMPACT TREATMENT ON THE CORROSION RESISTANCE OF BIOMEDICAL AND INDUSTRIAL ALLOYS

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It is well known that many service properties of metallic materials depend on the structure and properties of their surfaces that predetermine durability of the materials before their failure. Methods of surface severe plastic deformation (SPD) are frequently sufficient to grain refinement and thence to enlarge load bearing capacity of construction materials. Last decade, methods of surface modification by repetitive impact loads, such as shot peening, surface hardening and nanocrystallization (SHN), surface mechanical attrition treatment (SMAT), and ultrasonic impact treatment (UIT), which are frequently effective in production of ultrafine-grained (UFG) and nanocrystalline (NC) structures, are in focus of investigations.

In present work we have analyzed structural modification and polymorphic transformation in the surface layer of Co-Cr-Mo alloy, Zr-Ti-Nb alloy and VT-6 alloy undergone the UIT process. The structural factors were also discussed as possible reasons to enhance the microhardness and corrosion behaviors of these alloys.

Equipment for the UIT process is described in detail in Refs. [1-2]. Structural analysis of the deformed surface layers were carried out by means of optical microscopy, X-ray diffraction (XRD) method, transmission electron microscopy (TEM) and selective area electron diffraction (SAED) analysis. The corrosion behaviors of original and UIT-processed specimens were evaluated based on the measurements of open circuit potentials by specimen's immersion into a 0.9%NaCl solution, which is an inherent component of various physiological fluids, at a temperature of 37 °C for 1500 s. Besides, a three-electrode cell with platinum plate counter electrode and a saturated calomel (SCE) reference electrode (240 mV vs. standard hydrogen electrode) was used to study potentiodynamic polarization behaviors. Potentiodynamic curves were recorded using a potentiostat P-5827M. The area for measurements was 20mm^2. The following electrochemical parameters were measured and estimated to characterize the corrosion behavior: the corrosion potential (E_{corr}), the corrosion current (i_{corr}), the passivation-maintaining current density (i_{p}).

The obtained results are important for development of thermo-mechanical techniques that would ensure the safe long-termin *in vivo* application of the Co-Cr-Mo alloy. The UIT process provides the following beneficial characteristics: (i) it has the noble properties of inert metal due to stable chromium containing passive films, which manifest themselves with less negative corrosion potential and lower corrosion and passivity currents in potentiodynamic curve, and (ii) the hardness that is high enough to provide wear resistance for metal-to-metal bearing and avoiding production of wear debris from articulating surfaces. The UIT of the Zr-Ti-Nb alloy in air with duration up to 30 s was found to cause the deformation-enhanced oxidation and deformation-induced surface segregation of the components and impurities from the bulk of a Zr-Ti-Nb alloy. The UIT of the titanium alloy in different environment with duration 120 s is optimal regime for maximum thickness of deformed layer, high level of microhardness, wear and corrosion resistance, as well as the formation of UFG and NC structure in modified surface layer.

1. B.N.Mordyuk, G.I. Prokopenko Ultrasonic impact peening for the surface properties' management // J. Sound Vib. – 2007.– 308. – P. 855–866.
2. B.N. Mordyuk, O.P. Karasevskaya, G.I. Prokopenko, N.I. Khripta Ultrafine-grained textured surface layer on Zr-1%Nb alloy produced by ultrasonic impact peening for enhanced corrosion resistance // Surf. Coat. Technol. – 2012. – 210. – P. 54–61.

INNOVATING TECHNOLOGY OF THE SURFACE HARDENING WITH THE ECOLOGICAL SAFETY STEEL CORROSION PROTECTION

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The surface hardening, especially treatment on «white layer» by special regimes turning (MT), mechanical-supersound (MST) and laser (LT), occupy the particular place among the effective methods of steel corrosion protection. This innovating technology has been developed in Karpenko PMI under guidance d.t.s., prof. Babeya Ju.I. [1, 2]. «White layers» are rendered the positive influence on steel corrosion resistance as at static, so and at cyclic load in different working mediums, due to concentrate (in several times) of metal surface zones C, Cr, Ni a.o.by chemical processing [2, 3]. But also it require of «white layers» efficiency study, in conditions of intensified environmental contamination, especially, by heavy metals as supertoxicants XXI cent [4, 5] and by radioactivity of natural mediums (soil, river water a.o.) as consequence of Chernobil catastrophe [6]. It is shown that «white layer» on carbonic steels 45, low-alloy steel 40Kh and high-alloy steel Kh12M have been ensured high technological efficiency of corrosion protection, in different natural and technological mediums, contaminated by heavy metals (soil, river and drainage waters) and radioactivity (Cs-137, Sr-90). The technological efficiency in river water (ICW=5.8 [7]) and drainage water (ICW=7.5) is reached 83.6…84.2 % (on i_a) and in soil (Zc=61 [8]) 89.2%, in conditions of the radioactive soil (A_Σ=0.36 Ku/km^2) – 88.1%, and increase to 94.2% with complex protection at the additional treatment soil by metalochelating synergist protection composition (on secondary raw materials), due to intramolecular and intermolecular synergism in the nanoscale modification of metal surface [5, 6, 9-11].

1. V. I. Pokhmurs'kyi. Development of investigations in the field of corrosion and stress-corrosion fracture of metals and the methods of their protection (A Survey) // Mater. Sci. – 2019. – Vol. 54. Iss. 4. – P. 451–464.
2. Ju. I. Babey. Fisicheskie osnovi impulsnogo uprochnenija stali i chuguna. – K.: Nauk. dumka, 1988. – 240 p.
3. Ju. A. Kljachco, V. G. Starchak, Ju. I. Babey. Issledovanije chimicheskoi prirodi belogo sloja stali // Shurnal V Kh Oim. D.I. Mendelejeva. – 1971. – Vol. 16. №5. – P. 596–597.
4. S. L. Davidova, V. I. Tagasov. Tiashelije metallic kaksupertoxicani XXI c. – M.: RUDN. – 2002. – 140 p.
5. V. G. Starchak, S. D. Tsybuliaa.o.Vpliv ecologichnoi situacii na proticorosiinii zachist metalokonstrukcii // FkhMM. – 2012. – Specvip. – T.2. №9. – P. 767–772.
6. S. D. Tsybylya, V. G. Starchak, K. N. Ivanenko, a. o.Effect of radioactive contamination of the medium on the durability of steel 20 //Radiochemistry. – 2017. – Vol. 59. №5. – P. 535–540.
7. V. Khilchevski. Wodopostachannia ta wodovidvedenia. – K.: KDU. – 1999. – 319 p.
8. SanPiN 2.2.7.029-99. Ocinka zabrudnennia gruntu.
9. V. G. Starchak, S. A. Alexejenko, N. P. Bujalska. Rol heteroatomovv obrazovanii metallochelatnich nanostructure pri poverchnostnoi modificacii materialow // Nanostructurnoje materialovedenie. – 2008. – №2-4. – P. 70-84.
10. V.G. Starchak, S.D. Tcibula, N.P. Bujalska The surface modification of the metal and composite materials for the nature mediums / // HighMatTech-2009. – K.: ІПМ НАНУ, УМТ. – 2009. – P. 336, 350.
11. F. H. Walters. Design of Corrosion inhibitors use the Hard and Soft Acid-Base (HSAB) Theory //J. Chem. Educ. – 1991. – Vol. 68, №1. – P. 29–31.

DEVELOPMENT OF A HIGH EFFECTIVE DIFFUSION METALIZATION METHOD OF CAST IRON AND STEEL CHEMICAL EQUIPMENT PARTS

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In recent years, more and more attention has been paid to the development of protective coatings that provide steels and alloys with increased physical, chemical and mechanical properties, which allows the task of replacing expensive high-alloy chromium-nickel steels with cheaper carbon ones. This primarily applies to coatings based on silicon, chromium, titanium, aluminium, which provide steels and alloys with increased corrosion resistance, wear resistance, heat resistance [1, 2].

According to the results of the researches, it is established that the operational properties of gray cast iron parts (corrosion resistance, heat resistance, wear resistance) can be increased (by 10…15 times) due to diffusion saturation of the surface layer by one or more elements of the group: Cr, Ti, Cd, Al, Mn, Si. It is established that the level of performance characteristics of gray cast iron parts subjected to diffusion metallization is determined by the set of parameters of the saturated layer: depth, phase composition, nature of phase distribution, porosity, and structure of the sublayer and layer.

Among the relatively available salts of NH_4Cl, NH_4F, NaCl, NaF, etc. used as activator in mixtures for diffusion metallization of gray cast iron, high-quality layers that provide the acquisition of high performance properties can be obtained by dosing into a saturated mixture of NH_4Cl, NH_4F salts. Based on the mathematical models obtained, the "diffusion property – mixture composition" diagram are constructed, which allow to determine the optimal composition of the saturating mixture to obtain a necessary level of diffusion coating properties on gray cast iron.

It was found that the highest level of performance properties of gray cast iron parts is achieved after titanium and chromium plating in mixtures of 10...13% of activators containing NH_4Cl or NH_4F. To obtain a non-porous siliconized layer, a mixture of NH_4Cl and NH_4F salts in a 1:1 ratio should be used as the activator, with a total content of ~ 4% (by weight) of a saturating mixture. It is shown that the efficiency of diffusion titanium substantially increases with the introduction into the saturating mixture of aluminum. When the titanium saturating mixture contains, 8…10% aluminum, it is forms on the surface of gray cast iron the layer, the corrosion resistance of which is 10 times, and the hardness – 5…7 times more from the resistance of steel X18H10T.

At the diffusion saturation by chromium of steel and gray cast iron, an additional increase in the coefficient of stability can be achieved by introducing into the saturating mixture FeMn and Cr_2O_3. After chromium plating in a mixture containing ~ 15% Cr_2O_3 and ~ 3.5% FeMn, the corrosion resistance of steel is 2,5 times and that of gray cast iron is 6 times higher than the corrosion resistance of steel X18H10T.

It was found that chromium plating in the mixture containing ~ 3.5% FeMn along with the main components leads to an additional increase in the wear resistance of steel by 10…15 times, and of gray cast iron by 30…35 times, compared to the layer obtained in chromium-free mixture without FeMn.

1. Multicomponent diffusion coatings based on titanium, aluminum and silicon on nickel / V.G. Khizhnyak, T.V. Loskutova, A.E. Datsyuk, O.V. Khizhnyak // Scientific News of NTUU "KPI": scientific and technical magazine. – 2015. – № 1 (99). – 79 – 84.
2. Phase and chemical composition of diffusion titanoalumochrome coatings. / O.E. Datsyuk, V.G. Khizhnyak, T.V. Loskutova, and other // Journal. nano- and electron. physics. – 2018. – 10. – № 3. – P. 03015-2 – 03015-4.

RESEARCH OF CORROSION RATE OF ADDITIVE GROWING PARTS

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The production of competitive machines is associated with the development of new materials and the enhancement of their properties, which can be achieved by improving production technologies. The samematerial, which is the same in chemical composition but obtained by different technologies, has differences in structure and properties.

The necessity of introducing resource-saving production methods led to the emergence of volume metal-powder printing technologies (additive technologies). Additive technologies have occupied a special place in the industry and now they are classified into a separate category of molding. Every year, they are gaining more and more market segments that are replacing classic parts manufacturing technologies. This is due to the possibility of obtaining a finishing surface with the necessary tolerances for one cycle of cultivation. The main raw material in the setechnologies is powder.

Equally important in the additive manufacturing of high-tech industry parts is the provision of operational properties. Additive technologies have a number of features that imprint on the performance of these properties. The formation of alloy layers from different thickness technological layers of the powder, which is caused by the different fractional composition of the latter, can lead to a decrease in performance. It is powders that are the main creators of the properties of the final products. The very question of the corrosion behavior of alloys obtained by additive technologies is poorly understood.

The purpose of this study was to investigate the corrosion behavior of additives of domestic powders BT1-0 and BT20, which were fused by additive technology, which had non-spherical particle shape. For this purpose, within the framework of GD 2116, additive growing of specimens of BT1-0 and BT20 powders was carried out on an electron beam 3d printing unit, and substrates of BT20 and BT1-0 alloys were used, respectively. The powder fraction from 100 µm to 150 µm was used. 3d printing was performed on equipment and modes developed at the Institute of Electric Welding named after E.O. Paton NAS of Ukraine. Samples 10 × 10 × 5 mm in size were cut from the workpieces. Changes in the structure of the samples and their corrosion rate in a 20% solution of perchloric acid were investigated.

It has been established that the corrosion rate of the fused zone is higher compared to the substrate, as a result of not providing the proportionality of its components. The corrosion rate of the BT1-0 alloy is 2.7 times higher than substrates made of VT20 alloy. For the BT20 alloy obtained by additive technology, the highest corrosion rate is inherent in the fused zone, which is 1.4 and 1.7 times higher than the corrosion rate of the deposited layers. Studies of changes in the corrosion potential revealed that for the substrate zone, the potential shifts rapidly to the region of negative values; for the fused zone, the potential is positive throughout the test; for the deposited titanium zone, the potential changes in the positive region for the first 1210 s, then rapidly shifts to the negative region, then increases again to positive values. For all zones of the deposited BT20 alloy, the potentials are in the negative region, which characterizes the corrosion-unstable state of the material. The potential fluctuation may be predetermined by the specificity of oxidation of the formed structures. The fusion zone provides the highest corrosion-electrochemical properties.

CORROSION PROTECTION OF CARBON STEEL BY COMPOSITION BASED ON NATURAL POLYSACCHARIDE

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One of the effective methods of controlling metal corrosion is the inhibition of working environment. Since a number of known corrosion inhibitors, including chromates, are toxic to humans, environmentally hazardous and difficult to dispose of, ecologically safe substitutes are being studied, in particular on the basis of water-soluble natural polymers [1]. These polymers are non-toxic, contain numerous polar functional groups and are better adsorbed to the metal surface than monomers and oligomers. Biopolymers provide two advantages in corrosion inhibition: a polymer chain displaces more water molecules from the metal surface, and the presence of multiple adsorption sites makes their desorption more difficult [2]. Natural polymer xanthan gum (XG) is a biogenic polysaccharide obtained by aerobic fermentation of corn, soybeans or other plant materials using *Xanthomonas campestris* bacteria. It is environmentally safe and biodegradable. However, in a neutral chloride-containing corrosive environment, its effectiveness is low. The purpose of this study was to investigate the possibility of enhancing the protective effect of XG by combining it in one inhibitory composition with potassium sodium tartrate (PST) [3].

Corrosion of carbon steel St.3 was investigated in 0,1 % NaCl solution, to which XG and PST were added separately and in the composition. Characteristics of corrosion processes were investigated by electrochemical impedance spectroscopy using Gill AC potentiostat.

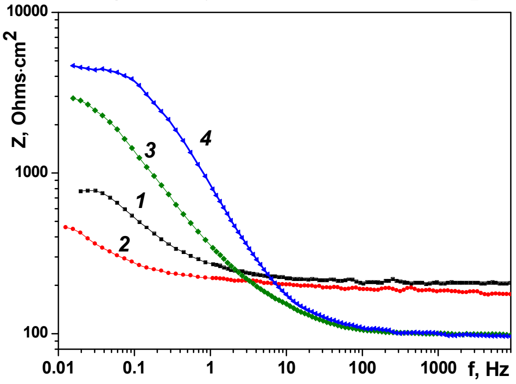

Fig. 1. Impedance dependence of carbon steel after a week of exposure at: *1)* uninhibited 0,1 % NaCl; *2)* 0,1 % NaCl+ 0,5g/l PST; *3)* 0,1 % NaCl + 2 g/l XG; *4)* 0,1 % NaCl +2 g/l XG and 0,5g/l PST

Electrochemical studies revealed (fig. 1) that with the use of the XG inhibitor, the charge transfer resistance of carbon steel after a week of exposure in a corrosive environment inhibited by XG was no more than 3000 $\Omega\cdot cm^2$, which corresponds to a degree of protection of 75%. At the same time, PST was generally ineffective under the circumstances. The composition of XG + PST showed higher protective properties – the resistance of the charge transfer of steel in the chloride solution increased to the level of 5000 $\Omega\cdot cm^2$, and its degree of protection was about 90%.

Microscopic studies of the surface of steel samples after exposure in inhibited solutions correlate with the data of electrochemical studies and confirm the effectiveness of the protective action of the composition XG + PST in chloride-containing solution.

Thus, it was found that the anti-corrosion effect against carbon steel of the natural polymer of xanthan gums in chloride-containing 0.1% NaCl solution can be increased by combining it in one composition with potassium sodium tartrate.

1. A. Ali Fathima Sabirneeza, R. Geethanjali, S. Subhashini. Polymeric corrosion inhibitors for iron and its alloys: A Review // Chemical Engineering Communications. – 2015. – Vol. 202. – P. 232–244.
2. S.A. Umoren, O. Ogbobe, I.O. Igwe, E.E. Ebenso. Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives // Corros. Sci. – 2008. – Vol. 50. – P.1998–2006.
3. F. Garcia-Ochoa, V.E. Santos, J.A. Casas, E. Gomez. Xanthan gum: Production, recovery, and properties // Biotechnology Advances. – 2000. – Vol. 18. – P.549–579.

ALUMINIUM ALLOY CORROSION INHIBITION BY ZEOLITE/ PHOSPHATE PIGMENT

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Zeolites are nano/micro crystalline aluminosilicate with 3D porous structure, which is represented by the following formula: $m_{2/n}\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$, where m is an exchangeable cation, n – is the cation valence, x is ≥2 (as Al^{3+} does not occupy the adjacent tetrahedral) and y is the degree of hydration [1]. The anticorrosion properties of a zeolite coating is affected by many factors, such as the structure and its crystallinity, the film thickness and its packing density as well as the roughness and hydrophobicity of the coating surface [2, 3].

The aim of the work is to develop complex anticorrosion pigments based on ion exchanged zeolite followed by zinc phosphate deposition on its nanoporous surface and to study their protective action on aluminium alloy.

Aluminium alloy corrosion inhibition by complex zeolite and phosphate pigment was studied by DC polarization method. Suspensions of zinc phosphate pigment Novinox PZ02 and Ca-modified zeolite/zinc phosphate blend in artificial acid rain with pH = 4.5 were prepared for this purpose. The concentration of an inhibiting component in each suspension was 1000 ppm. Aluminum alloy samples were dipped into inhibited acid rain solutions, and their polarization characteristics were recorded by a Gill AC potentiostat, using a saturated Ag/AgCl reference electrode and a counter platinum electrode. The potential scan rate during potentiodynamic polarization experiments was 1 mV/s.

Potentiodynamic polarization studies of the D16T alloy in acid rain pigments suspensions revealed (Fig. 1), that the complex pigment "zeolite-Ca^{2+}/$Zn_3(PO_4)_2$" is significantly superior to commercial zinc phosphate pigment Novinox PZ02 and zeolite-Ca^{2+}, taken separately.

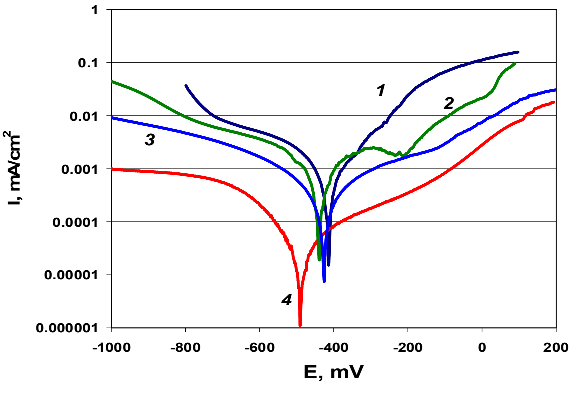

Fig. 1. Potentiodynamic polarization curves of D16T aluminium alloy after 24 hours exposure in acid rain solution: 1 – uninhibited, 2 – suspension with Ca-zeolite, 3 – suspension with phosphate Novinox PZ02, 4 – suspensions with complex pigment Ca-zeolite/zinc phosphate

The corrosion rate of the aluminum alloy in the suspension of the complex pigment is reduced in about 8-12 times compared with the uninhibited acid rain solution. The complex pigment is characterized by strong cathodic control of corrosion of aluminum alloy, indicating the formation at its presence of corrosion-resistant film.

1. C. Banerjee, R. P. Woo, S. M. Grayson, A. Majumder, R. K. S. Raman Influence of Zeolite Coating on the Corrosion Resistance of AZ91D Magnesium Alloy // Materials. – 2014. – Vol. 7. – P. 6092–6104.
2. L. Rassouli, R. Naderi, M. Mahdavain The role of micro/nano zeolites doped with zinc cations in the active protection of epoxy ester coating // Appl. Surf. Sci. – 2017. – Vol. 423. – P. 571–583.
3. L.-Y. Huang, Y.-Ch. Hao, W. Ch. Changjean, M.-J. Wang, A. S.T. Chiang, T.-Ch. Tsai Growth of MFI zeolite film as corrosion protection layer of aluminum alloy // Micropor. Mesopor. Mat. – 2015. – Vol. 217. – P. 71–80.

ALUMINUM ALLOY CORROSION INHIBITION BY TECHNICAL GLYCEROL

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The use of synthetic organic corrosion inhibitors and traditional inorganic, in particular chromates, is gradually being restricted in developed countries due to their toxicity. These compounds are accumulated in the environment, and their disposal requires significant costs. In this regard, environmentally safe corrosion inhibitors are being actively studied in Ukraine and abroad. During the production of biodiesel a byproduct - technical glycerol (TG) is formed. It contains glycerides, free fatty acids and their esters and is biodegradable [1]. Therefore, it was of interest to evaluate technical glycerol as a potential “green” corrosion inhibitor of aluminum alloys in neutral chloride-containing environment.

Samples of an aluminum alloy D16T in the delivery state with a working surface area of 1 cm^2 were used in the work. The protective effect of TG was studied by electrochemical impedance spectroscopy with Gill AC potentiostat. The corrosive environment was a 0,1% sodium chloride solution, to which TG was added in an amount of 2,5 g/l. Charge transfer resistance of the metal in corrosive solution was calculated from impedance spectroscopy data using software EIS Spectrum Analyzer.

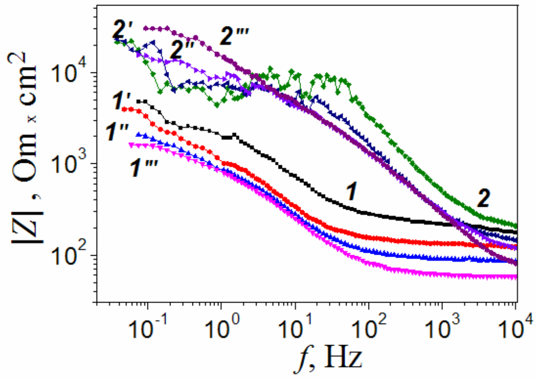

Fig. 1. Frequency dependencies of the impedance modulus of aluminum alloy samples in a non-inhibited solution of 0,1% NaCl (1) and with the addition of 2,5 g/l inhibitor TG (2) for temperatures: 1, 2 - 293 °K; 1′,2′- 313 °K; 1″,2″ - 333 °K; 1‴, 2‴- 353 °K.

A decrease in the impedance modulus of the D16T alloy samples at low AC frequencies with increasing temperature of the uninhibited corrosive solution was revealed (Fig. 1). At room temperature (293° K) the value | Z | of the alloy sample at frequencies of 0.1 Hz was $4{,}72 \cdot 10^3 \cdot$cm^2, and for 313; 333; 353°K, this value decreased to $3{,}97 \cdot 10^3$; $2{,}08 \cdot 10^3$ and $1{,}61 \cdot 10^3$ Ohms·cm^2 respectively. Instead, when adding 2,5 g/l TG in 0,1% NaCl solution, the index |Z| with increasing temperature slightly increased. The calculations show that in the studied temperature range, the charge transfer resistance of the aluminum alloy in the inhibited solution increases from 3 to 12 times compared with 0,1% sodium chloride solution. And at higher temperatures the protective effect is greater. The data obtained indicate that the adsorption nature of the TG inhibitor on the aluminum alloy in the chloride-containing solution can be physical and but partly chemical in nature.

Thus, it was found that the by-product of biodiesel synthesis - technical glycerin at a concentration of 2,5 g/l effectively inhibits corrosion of aluminum alloy in 0,1% NaCl solution, and with increasing temperature of the environment to 353°K its protective effect is still high.

1. F. Yang, M. Hanna, R. Sun. Value-added uses for crude glycerol – a byproduct of biodiesel production // Biotechnology for Biofuels. – 2012. – Vol. 5. – P. 13.

EVALUATION OF INHIBITION EFFICIENCY OF APRICOT POMACE EXTRACT AS A POLYFUNCTIONAL CORROSION INHIBITOR OF STEEL

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One of the key trends in the development of the modern field of chemical resistance of materials and metal protection from corrosion is the concept of ecologization and introduction of "green" technologies [1,2]. At the same time, food/plant waste is the source of a mixture of organic compounds of different classes (polyphenolic compounds, aldehydes, ketones, monoterpene compounds, etc.), which in the defined selection of solvent / solvent system can provide multifunctional corrosion protection in various corrosion environments. The authors have previously studied the component composition of 2-propanol, ethanol and aqueous extracts of apricot pomace (EPA) [3,4] and found that, depending on the type of extractant, the selectivity of the inhibitory action in a certain corrosive medium is observed.

Therefore, the effectiveness of the evaluation of the extract obtained by the mixture of solvents as a multifunctional steel corrosion inhibitor for various corrosive media is investigated, namely in air (atmospheric corrosion conditions), neutral aqueous (3% NaCl) and alkaline media ($Ca(OH)_2$ + NaCl).

The chemical profiles of the extracts were analyzed using liquid chromatography mass spectrometry (LC-MS) and HPLC methods. Total phenolic content and total flavonoid content of extracts were determined. The antioxidant activity of the extracts were evaluated by DPPH (1,1-diphenyl-2-picrylhydrazyl), ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonicacid)) and reducing power assays.

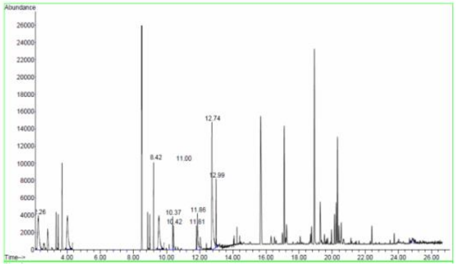

Fig. 1 GC-MS spectral chromatogram of the apricot pomace extract (APE).

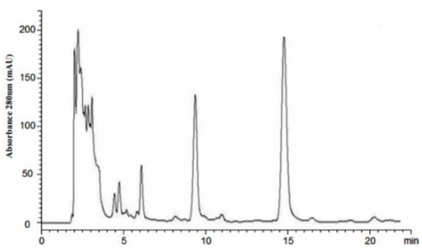

Fig. 2 HPLC chromatogram of APE

The results showed that the extracting solvent significantly altered the inhibition property. The combination of scientific research of the authors outlines that the required period of film formation for the ACE is the exposure time from ~ 12 to 40 hours. This period refers to the main stage of the formation of the protective film, during which there is an increase in the effectiveness of the protective action. To characterize the surface morphology of the film formed on the surface of the steel after the exposure to a corrosive solution with addition of ACE, microscopic studies has been carried out with the use of scanning electron microscopy (SEM) and atomic force microscopy (AFM).

1. Devikala S., Kamaraj P., Arthanareeswari M., Milin B. Patel. Green corrosion inhibition of mild steel by aqueous *Alliumsativu* mextractin 3.5% NaCl // Mat. tod.: Proc. – 2019. – Vol. 14. – P. 580–589.
2. M. B. Radovanović, M. B. Petrović, et al. Cysteineas a green corrosion inhibitor for Cu37Zn brass in neutral and weakly alkaline sulphate solutions // Env. Sci. Pollut. Res. – 2013. – 20. 4370–4381.
3. Vorobyova V., Apricot cake extract as corrosion inhibitor of steel: chemical composition and anti-corrosion properties V. Vorobyova, M. Skiba, Chem. J. of Moldova. – 2019 – Vol. 14. 1. – P. 77–87.
4. V.I. Vorobyova, M.I. Skiba, I.M. Trus Apricot pomaces extract (*Prunus Armeniaca L.)* as a highly efficient sustainable corrosion inhibitor for mild steel in sodium chloride solution. Int. J. Corros. Scale Inhib. – 2019. 8, No. 4. – 1060–1084.

PECULIARITIES OF INHIBITORY ACTION OF SECONDARY AMINES ON STRUCTURAL STEEL CORROSION IN ACID CHLORIDE MEDIUM

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The influence of the degree of protonation of the molecule on the efficiency of structural steel corrosion inhibition in acid chloride medium by secondary amines with triazoloazepinmethyl and aryl substituents was considered in this work [1]. It was shown by quantum-chemical calculations that for investigated secondary amines with different radicals (R = H, F, Cl, I) in benzene ring showed different form of the existence of molecules in a solution depends on the pH of the medium, and its greatest influence is found within the pH range from 0 to 2. It has been established that for all investigated compounds, the inhibition efficiency (IE) in the range of pH 0…2 changing in waves (Fig. 1). It is caused by the complication of the adsorption of the compounds on the metal surface due to the redistribution of charges on the main adsorption reaction centers and consistent with [2]. The highest inhibition efficiency (88.58% - 96.09% at a concentration of 1 mmol/l) of these compounds is found in solution of hydrochloric acid pH = 0.7–1.0 (Fig. 1). In this pH the molecules are mainly protonated by a nitrogen of triazole cycle, that shown with quantum-chemical calculation.

Using polarization measurements (Fig. 2) and Auger electron spectroscopy it has been concluded that the highest inhibition efficiency of the compound with a para-iodinebenzene substitute is explained by the formation of a strong protective inhibitor layer on the steel surface. Film thickness is up to 10 nm [3].

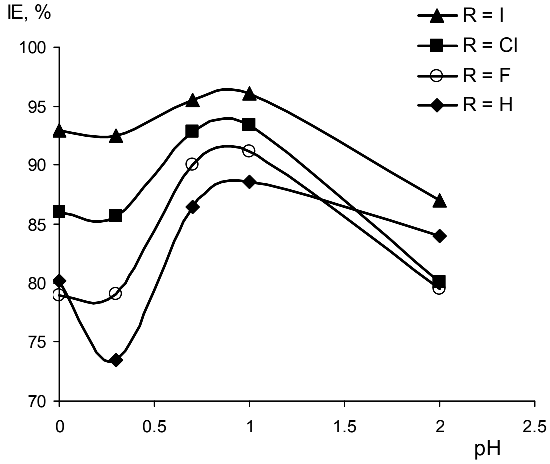

Fig. 1. Dependence between inhibition efficiency of secondary amines and pH of solutions of hydrochloric acid

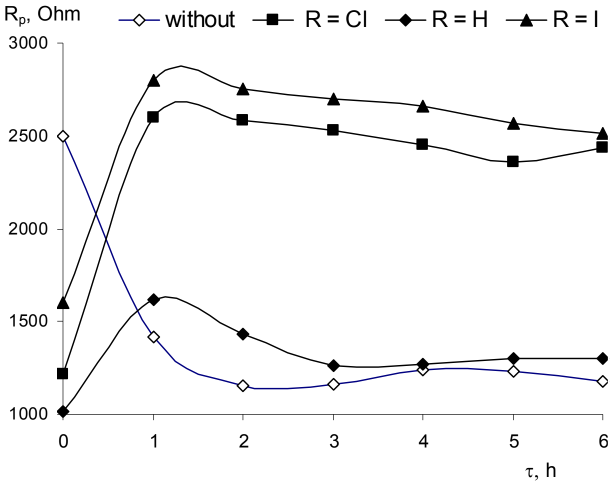

Fig. 2. Dependence between polarization resistance and sample soaking time in 0.2 M HCl solution (pH = 0.7)

1. Demchenko A.M., Nazarenko K.G., Makey A.P., Prihodko S.V., Kurmakova I.N., Tretyak A.P. Sintez, protivokorrozionnaya i biotsidnaya aktivnost proizvodnyih triazoloazepina // Zhurnal prikladnoy himii – 2004. –T.77. Vyip.5. – P. 794–797.
2. Vdovenko I.D., Perehrest N.A., Lisogor A.I. Issledovanie assotsiatsii alkilammonievyih soley v kislyih rastvorah // Elektrodnyie protsessyi pri elektroosazhdenii i rastvorenii metallov.
3. Nanostrukturni protsesy pry inhibuvanni korozii stali nitrohenovmisnymy kondensovanymy heterotsyklamy // Fizyka i khimiia tverdoho tila.. – 2012. – T. 13. № 4.

INHIBITORY PROTECTION OF PIPE STEELS FROM THE COMBINED EFFECTS OF SULFATE REDUCING AND TIONIC BACTERIES

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In the course of long-term operation, underground pipelines are subject to corrosion damage by soil microorganisms (MOs). Among the association of soil microorganisms, sulfate reducing (SRB) and thionic (TB) bacteria are the most corrosive to the metal of pipe steels in the underground environment. To date, the effects of SRB and TB bacteria on corrosion of pipeline steels in individual Postgate «B» and Beyerinka media have been sufficiently studied. The question of their joint influence in the mixture of nutrient media on the kinetics of biocorrosion processes and structural changes in the metal of the pipeline systems remains open.

The purpose of this work is to evaluate the effect of cells of the *Desulfovibriosp* SRB. piece Kyiv-10 and *Thiobacillus* sp. piece PAC-7 for their joint action in a mixture of Postgate "B" and Beyerinka nutrient media for the corrosion rate of pipe steels 17G1C-U and Art. 20 and structural changes of metal under the influence of corrosion damage. The object of the study was samples of 17G1C-U and Art. 20 steel tubes with a size of 10x30x1.0mm from a non-operated pipe. SRB cells of the genus *Desulfovibrio* sp. piece Kyiv-10 was grown on Postgate «B» in a thermostat at a temperature of 28°C for 14 days. Pure sulfate reducer colonies were obtained on Postgate «B» semisolid medium by sowing by ten-fold dilutions. *Thiobacillus* sp. piece The PAC-7 was isolated from gold ore dumping in South Africa. For the cultivation of thionic bacteria used Beyerinka medium composition (g/l): $Na_2S_2O_3$ $5H_2O$ - 5.0; $NaHCO_3$ - 1.0; Na_2HPO_4 $2H_2O$ - 0.2; NH_4Cl - 0.1; $MgCl_2$ $6H_2O$ - 0.1; Distilled water - 1.0 l. The control medium was a mixture of sterile Postgate» B» and Beyerinka media in a 1: 1 ratio. For the study, inhibitors based on dioxodecahydroacridine derivatives (Ing. 1) and Quaternary ammonium salts (Ing. 2) were used. Upon completion of the studies, the metal samples were subjected to mechanical and chemical treatment to remove corrosion products from their surface.

The corrosion rate of metallic specimens was determined by the gravimetric index of the corrosion rate Kgr. = m - m_0/S τ (mg/(dm^2 days), where: m is the final mass of the sample, mg; m_0 is the mass of the sample before corrosion, mg; S is the surface area of the sample, dm^2; τ is the exposure time, days. of the inhibitors tested were determined according to DSTU 3999-2000.The inhibitor concentration was 0.5 and 1.0%, and the effectiveness of the inhibitors tested was characterized by the degree of protective effect of the inhibitors (Z) calculated by the formula: Z = Kgr.- Kgr.$_1$/ Kgr. • 100%, where: Kgr - corrosion rate in uninhibited medium, mg / dm^2 day; Kgr.$_1$ - corrosion rate in the presence of inhibitors, mg / dm^2 day.

It was found that in a mixture of sterile Postgate «B» and Beyerink media in a 1: 1 volume ratio inoculated with SRB and TB cells, the corrosion rate is higher compared to the effect of SRB and TB monocultures. Under the comparative conditions of experiments, steel 20 in corrodes at a speed of 4 (4.3) times lower, compared to steel grade 17G1C-U, which is probably due to the influence of the component composition of steel. The highest degree of protection of the metal against biocorrosion (94.6%), caused by the combined effect of SRB and TB by bacteria, was shown by Ing. 2 at a concentration of 0.5% for 17G1C-U steel.

THIOSULFONATES AND RHAMNOLIPIDS AS BIOCORROSION INHIBITORS

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Protection of materials from biodeterioration is an actual scientific and practical problem. Metal structures are destroyed not only under the electrochemical corrosion influence, but also biological corrosion. The main factors of biocorrosion are microorganisms, as well as their metabolites (CO_2, H_2S, etc.). Especially dangerous are sulfate-reducers of the genera *Desulfovibrio* and *Desulfotomaculum* and thionic bacteria *Tiobacillus*, which oxidize sulfur and its compounds to sulfuric acid, lowering the pH of the medium. Today, synthetic biocorrosion inhibitors are mainly used to protect metals, but the development of environmentally friendly biocidal agents is an important task. The effect of the ethyl thiosulfanilate biocide (Lviv Polytechnic National University) [2], the rhamnolipid biosurfacatant of the strain *Pseudomonas* sp. PS-17 (Department of Physical Chemistry of Fossil Fuels InPOCCC, NAS of Ukraine) [3] for the growth of bacteria *Desulfovibrio desulfuricans* IMO K-6 (Ivan Franko National University of Lviv) [1] for 10 days (Table.1).

Table 1. The effect of ethylthiosulfanilate and rhamnolipid biocomplex on the growth of *Desulfovibrio desulfuricans* IMO K-6

Contents of preparations, g/l	Bacteria biomass, g/l			
	RBC	ETS	ETS+ RBC 1:1	Control (H_2O)
0,5	0,68	1,03	-	1,18
0,25	0,7	0,79	2,87	
0,125	0,66	0,7	0,8	
0,063	0,75	0,7	0,59	
0,031	0,89	0,34	0,75	
0,016	-	-	0,81	

Notes: Kravtsov-Sorokin nutrient medium in the Kravtsov-Sorokin's liquid medium; RBC – rhamnolipid biocomplex; ETS – ethylthiosulfanilate

It was shown that ETS and RBC at concentrations of 0.03-0.5 g/l, as well as their compositions in 1: 1 ratio (0.016-0.125 g / l), effectively inhibit the growth of sulfate reducer *Desulfovibrio desulfuricans* IMO K-6.

So, the developed preparations based on thiosulfonates and rhamnolipid biosurfactants are promising biocides for metals protecting from anaerobic biocorrosion.

1. G. Zvir, O. Moroz, S. Hnatush. Dissimilatory sulfate reduction in bacteria Desulfovibrio desulfuricans IMV K-6 upon influence of Uragan and Raundup herbicides // Vìsn. Dnìpropetr. Unìv. Ser. Bìol. Med. 2015. 6(1). – P. 40–44.
2. V. Lubenets, N. Stadnytska, D. Baranovych, S.Vasylyuk, O. Karpenko, V. Havryliak, V. Novikov. Thiosulfonates: the Prospective Substances against Fungal Infections. “Fungal infection”/EditedbyEricoSilvadeLoreto.IntechOpen. 2019. P. 1-25.
3. T. Pokynbroda, I. Karpenko, H. Midyana, O. Karpenko. Isolation of Surfactants Synthesized by the *Pseudomonas* Bacteria and Study of Their Properties // Innov Biosyst Bioeng. – 2019. – Vol 3.- No 2.- P. 70–76.

PECULIARITIES OF THE PROTECTIVE ACTION OF PLANT – BASED INHIBITORS IN DIFFERENT PH SOLUTION

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The methods of obtaining inhibitors from different plant raw materials were comparatively by analyzed and a 3 - stage method of separation of active components from wood: beech, pin, birch, oak, walnut processing wastes was developed. It was found that the protective properties of these extracts with same concentrations (0.1-0.8 g/l) in respect to 20 steel and copper in neutral media and 3% NaCl are virtually indistinguishable.

The degree of protection for increasing the concentration of the extracts from 0.1 to 0.8 g/l is slightly increases and is held for steel at 80 – 85% and for copper at 56 – 65%. Electrochemical studies show that chemisorption of the components, followed by formation of the cluster protective film, which inhibits the catodic and anodic electrode reactions is the mechanism of protective action of such extracts.

In acidic media (5% HCl) increas of the exposure time from 3 no 9 hours of steel and copper samples leads to an increase corrosion rate, but in the presence of 0,8 g/l of the extract the degree of 20 steel protection in 5% HCl increases from 80 to 89% and of copper to 52-68%. The magnitude of the displacement of adsorption potential under the influence of extract indicate the chemisorption mechanism of the inhibitory protection of these metals calculated on the basis of electrochemical tests.

From the temperature dependences of the corrosion rate of 20 steel in water and 5% hydrochloric acid the activation energies of the corrosion process were determined in the absence and presence of the extract. It is shown that activation energy under the influence of extract increases on average in 1.5-2 times due to the formation of additional potential barriers.

The test of the extract in medium of lubricated – cooling liquid also confirms its protective properties concerning 20 steel. This inhibitor at concentration of 0.8 g/l protects 20 steel in a 5% lubricated – cooling liquid by 76% and copper by only 44%, which is lower than in water and 5% hydrochloric acid. The corrosion potentials of 20 steel and copper in 5% lubricated – cooling liquid are shifted towards less negative values, while corrosion currents are reduced in 5-6 times for steel and 1.6-2 times for copper.

Increases of the protective ability of plant raw material extract is achieved through the use of synergist of plant origin: gums, rhimnolipid surfactants, ets. Such composition in neutral and acid medium can have protection degree of 95%.

CORROSION BEHAVIOR OF 20 STEEL, COPPER, BRASS IN INHIBITED ACID SOLUTIONS FOR HEAT-POWER EQUIPMENT CLEANING

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Methods of providing reliable and productive operation of heat-power equipment were analyzed. The peculiarities of different methods of cleaning the internal surfaces of boilers, condensers, etc. from salt deposits and corrosion products, the technological and economic advantages of acid removal of salt and corrosion deposits were substantiated. The necessity of the effective acid corrosion inhibitors use, particular environmentally safe, in the process of scale purification was shown.

Gravimetric and electrochemical studies showed that depending on the intensity of corrosion action on 20 steel, copper and brass, the acids, most commonly used for dissolving deposits, can be placed in a row: HC1 > CH_3COOH > low-molecular dicarboxylic acids > OEDF (hydro -) > citric acid. This series was responsible for both reducing metal specific mass losses and corrosion currents. At the sometime it was shown that the use of HC1 with comparision with other acids provided the most complete and fast removal of scale from heat exchange surfaces. The influence of two inhibitor types: HOSP-10 (based on pyridine and quinoline compounds) and TIS-5 (based on plant extract) on this metals corrosion resistance 5% in hydrochloric, citric and low-molecular dicarboxylic acids at temperatures of 25, 40 and 80^{o}C was investigated.

It was found that these inhibitors at 2g/l concentration protected 20 steel by 90-95%, brass – by 60-70% and copper – by only 40-45%. The calculated activation energies of corrosion process of 20 steel in the presence of HOSP-10 and TIS-5 increased by 30-40% compared to the non-inhibited medium. The mechanism protective action of both inhibitors is chemisorption with retarded partial electrode reactions and decreased corrosion currents. Anti - corrosion ability of the TIS-5 is not worse than HOSP–10, but it is eco-safe.

Investigation of the TIS-5 effect on the rate and completeness of calcium carbonate dissolution in 5% HCl revealed the following. Certain differences between the influence of 5% HCl and its inhibited solution on the kinetics of calcium ions transition to the soluble state were observed during the first 30 minutes. Dissolution of calcium carbonate slowed down at this stage was the result of complex formation of inhibitor functional groups with Ca^{2+}, which upon further interaction with inhibited solution was exhausted and dissolution rate even slightly exceeded the uninhibited acid dissolution. Fool-scale test of TIS-5 as a part of the wash solution for cleaning the EVACO-200 condenser confirmed the absence of a negative impact on the process efficiency of salt deposits removal and significant decrease in iron and copper leaching.

INTERCALATION OF NANOPOROUS OXIDE COATING ON ALUMINIUM ALLOY BY CORROSION INHIBITORS

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The most reliable method of protecting aluminum alloy products from corrosion is the electrochemical anodizing of their surface before paint application. Anodizing makes possible to obtain oxide coating of sufficient thickness with a nanoporous structure, which have a high adsorption capacity and provide a high adhesion of the paint coatings to the metal surface. Further enhancement of protective properties of oxide coatings is achieved by performing operations of filling and sealing the anode layer, which expands the use of oxidized aluminum and its alloys.

The corrosion-electrochemical characteristics of anodized D16T alloy in corrosive environment - 0.1% NaCl solution were investigated. Anode films with a thickness of 12 … 15 μm were applied from a mixed sulfate-oxalic acid electrolyte at a current density of 2.5A / dm^2 and a temperature of 18 ... 24^{O}C. The presence of oxalic acid in the electrolyte leads to a decrease in its thermal sensitivity and etching effect on the anodized surface, which allows to increase its service life and hardness of the oxide coating. Electron-microscopic analysis of the cross-sections indicates the formation of a regular microporous structure of the layer with pore sizes of 20 ... 35 nm.

The obtained films were filled in solutions of nickel acetate, potassium dichromate, imidazole and xanthan gum and sealed in distilled water at 95...98^{O}C. This treatment is accompanied by the conversion of anhydrous aluminum oxide into a low-soluble form of hydroxides or major salts, which occupy a larger volume, thereby closing a large portion of the cross-section of the film, which has a protective effect.

The corrosion of the anodized D16T alloy was studied by electrochemical impedance spectroscopy in 0.1% NaCl solution. The corrosion resistance of the samples impregnated with the corrosion inhibitors was evaluated by the integral index - breakdown function $D = \log (Z_0/Z_t)_{1Hz}$, where Z_0 and Z_t - the impedance modulus of the samples at the beginning of the tests and after seven days of exposure, respectively, with an AC frequency of 1 Hz. The lowest values of D in the range 0.1-0.2 and correspondingly the highest corrosion resistance were observed in anodized samples sealed with dichromate and natural polysaccharide. However, polysaccharide is an environmentally safe inhibitor that gives it a significant advantage over dichromate. The results of electrochemical studies of anodized and compacted inhibitors of aluminum alloy samples are correlated with microscopic analysis and polarization studies.

INHIBITION OF LOW-CARBON STEEL BIOCORROSION BY ZnO NANOPARTICLES

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Nanoparticles of metal oxides comprise a new class of important materials, which are designed for use in scientific studies and various areas human activity. Latest achievements in the area of nanotechnology, for instance, ways to produce highly ordered metal nanoparticles of different shapes and sizes, have allowed development of new approaches, which include use of nanoparticles as biocidal agents. Latest studies have shown that nanoparticles can be used as efficient bactericidal agents and materials in medicine (Tiller et al., 2001; Lin et al., 2002; Kuhn et al., 2003; Sunada et al., 2003 p .; Sondi & Salopak-Sondi, 2004; Lewis & Klibanov, 2005).

Aim of the study – to investigate influence of ZnO nanoparticles on process of microbial corrosion of steel in neutral water-saline medium in presence of sulfate-reducing bacteria.

The influence of ZnO nanoparticles (NPs) (concentrations 0,03 mg/ml and 0,3 mg/ml) on the process of biocorrosion and on the growth of bacteria has been studied in liquid Postgate's B medium, which has been inoculated with sulfate reducing microbial community. Postgate's B medium with microbial community, but without nanoparticles has been used as control. The efficiency of ZnO nanoparticles as biocides-inhibitors of microbial corrosion of low-carbon steel has been evaluated.

Nanoparticles have been synthesized by the method of electric-impulse ablation (Kaplunenko and Kosinov, 2009). By the method of transmission electron microscopy, it has been established that samples of ZnO contain separate NPs and their aggregates of triangular, elliptic and amorphous shapes. Triangular NPs have length of side about 30–50 nm, sizes of elliptic and amorphous NPs were 30–60 nm. Nanoparticles of metal oxide have been resuspended in double distilled water using ultrasound to obtain uniform colloid system. Freshly obtained colloid systems have been used in all studies.

The study has shown that NPs addition at concentration of 0,03 mg/ml to the corrosive medium does not inhibit the process of microbial corrosion, though sulfate-reducing activity of bacteria is inhibited: concentration of biogenic hydrogen sulfide is decreased three times as compared to control. The speed biocorrosion is decreased in 6,7 times if the concentration of NPs in increased to 0,3 mg/ml. The protective effect is 85,0 %. Inhibitory effect of NPs on the growth of sulfate-reducing bacteria has been shown: the amount of corrosion-hazardous bacteria in plankton is decreased by five orders of magnitude as compared to control, the concentration of biogenic hydrogen sulfide is decreased in 4,4 times. It has been shown that the presence of NPs (0,3 mg/ml) in corrosive medium decreases the amount of bacteria by three orders of magnitude.

Thus, the possibility of ZnO nanoparticles use to inhibit low-carbon steel biocorrosion with simultaneous inhibition of corrosive-hazardous sulfate-reducing bacteria growth has been shown. It can be considered to be a new alternative in prevention of steel microbial corrosion.

ANTI-CORROSIONACTIVITY OF NEW CLASS THE FOUR-MEMBERED HETEROCYCLIC COMPOUNDS' DERIVATIVES

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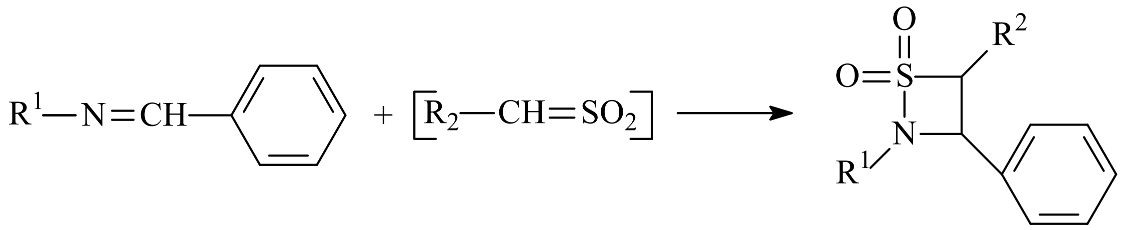
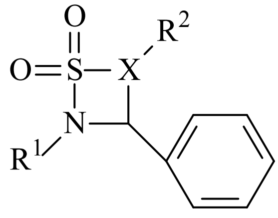
In order to find ways of practical use of products of cyclic addition of sulfenes and sulfonimines to compounds which containing in their composition the double bond N = C, we investigated the reactions with Schiff bases with a heterocyclic substituent at a nitrogen atom, the course of which in organic solvents (methylene chloride, acetonitrile, dimethylformamide) occurs according to the scheme:



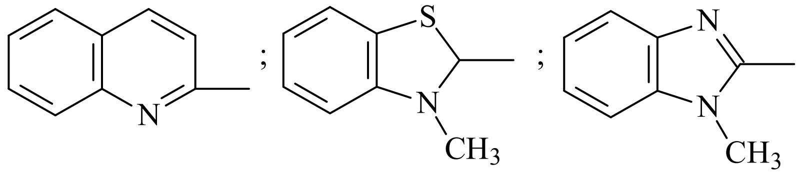
The influence of structure and conditions on the anticorrosive activity of the synthesized series of compounds of the general formula was investigated:



X = CH, N.

R^2 = H; Me; Ph.

R^1 =



This has allowed us to propose and investigate the serie of new effective inhibitory compositions of complex action. In particular, anti-corrosion wear resistant coating by introducing into the compound reinforcing additives and heterocyclic compounds (2-5% by weight) ((3,4-diphenyl-1,1-dioxide-1,2-thiazetidin-2-yl) -2- hetaryls), which have proven to be most effective as inhibitory supplements among the studied series of products of sulfenecycloaccession.

Physical-mechanical (impact resistance, abrasion resistance, elasticity), anti-corrosion (variation of the inhibitor concentration and retention time of the composite samples on metal) and adhesive (swelling) properties of the coating were investigated. The increase of wear resistance (by 1,3-1,5 times) and the anti-corrosion activity (by 10-15%) of the proposed coating in corrosion-aggressive environment compared to the standard samples that are used in industry was demonstrated.

Based on the results of the laboratory experiments, it was possible to provide recommendations on the effective use of the investigated coating for the working elements of steel equipment (steel 20) against wear and acid corrosion.

MODELING THE ADSORPTION OF *N*-ALKYLATED QUINOLINES ON THE SURFACE OF IRON IN ACID ENVIRONMENT

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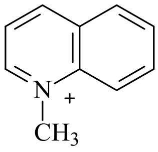
Quantum-chemical calculation methods have been successfully used for research the relationship of simple molecular structures with their inhibitory properties [1, 2]. The researchers also can successfully apply this approach for more complex systems if they accept the following assumptions: 1) the effect depends only on the properties of the inhibitor molecule; 2) the entire molecular environment in the vicinity of the inhibitor molecule is neglected when considering adsorption competition on the surface of iron.

In this research, with using the Accelrys Material Studio 5.0 program using the “Adsorbtion Locator” module and the force field module COMPASS, we conducted a simulation on the surface of iron of the adsorption of *N*-alkylated quinolines (cations) with the following structure:


(1)

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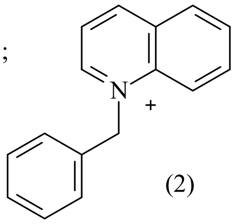
(2)

We studied the tendencies in the change of the adsorption capacity of these molecules (table) depending on the nature of the substituent at the quinoline nitrogen atom towards the surface Fe (100).In each case we considered the interaction of one *N*-substituted quinoline molecule with the surface of iron to determine the binding energy.At first, an iron crystal was built by preliminary optimization of the unit cell, and then supercells (8 atomic layers) were constructed.To account for the influence of the aqueous environment, we introduced 50 water molecules into the system.The gravimetric method was used to study the effectiveness of the inhibitors in an acidic environment (1 *M* solution H_2SO_4).

Table. The calculation values of energies (kcal/mol) adsorption of cations

n/n	Rigid adsorption energy	Deformation energy	Adsorptionenergy
1	-64,3	-8,5	-72,8
2	-108,4	-10,2	-118,6

The transition from the 1-benzylquinolinium cation (2) to the 1-methylquinolinium cation (1) is accompanied by a noticeable decrease of the adsorption energy (1,5 times).This is due to a decrease of the total steric volume of the molecule and reduces the likelihood of a manifestation of blocking effect on the surface.The analys of the results of corrosion tests shows that the change the inhibitory efficiency of the corresponding *N*-alkylquinolinium cations is in good agreement with the results of quantum chemical calculations.

Thus, molecular modeling can be used for design and development of new organic corrosion inhibitors.

1. K.F. Khaled, K. Babic-Samardzija. N. Hackcrman. Theoretical study of the structural effects of polymethylene amines on corrosion inhibition of iron in acid solutions // Electrochimica Acta. – 2005. – Vol. 50. № 12. – P. 2515–2520.
2. M. Finsgar and J. Jackson Application of corrosion inhibitors for steels in acidic media for the oil and gas industry. Areview // Corros. Sci. – 2014. –Vol. 86. № 9. – P. 17–41.

ELECTROCHEMICAL INVESTIGATION OF SOME DERIVATIVES OF 1.8-DIOXODECAHYDROACRIDINES AS CORROSION INHIBITORS FOR MILD STEEL IN GROUNDWATER IMITATS

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The use of corrosion inhibitors remains one of the effective methods of corrosion protection. Among the nitrogen-containing heterocycles for protection of metals from corrosion in acidic environments, pyridine derivatives are the most common [1,2]. High degree of corrosion protection of steels in acidic environment is provided by quinazoline derivatives [3], acridine [4], quinoline [5,6]. To protect industrial systems, the authors [7] have proposed the use of complex inhibitors based on pyridine and polyamine derivatives.

Despite the large number of corrosion inhibitors, the search for new inhibitors and the creation of compositions that will be effective for specific conditions are continuing.

The aim of this work is to synthese nitrogen-containing heterocycles from aniline and p-nitroaniline, dimedone and ethanol (ING1, ING2) and to study their efficacy as inhibitors in NS1 groundwater imitation. The synthesized compounds are crystalline substances, insoluble in water, soluble in alcohols. An ethanol solution of the inhibitor was used for the studies. The studies were performed on NS1 groundwater imitation: KCl - 0.149 g / l, $NaHCO_3$ - 0.504 g / l, $CaCl_2 \cdot 2H_2O$ - 0.159 g / l, $MgSO_4 \cdot 7H_2O$ - 0.106 g / l.

To investigate the mechanism of action of inhibitors on the corrosion behavior of steel in NS1 medium, an electrochemical method of removing the polarization curves on the MTech COR-410 potentiostat was used.

As a result of the studies, it was found that the tested compounds in the environment of NS1 under free corrosion conditions affect the anodic process of dissolution of the steel, slightly shifting the stationary potential to the positive region. With the imposition of polarization, a further increase in the corrosion potential was observed in the region of positive values (from -0,746V to -0,699V), indicating anode protection. The corrosion current density when injected with ING1 alcohol solution decreased slightly, while for ING2 it was almost an order of magnitude (from -2.87 to -3.70), indicating its high efficiency as a corrosion inhibitor. The influence of the concentration of compounds on the electrochemical properties is investigated.

1. R.M. Vyshnevs'kyj. Cyklichni ta acyklichni aminy, yak potencijni ingibitory koroziyi metaliv / R.M. Vyshnevs`kyj, B.L.Lytvyn, A.S.Fedoriv // Fizyka i ximiya tverdogo tila. – 2010. – T.10. – 2. – P. 332–345.
2. Issledovaniye ingibiruyushchego deystviya razlichnykh piridiniy galogenidov i ikh smesey na korroziyu stali v sernokisloy srede / R. I. Yurchenko. S. V. Ivashchenko. T. N. Pilipenko. I. S. Pogrebova // Zhurnal prikladnoy khimii. – 2005. – T. 78. – V. 3. – P. 517–519.
3. Synthesis and investigation of quinazoline derivatives based on 8-hydroxyquinoline as corrosion inhibitors for mild steel in acidic environment: experimental and theoretical studies / Rbaa, M., Galai, M.,Benhiba, F., [et all.] // J. of Ionics. - 2018. – P.1–19. https://doi.org/10.1007/s11581-018-2817-7
4. 2, 10-dimethylacridin-9(10H)-one as new synthesized corrosion inhibitor for C38 steel in 0.5 M H_2SO_4 / Salghi,R., Ben Hmamou, D., Ebenso, E.E., [et all.] // Intern. J. Electrochem. Sci. – 2015. – V.10. Iss. 1. – P. 259–271.
5. Ivshin Ya.V. Ingibitory korrozii na osnove geterotsiklicheskikh aminov. 1. Vliyaniye struktury molekuly na zashchitnyye svoystva / Ivshin Ya.V.. Ugryumov O. V.. Varnavskaya O.A.// Vestnik KGTU. – 2015. – T.18. - 3. – P.77–80.
6. Ivshin Ya.V. Ingibitory korrozii na osnove geterotsiklicheskikh aminov. 1. Vliyaniye kontsentratsii ingibitora i sostava korrozionnoy sredy na zashchitnyye svoystva / Ivshin Ya.V.. Ugryumov O. V.. Dzhanbekova L.R.// Vestnik KGTU. – 2015. – T.18. – 18. – P.125–126.
7. Voloshin V. F. Ingibitory korrozii dlya zashchity magistralnykh nefteprovodov v serovodorodsoderzhashchikh elektrolitakh / V. F. Voloshin. V. S. Skopenko. V. V. Voloshina // Stroitelstvo. Materialovedeniye. Mashinostroyeniye. Seriya: Energetika. ekologiya. kompyuternyye tekhnologii v stroitelstve. – 2014. - V. 76. – P. 80–85.

ANTIMICROBIAL ACTIVITY AND BIODEGRADABILITY OF GUANIDINE-CONTAINING POLYETHYLENE OXIDE HYDROGEL

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Polyethylene oxide hydrogels have been widely used in various fields of science and technology due to their non-toxicity, high degree of swelling, and biodegradability. One method of producing such hydrogels is based on the urethane formation reaction in the presence of a crosslinking agent. Of particular importance is the construction of pH-sensitive hydrogels, which is carried out by introducing a controlled number of ionic groups, by co-polymerizing of acrylic derivatives of oligooxyethyleneglycols with acrylic monomers containing such groups, or by adding ion-containing additives during the urethane formation reaction. Of special interest is obtaining of polyethylene oxide hydrogels with the use of derivatives of a highly basic compound such as guanidine, which also demonstrates antimicrobial activity.

The aim of this work was to obtain guanidine-containing polyethylene oxide hydrogel, to determine its antimicrobial properties and biodegradability under the influence of bacteria which had been identified and singled out by us earlier from damaged protective coatings of gas pipelines.

In order to perform this task, guanidine-containing oligomer having linear structure with terminal guanidine fragments was synthesized via the reaction between bifunctional aromatic oligoepoxide (MW 365) and guanidine, with the molar ratio of components 1:2. The obtained oligomer structure is characterized by IR and NMR spectroscopy.

Polyethylene oxide hydrogel was synthesized in two steps. The first step was obtaining of guanidine-containing oligomer, the second step was obtaining of hydrogel by reacting oligooxyethylene glycols MW 6000 with toluene diisocyanate and guanidine-containing oligomer at room temperature. The latter acts simultaneously as a cross-linking, ion-containing and antimicrobial agent.

Synthesized hydrogel demonstrates antimicrobial activity with respect to gram-positive and gram-negative bacteria: the diameter of growth suppression zone of *Rhodococcus erythropolis* 102 is 20 mm, *Bacillus subtilis 138* - 24 mm, *Pseudomonas pseudoalcaligenes* - 15mm.

An indicator of the material degradation is the sample weight loss under the influence of bacteria. After 60 days of the experiment, weight loss of the samples in Towson medium with meat peptone broth under the influence of heterotrophic bacteria was 0.19-0.22 g with the initial weight of 0.32-0.34g. Presence of the researched materials in the medium, contributed to the reduction of catalase and lipase activities of bacteria by 1.4 - 2.5 times as compared to the control (medium inoculated by bacteria without introducing of the materials).

Thus, the research has shown that the obtained hydrogel has pH-sensitivity within the range of pH 4-5, is biodegradable and demonstrates bactericidal activity against a number of bacteria.

USE OF NITROAMINO-CONTAINING WASTES AS CORROSION INHIBITORS IN ACID SOLUTIONS

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We have previously studied the inhibitory properties of nitroamine containing resinous wastes and used them as components of protective coatings

In this regard, it is of great interest to study the possibility of using these wastes as inhibitors for etching solutions

The work is devoted to the study of metal protection in acidic solutions (20% HC1, 1н and 2н H_2SO_4 solutions) on steel images (St.3) using two methods: potentiodynamic and gravimetric.

Since the studied waste consists of a mixture of primary, secondary and tertiary nitrooxyamines, it was necessary to study the inhibitory properties of individual components and identify the contribution of each of them to the total protective effect. Since the basicity of primary amines is more pronounced, to illustrate the inhibitory effect, the primary amine was studied using the methods used: $O_2N\text{-}C_6H_4\text{-}CH(OH) - CH_2\text{-}NH_2$, called "oxy-amine".

Calculated on the basis of experimental data, the kinetic characteristics of dissolution of samples of steel St. 3 in acid solutions with the addition of inhibitory additives indicate that both pure oxy-amine and resinous waste dissolved in acid belong to the inhibitors of the mixed type under mixed control, since there is an increase in the polarizability of both chemical processes (anode and cathode) in both pure acid (background solution) and acid solution with the additives used. In addition, depending on the concentration, the latter can both inhibit and stimulate (catalyze) iron corrosion.

By applying the dependence of the inhibition coefficient (γ) on —lgC obtained by two independent methods, it was possible to determine the range of concentrations where the additive behaves as a corrosion inhibitor (from $1 \bullet 10^{-3}$ to $8 \bullet 10^{-3}$ mol / l in 1н. sulfuric acid solution for oxy-amine or from 0.035 wt.% to 0.55 wt.%. for nitrooxyamines waste).

HIGH-VOLTAGE SPARK INSPECTION OF NONCONDUCTIVE ANTICORROSIVE COATINGS ON METALLIC SUBSTRATE

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The inspection of anticorrosive coating integrity is an important part of the maintenance of the metallic structures exploited in the corrosive environment. The applications of the high-voltage spark inspection techniques for monitoring of nonconductive coating quality are regulated by some foreign and national documents [1-4]. Many of the International Societies propose the standards about the application of high-voltage holiday detectors, including NACE (National Association of Corrosion Engineers), ASTM and ISO. The main interest to high-voltage inspection technique is related to the possibility to detect the discontinuities (holiday) in the coating possible to deteriorate the anticorrosive properties, such as porosity, cavity, pinhole, inclusion or crack. The inspected coating must be deposited on the surface of a conductive substrate (metals or concrete with sufficient moisture content to be conductive). There are two types of high-voltage inspection techniques related to the continuous or pulsed types of test voltage. The energy in the pulsed systems is contained within the short-time pulses. In this case, the test voltage can be maintained on slightly conductive coatings and only significant release of energy through a defect is monitored. But the lower energy released by dirt or moisture on the coating are ignored. Modernized PULSAR type holiday detector is based on the pulsed voltage applied to the test electrode can detect of the pinhole type defects with 0.3 mm diameter in 9.5 mm thick dialectic protective coatings. The maximal speed of the test electrode scanning – 0.35 m/sec. The defect presence is alarmed by sound and light indications. PULSAR type holiday detectors have a relatively low size and weight due to the high-voltage transformer application with high- performance characteristics. The generalized scheme of PULSAR type holiday detector contains the next components (fig. 1): 1 – generator, 2 – intermediate voltage transducer, 3 – the switch synchronizer, 4 – capacitive energy storage, 5 – thyristor-diode switch unit, 6 – remote high-voltage transformer, 7 – indicator, 8 – high-voltage test electrode, 9 – inspected coating, 10 – metallic substrate. PULSAR type holiday detector was successfully applied in many enterprises and in the Pipeline Protective Coating Certification Center of our institute.

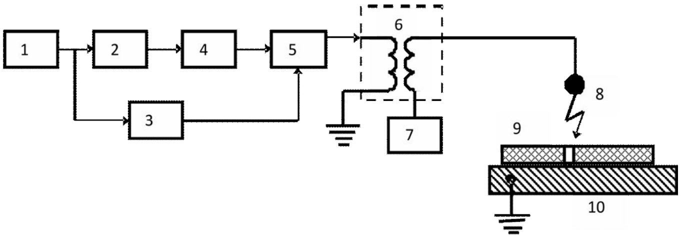

Fig. 1. Generalized scheme of PULSAR type holiday detector.

Some methodological aspects of high voltage spark method application are needed to be investigated to improve the inspection reliability. For this purpose, the optimal test voltage must be adjusted in accordance with the electric strength of inspected material.

1. ASTM D 5162:2015. Standard practice for discontinuity (holiday) testing of nonconductive protective coating on metallic substrate.
2. NACE International SP0188. Standard Practice – Discontinuity (holiday) testing of new protective coatings on conductive substrates.
3. ISO 29601. Paints and varnishes — Corrosion protection by protective paint systems — assessment of porosity in a dry film.
4. DSTU 4219-2003. Steel pipe mains. General requirements for corrosion protection (in Ukrainian).

EDDY CURRENT EVALUATION OF INTERNAL CORROSION DAMAGES IN TWO-LAYER AIRCRAFT STRUCTURES WITHOUT DISASSEMBLING

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The well-timed detection of corrosive damages is very important for the accident-free operation of aircraft structures. It is especially important for long-term exploited (aging) aircraft [1,2]. Therefore, the corrosive monitoring of aircraft structures is an important part of aircraft maintenance [3]. The most susceptible to corrosive damage are aluminum alloy units (for example, internal surfaces of double-layer structures, skins of a fuselage and wings, the areas of the bathrooms).

From the eddy current (EC) inspection method, all types of corrosion damage can be divided into total and local corrosion, depending on the ratio of the damaged area and the size (sensitive area) of EC probe (ECP). Thus, local corrosion can be attributed to total corrosion when the damaged area is larger than the ECP diameter. Generally, the total corrosion can be evaluated by low-frequency absolute type ECP. In this case, the corrosive damages can be interpreted as sheet thinning and evaluated by EC sheet thickness measurements. For local corrosion detection, low-frequency double differential type ECP can be applied [1, 4]. The more complicated situation for corrosion monitoring occurs when corrosive damages are situated in internal surfaces of the double-layer aircraft structure (bottom surface of a first (top) layer or top surface of the second layer).

Low-frequency absolute type EC probe was developed to investigate the detectability of the total corrosion thinning in aluminum alloy double-layer structures. EC probe consists of one driver coil for primary electromagnetic field creation and two serially connected secondary coils. All coils were wounded on an 8 mm diameter ferrite for sensitivity improvement. Signals of developed EC probe were investigated in the complex plane by universal EDDYCON C type EC flaw detector on different operational frequencies (from 1 to 10 kHz). The different levels of the total corrosion damages were simulated by different depths thinning fabricated mechanically in aluminum alloy sheets.

The EC signals created by local type corrosive damages also were investigated. In this case, two low-frequency double differential type EC probes characterized by operational diameters 8 and 10 mm were developed [4]. The local type corrosive damages were simulated by drilled depths holes characterized by different diameters and depths. Signals of developed EC probe were investigated in the complex plane by universal EDDYCON C type EC flaw detector as presented above.

Results obtained show the possibility of EC method to evaluate different types of corrosive hidden damages in aircraft double-layer structures without disassembling. High enough detectability and inspection selectivity can be achieved by proposed low-frequency EC probes. All inspection procedure details (like applied operational frequencies) will be developed by taking into account the inspected structure parameters (the skin thicknesses, the thickness of the dielectric protective coating, the clearance between layers and so on).

1. Structure mechanics and strength of material. Vol. 9. Strength and durability of airplane materials and structural elements / O. Ostash, V. Fedirko, V. Uchanin V. et al, Lviv: Spolom, – 2007.
2. Evaluation of aluminium alloys degradation in aging aircraft / O. Ostash, V. Uchanin, O. Semenets et al // Research In Nondestr. Evaluation. – Vol. 29. Iss. 3. – P. 156–166.
3. R. A. Smith Fine-tuning the eddy current detection of hidden first-layer corrosion in aircraft skins // Insight. – 1998. – Vol. 40. Iss. 10. – P. 712–721.
4. V. Uchanin Surface double differential type eddy current probes (in Ukrainian). – 2013. – Lviv: Spolom. – P. 267.

ANALYSIS OF THE INFLUENCE OF TEMPERATURE ON CORROSION STEEL BEHAVIOR IN ELECTROLITE

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We offer a model for predicting the dependence of the corrosion rate of steel on temperature. Increasing the temperature, decreases the molecular ion oxygen overstress and increases its diffusion rate to the metal surface, which ultimately leads to an increase in the corrosion rate [1].

We consider corrosion in a surface defect of a type of crack. The initial conditions, the activation energy of the corrosion process of steel in aqueous NaCl solution are taken into account. We use the generalized Kaeshe type relation for corrosion current [2], which includes: electrolyte conductivity, potential difference, crack opening and depth, parameter Tafelin corrosion current and metal corrosion potential, specific energy of plastic deformation of the surface (interphase) layer during the formation of a new (juvenile) surface. Additionally, to describe the pitting corrosion of steel, we apply the diffusion and mass transfer equations in the same way as in [3], which includes oxygen concentration and diffusion coefficient.

These ratios are the basis of a mathematical model for investigating the effect of temperature on the rate of corrosion process on a steel surface.

On the basis of the experimental data it was found that with increasing NaCl concentration the corrosion rate decreases.

For the ranges of variation of NaCl concentration 290… 310 g / kg and temperature 290… 360 K, the dependence of the corrosion rate on the temperature is approximated by the exponent.

Using the least squares method, it was found that the correlation coefficient between the f (T) (T - temperature) distributions for the two NaCl concentrations of 290 g / kg and 310 g / kg is approximately equal to 1.

The obtained results make it possible to establish (analytically describe) the correlation of the corrosion rate with the anode reaction overvoltage in the surface cavern at different temperatures.

1. Mychajlov B. N,, Nemykina O. V. Corrosion-electrochemical behavior steel in chlorine production environment // Polzunovsky Vestnik. – 2006. – № 21,. – P. 201–204.
2. Dzala R., Yuzevych V. Electrochemical corrosion in defects under coatings // Phys.-Chem. mechanics of materials. – 2018. – Special iss 12.– P. 318–322.
3. Scheiner S.Hellmich C. Stable pitting corrosion of stainless steel as diffusion-controlled dissolution process with a sharp moving electrode boundary// Corr. Sci – 2007 – Vol. 49. Iss. 2. – P. 319–346.

THE CORROSION CONTROL OF UNDERGROUND PIPELINES BY MEASUREMENTS OF CURRENTS AND POTENTIALS

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Diagnostic examinations of underground pipelines (UP) and related metal structures have traditionally been carried out by contact electrometric methods of potential measurement. These shortcomings can be eliminated by the use of non-contact methods [1, 2], among which the search and determination of the location and measurement of the depth of occurrence of the UP are widely used. However, non-contact current measurements (NCM) are underused. Special apparatus and methods of measurement processing are required for this purpose. In this paper, we describe a technique for controlling the corrosion of UP by priority NCM and in combination with contact measurements of alternating electrical voltages and potential differences.

The systems of parallax and gradient input converters have been developed based on the theoretical foundations of PhMI of NASU. New methods of NCM with azimuthal and radial orientations of the base of observation points, with arbitrary placement of the base in the transverse UP plane (with component and modular primary converters) are proposed. The possibility of using redundant information in the input data for estimation of errors of measurements of coordinates and current is established. The created BIT-KVP equipment [1] allows to determine the location, direction and depth of occurrence of pipelines and conductive communications and to measure the strength of the AC alternating current component with correction of relief error without connection to the pipeline and the ground. This instrument is additionally equipped with a voltmeter for traditional contact measurements and electronic memory. The results of measurements through a special program interface are translated into a personal computer for automatic processing and documentation. NCM excited by a cathodic protection unit (CP) or a test current generator in the UP make it possible to quickly check and control the corrosion protection at different sites of the UP [1]. Integrated, differential and local assessments of the condition of the corrosion protection of the UP are provided by the use of the NCM in order to determine the needs, types and amounts of repair to prevent damage and continue the operation of the UP. Their main advantages over traditional contact electrometric methods are greater efficiency and informativeness at lower labor costs.

The new method of simultaneous measurements of constant and alternating voltages gives the value of the polarization potential (without the ohmic component), which is the main criterion for the electrochemical protection of metal. The PPM equipment, created by this method, makes it possible to additionally detect damage to the insulation of the AC and at the potential difference.

The application of the Global Positioning System module in the created equipment of the BMC-K provides automatic fixation of geographical coordinates and time of measurement of current and depth of occurrence of PT, which significantly facilitates the processing and documentation of survey results. By coordinates, we determine the distance between the current measurements, which is necessary to find the distribution of current flow density, its subsidence and the pipe-to-ground transient resistance. There are examples of combined use of NCM and PPM that allow the determination of the density distributions of the direct current component of the cathodic protection unit, the specific soil resistance and the resistance of the insulation layer in different sections of the UP. This confirms the advantages of such a method over the traditional method of corrosion testing of UP.

1. Electrophysical methods of non-destructive testing of defect in structural elements / R.M. Dzhala, V.R. Dzhala, I. B. Ivasiv, V. G. Rybachuk, V. M. Uchanin. / Technical diagnostics of materials and constructions: Reference manual / Editor-in-chief Z. T. Nazarchuk. – Vol. IV. – Lviv. – 2018. – P. 356.
2. New methods for the corrosion monitoring of underground pipelines according to the measurements of currents and potentials / R.M. Dzhal, B.Ya. Verbenets', M.I. Melnyk, A.B. Mytsyk, R.S. Savula, O.M. Seменyuk // Materr. Sci. – 2016. – Vol. 52, No. 5 – P. 732–741.

UNCOORDINATED OPERATION MODE OF CATHODIC STATIONS

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The protective potential of the underground steel pipeline is formed by several cathodic protection stations. Cathodic protection stations (CPS) operate simultaneously [1,2].

The inconsistency in the simultaneous operation of the CPS is caused not only by the different condition of the insulating coating or by the currents that wandering. For CPS with a classic transformer circuit and unmanaged or controlled rectifier, the phase of connection to the power supply network - is an important perturbation factor. With the simultaneous operation of the CPS, which are galvanically interconnected by an underground steel pipeline, when they are connected to different phases, there is a mutual shift of the rectified voltage.

The voltage on output the one of the SKZ changes according to a certain law. The voltage between the ground and the point of connection of another CPS fed from a different phase than the first CPS has a different law of change over time. In this case, we have a difference between amplitude of potentials, which is formed by cathodic protection stations (curve 1, Fig. 2). If the second cathodic protection station is connected to the same phase as the first CPS, the potential difference will decrease (curve 2, Fig. 2).

The coordinated connection of the CPS to the power phases provides a reduction in the equalization currents caused by the potential difference caused by the uncoordinated mode of operation of the cathode protection stations. Connecting the different cathodic protection stations to the same phase leads to a decrease in the amplitude of the potential difference (curve 2, Fig. 2).

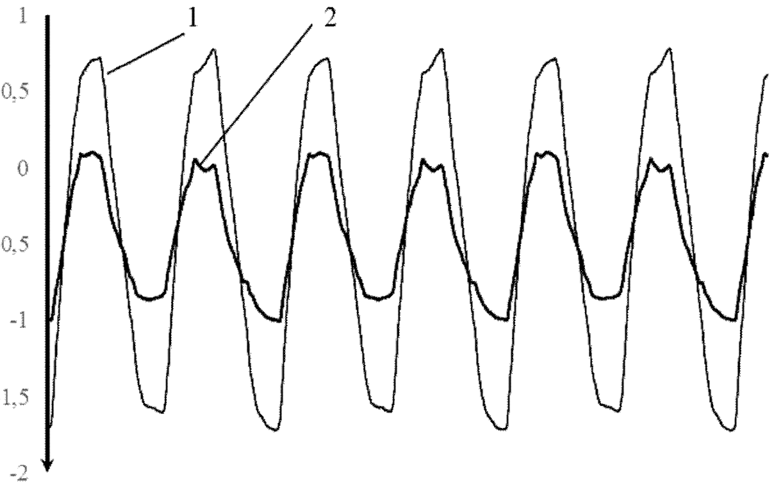

Fig. 2 Potential difference between adjacent CPS connection points in inconsistent (1) and consistent (2) operating modes

The positive impact on the corrosive situation by the coordinated connection to the eponymous phase of different CPS indirectly indicates the feasibility of joint control of cathodic protection stations galvanically linked by the object of protection in order to improve the corrosion protection.

1. Aziukovskyi O. System of electrochemical protection against corrosion with adaptation to change electrotechnical parameters of protection object // Electromechanical and energy saving systems – #4, 2018. – P. 60 – 67.
2. Aziukovskyi A. The electrochemical cathodic protection stations of underground metal pipelines in uncoordinated operation mode / A. Aziukovskyi // CRC Press. Balkema is an imprint of the Taylor & Francis Group, an informa business, London, UK 2013. – P. 47 – 55.

A LOW COST POTENTIOSTAT FOR CORROSION STUDIES

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The corrosion research scientists have a need for inexpensive potential control devices – potentiostats. Commercially available potentiostats range in price from $1,000 for a device with limited functionality, to over $10,000 for a multifunctional research quality workstation. Therefore, many low budget laboratories have started to design their own potentiostats [1-3].

A simple version of potentiostat MTech COR-500 based on microcontroller C8051F350 (Silabs, USA) and 12-bit voltage output digital to analog converter MCP4922 (Microchip, USA) has been designed (fig. 1). The C8051F350 chip is fully integrated, low power, mixed-signal system-on-a-chip microconroller unit. It includes high-speed 8051-compatible core, precision programmable 24.5 MHz internal oscillator, 8 kbytes of on-chip flash memory, 24-bit analog to digital converter with analog multiplexer and 2.5 V voltage reference. The potentiostat controls the potential between the working electrode and the reference electrode in range ±2.5 V, has five ranges of measured current with manual selecting: ±0.01, ±0.1, ±1, ±10 ±50 mA. The device can measure voltammograms under sweep rate up to 50 mV/s. The potentiostat is equipped with RS232-USB converter based on PL2303HX chip for communication with the computer through USB port [4].

Fig. 1. Potentiostat MTech COR-500

Specifications:
- Potential range ±2.5 V
- Compliance voltage ±14 V
- Minimum current range ±0.01 mA
- Maximum current range ±50 mA
- Sweep rate 0.01-50 mV/s

Techniques:
- Linear Sweep Voltammetry
- Cyclic Voltammetry
- Chronoamperometry
- Open Circuit Chronopotentiometry

Computer program for operating with potentiostat has been developed. This software allow to measure and visualize voltamperograms, chronopotentiograms and chronoamperograms. For reduction of influence of electromagnetic noise and improvement signal/noise ratio the program makes digital processing of measured polarograms by Savitzky-Golay filter. Potentiostat MTech COR-500 has been successfully tested on model systems using resistive electrochemical equivalents. Also, the potentiostat was tested using well-known techniques: linear sweep and cyclic voltammetries, chronoamperometry and open circuit chronopotentiometry.

1. A.A. Rowe, A.J. Bonham, R.J. White, M.P. Zimmer, R.J. Yadgar, et al. CheapStat: an open-source, “do-it-yourself” potentiostat for analytical and educational applications // PlosOne – 2011. – 6(9). – P. e23783.
2. R.W. Shideler, U. Bertocci. A low-noise potentiostat for the study of small amplitude signals in electrochemistry // J. Res. Natl. Stand. – 1980. – Vol. 85. Iss. 3. – P. 211–217.
3. C.Y. Huang, M.J. Syu, Y.S. Chang, C.H. Chang, T.C. Chou, B.D. Liu. A portable potentiostat for the bilirubinspecific sensor prepared from molecular imprinting // Biosens. Bioelectron. – 2007. Vol. 22. Iss. 8. – P. 1694–1699.
4. I.O. Patsay. Potentiostat MTech COR-500 // Retrieved from URL https://chem.lnu.edu.ua/mtech.

EFFECT OF TEMPERATURE AND CARBON DIOXIDE PRESSURE ON CORROSION AND CORROSION-MECHANICAL DESTRUCTION OF PIPE STEELS IN MODEL SEAM WATER

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The effect of temperature (t = 20, 60, 90 and 120°C) on corrosion and corrosion-mechanical destruction of martensitic steels JFE-13CR-80, JFE-13CR-95, JFE-HP1-13CR-110 and JFE-HP2-13CR-110 (table) in model seam water (MSW) under the carbon dioxide pressure P = 6 atm has been investigated.

Table. Chemical composition of steel*

Steel	JFE-13CR-80	JFE-HP1-13CR-110	JFE-13CR-95	JFE-HP2-13CR-110
Element	Mass %			
Si K	0.47	0.28	0.00	0.00
Cr K	13.45	13.50	12.83	13.09
Fe K	85.66	80.27	86.93	79.25
Ni K	0.05	4.52	0.00	5.23
Cu L	0.00	0.16	0.00	0.00
Mo L	0.36	1.07	0.24	2.25
Mn K	0.00	0.21	0.00	0.00
W M	0.00	0.00	0.00	0.18

*Carbon concentration is not presented in the table.

It has been established that the corrosion rate of JFE-13CR-80 and JFE-13CR-95 steels in MSW at carbon dioxidepressure P = 6 atmis 4… 40 times higher than JFE-HP1-13CR-110 and JFE-HP2-13CR-110 steels depending on temperature. The highest corrosion rate of JFE-13CR-80 and JFE-13CR-95 steels is observed at 60°C: 0.11… 0.16 g/(m^2·h).

Electrochemical studies in MSW at 20°C and P_{CO2} = 1 atm showed that JFE-HP1-13CR-110 and JFE-HP2-13CR-110 steels are more resistant to pitting corrosion than JFE-13CR-80 and JFE-13CR- 95.

Local corrosionof the steelswasnot found at static stresses $\sigma = 0.6\sigma_{0.2}$,under pressure of carbon dioxide P=6 atmin MSWat the temperature 20°C. At higher temperatures, ulcers appear on the surface of deformed steels JFE-13CR-80, JFE-13CR-95, whichcan initiate developmentof cracks. Local corrosionof the steelsJFE-HP1-13CR-110 and JFE-HP2-13CR-110 wasnot found at static stresses and higher temperatures.

Mechanical properties of steels JFE-HP2-13CR-110, JFE-HP1-13CR-110, JFE-13CR-95 does not significantchangeat the slow tensile (velocity 10^{-6} s^{-1}) in the MSWunder pressure of carbon dioxide P_{CO2} = 1 atm. The significant influence of the corrosive environment on the mechanical properties of JFE-13CR-80 steel is related to the high concentration of corrosion-active non-metallic inclusions, which exceeds the permitted limits.

Thegreatesttendencytolow-cyclic corrosion fatigue was found forJFE-13CR-80 and JFE-13CR-95 steels. The durability of JFE-HP2-13CR-110, JFE-HP1-13CR-110 steelsreducedbyonly 8… 9% atcyclic tension $\sigma = \pm 500$ MPa.

The research results were used by Ukrgasproekt LLC (Poltava) for the design of pump and compressor equipment for DTEK LLC.

CORROSION OF GALVANIZED PIPES IN HOT WATER SYSTEMS

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The studies were carried out in order to determine the causes of the formation of a through corrosion defect on the galvanized pipe of the hot water supply system (HWS) Ø42 × 3.5 mm, after operation for two years. The study included visual and optical inspection of pipes, analysis of the chemical composition of metal and corrosion products on the inner surface of the pipe, analysis of the chemical composition of water, as well as a set of electrochemical tests conducted at temperatures of 20 and 60 ° C. The chemical composition of water from the HWS system complied with current standards. After visual inspection of galvanized pipe was found that the zinc coating on the inner surface of the pipe in the initial state had considerable roughness, and its thickness is changed in a rather wide range of 4 to 55 μm. After two years of operation, the entire inner surface of the pipe was covered with corrosion products whose chemical analysis showed the presence of iron oxides and hydroxides as well as zinc hydroxide in them. According to the results of electrochemical studies, the corrosion potentials on the galvanized pipe in the initial state and after operation were determined (Fig. 1), it was shown that the potential of the zinc coating after operation shifts in anodic side and becomes close to the potential of the base metal of the pipe. The polarization resistance method [1-2] estimated the corrosion rate of the base metal and zinc coating at water temperatures of 20 °C and 60 °C. With increasing temperature, the corrosion rate of steel increases from 0.09 mm/year at 20 °C to 0.148 mm/year at 60 °C, and zinc coating - from 0.068 mm/year at 20 °C to 0.099 mm/year at 60 °C. Increasing temperature promotes shift of the stationary potential on the zinc coating to the anodic side from -1.1 V at 20 °C to -0.87 V at 60 °C (Fig. 2), at the anode curve at room temperature is observed the zinc passivation region, with further transition to the area of active dissolution. At 60 °C, zinc passivation at anode polarization is not observed. For the base metal of the pipe, raising the temperature accelerates both cathode and anode processes.

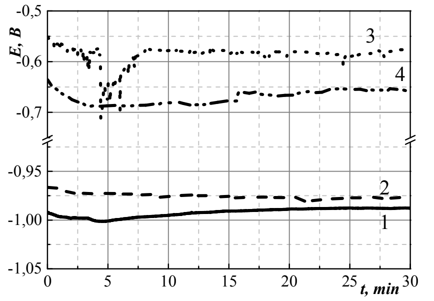

Fig.1. Corrosion potential of galvanized pipe in the initial state (1-3) and after operation (4): 1) Zn on the outer surface; 2) Zn on the inner surface; 3) base metal; 4) Zn on the inner surface

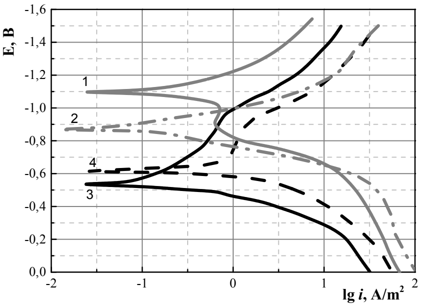

Fig. 2. Polarization curves on zinc coating (1-2) and steel (3-4) at different temperatures: 1) and 3) - 20 ºC; 2) and 4) - 60 ºC

The unevenness of the zinc coating on the inner surface of the pipe and the high corrosion rate at 60 °C results in the rapid dissolution of the areas where the zinc coating has the least thickness. Over time, the corrosion rate decreases due to the passivation of the zinc coating, with the potential becoming more positive than the steel potential, and the zinc coating losing its protective properties becoming cathodic with respect to steel. In the future, conditions are created for accelerated local anode dissolution of the sections of the galvanized pipe that lacks zinc coating, with the formation of through corrosion defects.

1. Klymenko A., Gerasimenko Yu. Methods and means of monitoring stress-corrosion cracking of gas pipelines // Physico-Chemical Mechanics of Materials. – 2012. – V.2. №9. – P. 647–652.
2. Klymenko A., Gerasimenko Yu., Belousova N. etc. The development of electrochemical methods for measuring the corrosion rate of metals of the scientific school of Professor L.I. Anthropova // Bulletin of NTUU "KPI". – 2013. – № 6. – P. 89–102.

DEMANDS' ANALYSIS OF REQUIREMENTS DOCUMENT IN THE FIELD OF CORROSION PROTECTION CONCERNING THE LEVEL OF PROTECTIVE POTENTIALS AND RESIDUAL CORROSION RATE OF MAIN PIPELINES

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The demands of requirements documents in the field of corrosion protection concerning the protective potentials and the residual corrosion rate of the main pipelines have been analyzed in order to correct the relevant schedules of DSTU 4219, Table. 1.

Table 1. Values of protective potentials according to requirements document of different countries

Requirements document	Potential, V			
	Minimum		Maximum	
	Polarisation potential	Potential with IR drop	Polarisation potential	Potential with IR drop
DSTU 4219-2003 [1]	from -0,85 to -1,05	from -0,90 to -1,20	from -1,10 to -1,15	from -1,50 to -3,5
GOST R 51164-98 [2]	from -0,85 to -0,95	from -0,90 to -1,05	from -1,10 to -1,15	from -1,50 to -3,5
EN 12954 [3]	from -0,65 to -0,95**	-	-	-
NACE SP0169 [4]	-0,85	-	-	-

Note.
* For operating steel pipelines up to their reconstruction and in the absence of the ability to measure polarization potentials depending on the design of the protective cover.
** At 40 ° C≤ T ≤ 60 ° C, the protective potential can be interpolated.

It is shown that the European and American standards have no requirements for the upper level of the protective potential without ohmic component, which is due to the differentiated approach to its choice taking into account the corrosive activity of the surrounding soils. However, experience has shown that the recommended protective potential values may sometimes be insufficient or excessive, which may cause to local corrosion, including cracking during operation, depending on local soil properties.

It was establish in the Amending No. 1 to DSTU 4219 that for pipelines of steel with a strength level higher than 580 MPa, the polarization potentials not permit more than minus 1.10 V. At that the protective potential must provide a technically sufficient protective effect at which the residual corrosion rate of the pipeline metal is less than 0.01 mm/year.

1. DSTU 4219-2003.STEEL PIPE MAINS. General requirements for corrosion protection.
2. GOST R 51164-98 STEEL PIPE MAINS. General requirements for corrosion protection.
3. EN 12954:2001 Cathodic protection of buried or immersed metallic structures.General principles and application for pipelines.
4. NACE SP0169-2007 International Standard Practice. Control of External Corrosion on Underground or Submerged Metallic Piping..

PECULIARITIES OF HYDROGEN-INDUCED DELAMINATION FRACTURE OF GAS PIPELINE

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Delamination cracking in pipeline steels is commonly observed, it can be both of metallurgical and operational origin. In the first case such damages are inherent to metallurgical products, while in the second one they are introduced in service under working stresses. Delamination is formed by plane with relatively weaker texture parallel to the rolling plane within the steel due to any aspect that leads to anisotropic microstructure, including: texture, banding, carbide and inclusions particles, inclusion alignment on the rolling plane, intergranular fracture, and anisotropic plastic deformation [1]. A common feature of delamination cracking in pipelines is that fracture propagates in the circumferential direction, which often results in pipeline fracture. Hydrogen induced cracking is typical for oil and gas pipelines, as pipe manufacturing technology involves rolling and consequently lengthening of nonmetallic inclusions and weakening cohesion with matrix. Hydrogen charging of a metal from inside the pipe due to electrochemical corrosion, leads to molecular hydrogen accumulation in certain trapping sites, e.g. in the formed intergranular defects "inclusion – matrix", and creation of high pressures in them. Such circumstances promote the formation, evolution and accumulation of microdefects in pipeline steel (so called accumulated damaging), deterioration of mechanical properties, especially, of plasticity and brittle fracture resistance. This leads to integrity violation of large areas of construction, often comparable with its characteristic dimensions.

In this paper, developing the studies [2-4], the appearance (Fig. 1) and peculiarities of hydrogen induced delamination fracture of gas pipeline, being long-term operated, have been considered.

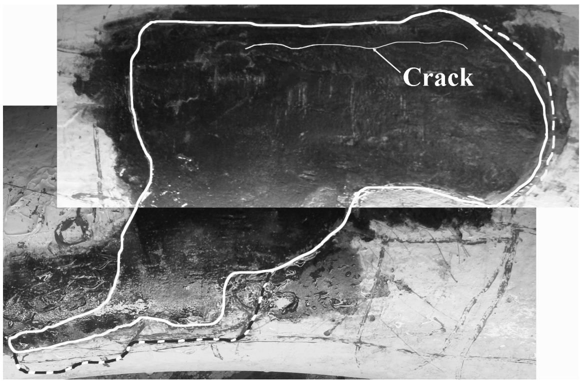

Fig. 1. Hydrogen induced delamination fracture of gas pipeline: delamination cracking under operation (solid line) and its extension after hydrostatic pressure testing (dotted line)

1. M. S. Joo, D.-W. Suh, J. H. Bae, H. K. D. H. Bhadeshia Role of delamination and crystallography on anisotropy of Charpy toughness in API-X80 steel // Mater. Sci. and Eng. A. – 2012. – Vol. 546. – P. 314–322.
2. H. M. Nykyforchyn, O. I. Zvirko, O. T. Tsyrulnyk Hydrogen assisted macrodelamination in gas lateral pipe // Procedia Structural Integrity. – 2016. Vol. 2. – P. 501–508.
3. L. E. Kharchenko, O. E. Kunta, O. I. Zvirko, R. S. Savula, Z. A. Duryahina Diagnostics of hydrogen macrodelamination in the wall of a bent pipe in the system of gas mains // Mater. Sci. – 2016. – Vol. 51. No. 4. – P. 530–537.
4. B. M. Stasyuk, N. V. Kret, O. I. Zvirko, I. P. Shtoiko In analysis of the stressed state of a pipe of gas pipeline with hydrogen-induced macrodefect // Mater. Sci. – 2019. – Vol. 55. No. 1. – P. 124–129.

CORROSION PROTECTION OF SUCKER RODS AGAINST FATIGUE FAILURE

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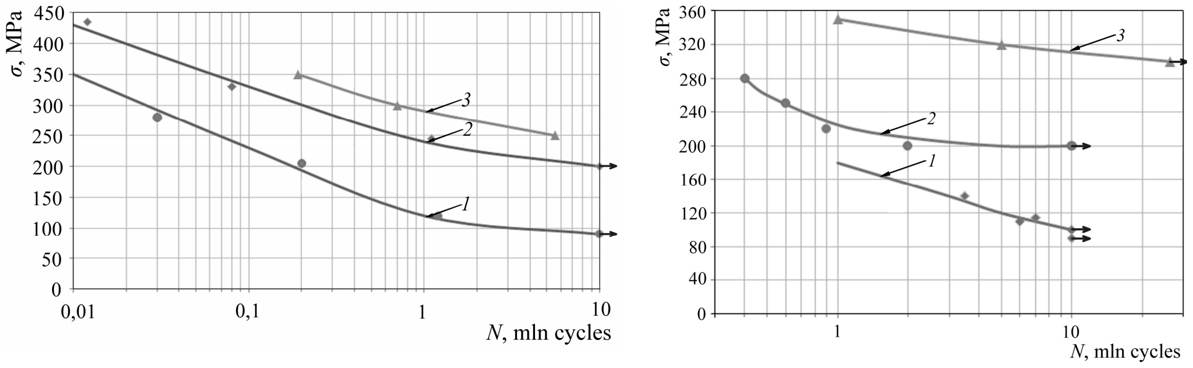
Most failures associated with the sucker rod form of artificial lifted wells using the sucker rod lift method can be attributed to one of three primary downhole components – subsurface pump, sucker rod string or tubing string. All of these components are defined as any catastrophic event requiring servicing personnel to pull or change-out one or more of these components.

In the paper the causes of integrity loss of steel sucker rods under operation were analysed. The sucker rods are made of a full-profile round section of low-alloyed steel and serve to transfer power from the surface to the subsurface pump [1]. Polished rod is one of the most important elements of sucker rod pump system since it is exposed to the highest loads. It takes maximum load capacity.

To increase the lifetime of rods it was proposed to use a special liquid technological environment, which retards fatigue cracks growth due to creation of artificial crack closure effect [2]. Scaled-down experiments on high cycle fatigue of long-term operated sucker rods made of the 20H2M and 35XM steels were carried out. It was revealed, on the one hand, the considerable negative influence of 3% aqueous NaCl solution and, on the other hand, – the significant positive effect of technological environment on fatigue durability of the investigated steels (Fig. 1). The noticeable increase in fatigue durability of rods in the technological environment in comparison with that in corrosion environment and in air was observed.



a *b*

Fig. 1. Fatigue strength curves for the 20H2M (*a*) and 35XM (*b*) steels tested in air (*1*), in 3% NaCl solution (*2*) and the special technological environment (*3*).

1. B. V. Kopei, A. B. Stefanyshyn, T. P. Venhrynyuk Fatigue strength of hybrid pump rods // Materials Science. – 2019. – Vol. 54. No. 5. – P. 739–742.
2. Ya. Khaburskyi, Z. Slobodyan, M. Hredil, H. Nykyforchyn Effective method for fatigue crack arrest in structural steels based on artificial creation of crack closure effect // Int. J. of Fatigue. – 2019. – Vol. 127. – P. 217–221.

IMPROVING PLATE HEAT EXCHANGERS PERFORMANCE WITH APPLICATION OF ULTRASOUND VIBRATION

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Plate heat exchangers are becoming the most widespread type of heat exchanging equipment in different fields of industry. The main advantages of plate heat exchangers are high heat transfer efficiency, low size and easily adjustable productivity by simply varying the number of heat exchanging plates. The heat exchanging plates are mainly manufactured from stainless steels such as AISI 316, AISI 304 and others alike. These steels are believed to be resistant to local corrosion attacks when chloride content is low. However, potable water of well origin may contain chloride concentration that is high enough to activate pitting corrosion. Moreover, the accumulation of corrosion products from water supply system on the heat exchanging surface may lead to the adsorption of extra chlorides. So, the surface chloride concentration may become higher than the bulk one. Another problem of heat exchanger operating with the untreated water is scaling. According to Ukrainian regulations water softening is not used in water supply systems, so when such water is heated the deposition of hardness salts occurs on the heat exchanging surface. The accumulation of scale deposits causes several problems, the most common are extra heat consumption and the rise of hydraulic pressure. Scale is usually cleaned periodically with acid treatment. So, scale and local corrosion attacks are two the most common problems of plate heat exchangers.

The present work is aimed on simultaneous solution of both problems by applying of ultrasound vibration to the operating heat exchanger. Literature survey and preliminary tests showed, that when ultrasound vibration can improve pitting resistance of stainless steel by lowering the adhesion of pit covers thus repassivating formed pits. Also, ultrasound is known to be used for surface cleaning due to high accelerations caused by ultrasound vibration. So, in this work ultrasound vibration was tested for both pitting suppression and scale removal.

The experimental procedure was performed with an electrochemical technique of potentiodynamic polarization. The three-electrode cell contained stainless steel plate working electrode made from AISI 304 stainless steel plate of 0.5 mm thickness, attached to the ultrasound horn. The horn was placed above the cell, so vibration was applied to the steel plate, not through the water solution. Platinum plate was used as an auxiliary electrode and saturated silver chloride electrode as a reference one. The anodic polarization was applied at scan rate of 0.2 mV/s and reversed as anodic current density reached 30 $\mu A/cm^2$. The same experiment was performed when ultrasound vibration was applied to the stainless steel. The ultrasound parameters were 28 kHz frequency and 10 W electrical power. After the pitting potential was established, the potentiostatic polarization was applied to compare the current density of vibrated and non-vibrated plates.

The scaling removal was tested in the laboratory set-up, which consisted of two water circles. One circle contained electric water heaters, pump and a heat exchanger. Another circle was connected to the same heat exchanger and contained a pump. The second circle was filled with a hard model water, saturated with $Ca(HCO_3)_2$ before the test. The temperature in the first circle was maintained at 95 °C in order to cause scale deposition in the heat exchanger from the side of the second circle. Scale deposition was performed for 30 hours. After this period, the second circle was connected to the tap water with controllable flow rate and heat transfer coefficient was measured based on the temperatures in the first and second circles before and after the heat exchanger. In the experiments, where ultrasound was used to clean the scale, the horn was attached to the side wall of heat exchanger. Sonication was performed simultaneous with scale deposition and heat transfer coefficients were compared.

THEORETICAL AND TECHNOLOGICAL METHODS OF INCREASING CORROSION RESISTANCE OF TUBES MADE OF LOW-ALLOY STEELS FOR THE GAS-AND-OIL PRODUCING INDUSTRY

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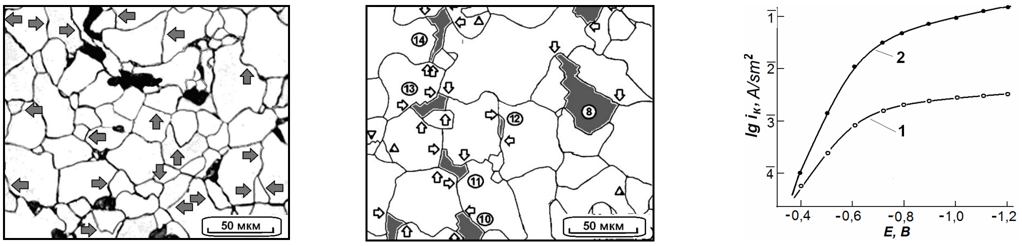
The study objective: Increasing corrosion resistance and operational reliability of tubes made of low-alloy ferrite-pearlite steels by applying a new concept of grain boundary engineering (GBE) of polycrystalline materials. For the first time, metallographic and electron microscopic procedures for the study of special boundaries (SB) of grains in ferrite-perlite steels were developed and content and energy level of special boundaries of ferrite-ferrite and interphase ferrite-perlite boundaries were evaluated (Fig. 1*a*, *b*) [1]. Based on the principle of GBE of materials, a comprehensive technology of production of oil and gas line tubes of high corrosion resistance made of low-alloy steels has been developed [2]. The obtained tubes of 06Cr1-U steel are characterized by a structure with a high content (up to 23%) of special low-energy boundaries (α-α and α-γ), a high complex of corrosion properties and a reduced tendency to hydration compared to tubes of steel 20 (Fig. 1, Table 1) [3].



a *b* *c*

Fig. 1. Structure of 06Cr1-U steel tubes (*a, b*): *a* – SB α-α; *b* – SB α-γ (arrows); *c* – cathode polarization curves of 06Cr1-U steel (*1*) and 20 steel (*2*); 1N H_2SO_4+1.5g/l $CS(NH_2)_2$

Table 1. Results of comparative corrosion testing tubes of steel 06Cr1-U and steel 20

Steel	V_{cor}. (mm/year) chloride-acetic solution	Lg I_a (A/cm^2) APC; 0,1 N NaCl; E= –0,1 V (n.h.e.)	Lg $I_к$ (A/cm^2) 1N H_2SO_4+1.5g/l CS $(NH_2)_2$; $E_к$= –1,2V, time 4 h	V_{cor}. (mm/year) NACE TM 0284
06Cr1-U	0,03	2×10^{-4}	0,5	0,3
20	1,2	5×10^{-2}	1,5	0,8

Heat treatment according to the developed technology including quenching and double short-term (up to 10 min.) tempering at temperatures $t_1=Ac_1-10°C$ and $t_2=Ac_1-20°C$ raises resistance against SSCC ($\sigma_{cr} \geq 0.85\ \sigma_{0,2}$) and the level of mechanical properties of tubes to the strength group X 56 (on API 5L) [4]. It has been proven that special boundaries are maintained after tempering steels. The integrated technology can be implemented in the metallurgical industry and tubes of high operational reliability – in the oil and gas industry.

1. Bolshakov V.I., Sukhomlyn G.D., Dergach T.O. Metodychni osnovy doslidzhennia zernohranychnoi struktury v staliakh z γ, α i α + γ fazovym stanom // Visnyk Prydniprovsk. derz. akademiy budivnytstva ta arkhit. – 2017. – № 3 – P. 10–21.
2. Sukhomlyn G.D., Dergach T.A. Prymenenye zernohranychnoho konstruyrovanyia staly dlia poluchenyia trub s vysokym kompleksom svoistv // Metallurhycheskaya y gornorudnaya prom. – 2008. – № 6. – P. 50–53.
3. Dergach T.A. Kompleksnie yssledovanyia neftehazoprovodnyh trub, yzghotovlennykh po enerhosberehaiushchey tekhnolohyy // Metallurhycheskaia y hornorudnaia prom. – 2009. – № 3. – P. 100–103.
4. Bolshakov V.I., Dergach T.O., Sukhomlyn G.D. Sposib polipshennya struktury i vlastivjstey trub z nyzkolegovanyh staley // Metaloznavstvo ta termichna obrobka metaliv. – 2019. – № 1. – P. 29–33.

INFLUENCE OF FORMATION WATER MINERALIZATION ON DRILLING PIPE CORROSION

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During long-term operation, due to the interaction with formation water and drilling mud, the elements of the drilling string, first of all drill pipes and their threaded connections, wear out. As the analysis of failures showed, their main causes are corrosion damages, corrosion-fatigue failure and wash outs (Fig. 1). [1-2]. Also for flooded wells is a significant danger of hydration, which intensifies inner pipe corrosion [3-4], causes increased localization of corrosion processes [5-6] and is one of the causes of erosion damage to industrial pipelines [7].

Fig. 1 Corrosion damages of drill pipes

Reservoir water sampling and chemical analysis were performed. It has been established that the main corrosive component of formation waters is soluble chlorides, the high concentration of which will pose a significant corrosion risk to oil and gas equipment.

Corrosion and corrosion-mechanical tests of drill string material (steel G105) were performed. It is shown that with increasing the level of mineralization, the corrosion rate significantly increases both the corrosion rate and the localization of corrosion processes, which leads to an increased risk of leaching.

The rate of total corrosion for highly mineralized formation waters with pH 5.5-6.8 is 0.4-0.7 mm / year, for media with pH 3.7-5 from 1.2 to 1.7 mm / year, respectively. It was also found that in acidic highly mineralized chloride formation waters is characterized by pitting corrosion, the speed of which at operating temperatures (110-150 ^{o}C) can reach 44.2-65.7 mm / year.

1. Lukin, O. Yu., Pryharina, T. M. Hazovyi potentsial nadr Ukrainy ta shliakhy yoho osvoiennia. // Zbirnyk naukovykh prats UkrDHRI. – 2018. – P. 78–89.
2. Kondrat, O. R., Hedzyk, N. M. Increasing natural gas production from tight terrigenous reservoirs. // SOCAR Proceedings. – 2017. – 4. – P. 42–51.
3. Zamani, S. M., Hassanzadeh-Tabrizi, S. A., Sharifi, H. Failure analysis of drill pipe: A review. // Engineering Failure Analysis. – 2016. – 59. – P. 605–623.
4. Lu, S., Feng, Y., Luo, F., Qin, C., Wang, X. Failure analysis of IEU drill pipe wash out. // International Journal of Fatigue. – 2005. – 27(10-12). – P. 1360–1365.
5. Obanijesu, E. O., Pareek, V., Gubner, R., Tade, M. O. Hydrate formation and its influence on natural gas pipeline internal corrosion. // Nafta. – 2011. – 62(5-6). – P. 164–173.
6. Poberezhny, L., Maruschak, P., Hrytsanchuk, A., Poberezhna, L., Prentkovskis, O., Stanetsky, A. Impact of gas hydrates and long-term operation on fatigue characteristics of pipeline steels. // Paper presented at the Procedia Engineering. – 2017 – 187. – P. 356 –362.
7. Fangpo, L., Yonggang, L., Xinhu, W., Caihong, L. Failure analysis of∅ 127mm IEU G105 drill pipe wash out. // Engineering Failure Analysis. – 2011. – 18(7). – P. 1867–1872.

INFLUENCE OF LIFT METHODS AND HYDRATION FORMATION ON CORROSION OF INDUSTRIAL GAS PIPELINES

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One of the main tasks of the oil and gas industry while product transportation is to guaranty the continuity of supply. Several negative factors, one of which is the overlapping of the pipeline cross-section by gas-hydrate formations, result in a serious problem of production pumping. In the aftermath of it,financial expenses rise while gas recovery experiences reduction. [1, 2]. Based on the lift methods of the Eastern oil-and-gas region plume, a range of load levels was selected for corrosion-mechanical tests. The stress concentration was taken into account. 7 model environments were selected for testing.

Table 1. Chemical composition of model environments (ME)

№ ME	TheconcentrationofNaCl, mol/l
1	0,01
2	0,05
3	0,1
4	0,5
5	1,5
6	2,5
7	3,75
8	5

According to the results of the study, which was conducted about corroded surfaces maintained in the gas hydrate, it became possible to establish the mechanism of its influence on the pipeline material corrosion. Corrosion hydrate itself does not cause the effect of corrosive components of the brine water. It only intensifies and localizes this effect [3].

It is established that as chloride ion concentration increases, the effect of mechanical factors raises significantly too. This dependence is accurate for both general corrosion degradation and local corrosion. There is a sharp increase in the corrosion rate during the transition from ME6 to ME 7 for in-pipe corrosion, in highly mineralized brine water. Supposedly, such corrosive behavior is caused by the accelerated destruction of passive films by chloride ions when a certain critical concentration is reached. The combined analysis of the corrosion behavior of the pipe material in corrosive chloride-type environments reveals similar patterns of the combined influence of the corrosive environment and mechanical factors on the corrosion processes rate. Thus, for both cases of corrosion, an intensification of the influence of a mechanical factor with increasing chloride concentration is observed. In ME 1, ME 4, and ME 5 slight changes in the dynamics of the process during the transition from elastic to an elastic-plastic zone are detected. In ME 2, ME 3, ME 7, and ME 8 these changes are more vivid.

As the level of mechanical stress in local corrosion increases, a significant intensification of corrosion processes is observed, especially in the area of elastic-plastic deformation. In order to have an accurate assessment of operational risks, resources, and safe resource residues, it is crucial to know the speed of pipeline wall thinning during operation to prevent possible emergencies in due course. Studies have shown that, depending on the load level and the relevant simulative environment, the increase in general corrosion rate due to the effect of gas hydrate for 17GS steel ranges from 0.1 to 0.67 mm/year.

1. Лукін, О. Ю., Крижанівський, Є. І., Геєць, В. М. Про перспективи нарощування видобутку нафти і газу в Україні (стенограма наукової співдоповіді на засіданні Президії НАН України 7 листопада 2018 р.). // Вісник Національної академії наук України. – 2018. – 1. – С. 38–54.
2. Єгер, Д. О., Лещенко, І. Ч., Гришаненко, В. П. Проблеми та перспективи стабілізації і нарощування видобутку природного газу в Україні.. // Проблеми загальної енергетики. – 2019. – 1. – С. 4–11.
3. Poberezhny, L., Hrytsanchuk, A., Hrytsuliak, G., Poberezhna, L., Kosmii, M. Influence of hydrate for mation and walls hears tress on the corrosion rate of industrial pipe line materials. // Koroze a ochranamaterialu. – 2018. – 62(4). – P. 121–128.

SENSITIVITY TO STRESS-CORROSION CRACKING OF LOW-CARBON 09G2S STEEL IN NEAR-NEUTRAL PH UNDER CATHODIC POLARISATION

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Peculiarities of stress-corrosion cracking (SCC) of pipe steel of ferrite-pearlite class 09G2S in NS4 solution under cathodic polarization using slow strain rate tests using the complex methodology [1] developed in E.O. Paton Electric Welding Institute of NAS of Ukraine, which includes the method of polarization curves, slow strain rate test method, the analysis of the morphology of fractured specimens and the determination of the degradation coefficients of properties (strength, relative elongation and relative narrowing of the specimens after destruction) were investigated.

It was shown experimentally when the polarization potential is shifted to more negative values, the sensitivity of the 09G2C steel to SCC (K_S) increases, Fig. 1 It is caused by changing in the mechanism of SCC.

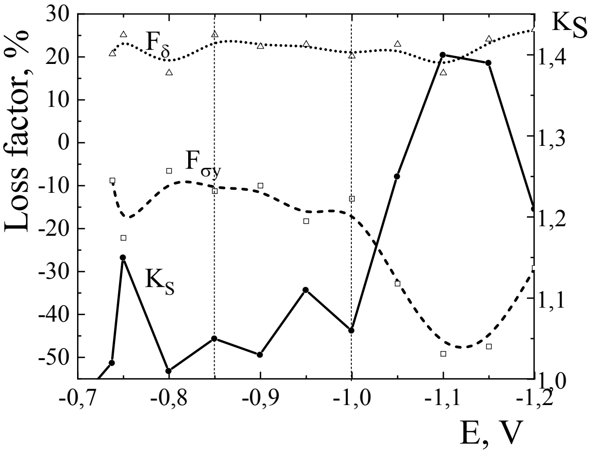

Fig. 1. Loss factors, F_δ (elongation) and $F_{\sigma y}$ (yield stress), and sensitivity to SCC (K_S) of 09G2S steel under cathodic polarization

To understand the observed regularities, a theoretical model based on the analysis of polarization curves under low and high scanning rate of the potential was applied [2]. According to this model, it was established that SCC of 09G2S pipe steel can undergoes by different mechanisms, depending on the cathodic potential. Investigation of the fracture surface by scanning electron microscopy method it was confirmed that samples' breaking occurs by a mixed (tensile-brittle) mechanism. When the polarization potential is shifting to more negative values, the brittle fracture becomes more evident.

Analyzing the change in the mechanical properties and the morphology of the fracture surface, it was assumed that, depending on the polarization potential, the SCC of 09G2C pipe steel can follow by different mechanisms. It was demonstrated that there exists the range of the potentials in which 09G2S steel stays in a non-equilibrium electrochemical state, and the reaction of anodic dissolution and hydrogen embrittlement can run simultaneously.

1. L.I. Nyrkova, S.A. Osadchuk, A.A. Rybakov, S.L. Melnychuk. Methodological approach and criterion of the estimation of pipe steel susceptibility to stress corrosion cracking // Physicochem. Mech. of Mater. – 2019. – Vol. 55. Iss. 5. – P. 14–20.
2. Z.Y. Liu, X.G. Li, Y.F. Cheng. Mechanistic aspect of near-neutral pH stress corrosion cracking of pipelines under cathodic polarization // Corros. Sci. – 2012. – Vol. 55. – P. 54–60.

INCREASING DURABILITY GAS COOLERS OF TBB-1000-4У3 TURBOGENERATOR.

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Cooling of the TBB-1000-4У3 turbine generator magnetic circuits is accomplished by four ГО-1800/5453-У3 gas coolers by circulating hydrogen gas between the rotor and stator windings and the interpipe cavities of the gas coolers. The heat is transferred to the ribbed aluminum alloy nickel silver tubes and removed by distilled water flowing through the heat exchange tubes. After long operation of gas coolers longitudinal through cracks are formed on certain sections of heat exchange tubes (between pipe boards and fins). Depressurizing the system requires stopping the turbine generator and replacing the damaged tubes.

Analysis of the conditions of operation of the gas cooler indicates that the main reason for the formation of cracks is the flooding of the surface of the nickel silver pipes in the gap between them and the openings of the pipe boards (steel 09Г2С) of the gas coolers. The presence of the gap is due to the under-compression of the tubes to the edge of the tube boards, which is provided by the standard for structural reasons. Hydrogen cooling system contains up to 1,2% O_2 and up to 20% moisture under normal conditions. This contributes to the condensation of moisture and the development of a corrosion process with the release of hydrogen in the said cracks and the subsequent flooding and cracking of nickel silver pipes tubes.

In order to improve the resource performance of gas coolers, the feasibility of replacing nickel silver tubes with copper or brass was investigated. For this purpose, the currents of copper - steel and nickel silver - steel and the mass losses due to contact corrosion of the studied materials and the concentration of hydrogen after corrosion tests were determined. It was found that the concentration of hydrogen in copper is 0.5 ppm, which is 35 times less than in steel 09Г2С, and 17 and 4 times less than respectively in nickel silver and in brass. Copper - steel and nickel silver - steel currents for 338 hours. the tests are close to each other and are 0.039 and 0.07 mA, and the corrosion rate of the steel specimens in these pairs is practically the same, 0.1781 and 0.1766 g / ($m^2 \cdot h$).

Successful two-year operation of gas coolers with copper heat exchange tubes manufactured by "Ukrspetsmash" LLC confirms their reliability.

PROVIDING THE RELIABILITY OF SEALING THE HEAT TRANSMISSION TUBES IN THE TUBE BOARDS OF THE HEAT EXCHANGERS

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Gas coolers of turbogenerators and transformer refrigerators operating at nuclear, thermal and hydroelectric power stations, contact with fire and explosive environments (hydrogen, liquid oil), so reliable sealing of heat exchange tubes in the pipe boards is a topical problem. Usually, for heat exchangers of this group in the refining and petrochemical industries, normative documents stipulate welding of heat transfer tubes in tube boards with their subsequent flaring.

This provides double protection for such joints against sealing and prevents crevice corrosion between them during prolonged operation. Such reliable connection of tubes with tube boards is possible if these materials are well welded with arc welding methods. Pipe boards for gas coolers and power plant refrigerators are made mainly of 09Г2С steel, and their heat exchange tubes are made of nickel silver or copper, since these materials are resistant to corrosion and flooding if moisture is present in working environments.

Copper and nickel silver are badly welded by arc welding with carbon and low alloy steels. It is suggested that steel pipe boards on the side of the tube ends should be coated with a layer of copper, followed by welding the ends of the heat exchange tubes with a copper coating layer of the tube board and flaring the tube in the tube board. Residual welding stresses can have a negative effect on the adhesion of the coating layer of such combined sealing of heat exchange tubes in tube boards. Certain requirements are laid down for the copper cladding layer and the interface between it and the base metal of the pipe boards. In particular, it is not permissible to bundle control, copper-clad specimens after their bending test through a prism with a radius of up to 3 mm at an angle of not less than 1500, and the tensile strength of the transition zone between 09Г2С steel and copper should be not less than 415 MPa. Such requirements are provided by the selected welding modes and the appropriate machining of the steel prior to the deposition of copper, which gives the surfaces of the toothed shape, providing, in addition to the metallic type of bonding, also the mechanical adhesion of the surfaces.

Based on the results of joint research with FMI NAS of Ukraine, LLC "Ukrspetsmash" produced eight gas coolers for cooling of turbogenerators of Zaporizhzhya NPP.

STUDIES OF CORROSION RESISTANCE OF STRUCTURAL MATERIALS IN OIL DEPOSIT PRODUCED WATER

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We propose a set of methods that allow in laboratory condition simulate corrosion processes occurring on the surface casing and tubing and hence predict its subsequent corrosion attack.

The relevance of this study is due to the real needs of the industry to extend the non-repair life of the oil field.

The objective was to study the combined effect of such factors as the depth of the oil reservoir, the degree of mineralization of the accompanying reservoir water, the content of CO2 and H2S on various samples of steels. The experiments were performed on a laboratory unit in the form of an autoclave, which simulated the mutual effects of various factors whose limit values were selected from the real conditions of several wells of the Iraqi Mishrif field.

The central composite (rotatable) plan of the second order are used for the planning of the experiment. The intervals of variation of the factors in the plan-matrix for the experiment were selected based on industry data. In particular, the temperature of the experiments was in the range of 50-110°C, salt content (Na Cl) - in the range of 80-160 g / l, the content of CO_2 - in the range of 0.1-4.1%, the content of H_2S - in the range of 0.02-2.42%. Steels, 12X18H10T and SAF2507 were selected as the steel samples. The corrosion rate (g / (m^2 * h) was selected as the target function. It wasstudiedthe nature of cyclic voltammetric of the selected steel samples at certain points in the factor space.

Analysis of the results.

The biphasic structure of SAF2507 steels is better resistant to corrosion because austenite and ferrite galvanically protect each other [1]. The sharp inhibition of metal dissolution processes is associated with the formation of stable molybdenum-containing protective films. It is shown that austenitic-ferrite steels exhibit high corrosion resistance under oil wells. The 12X18H10T steel is subjected to ulcerative corrosion in formation water at 80°C and it depends on the presence of hydrogen sulfide and CO2, which is indicated by bursts (sharp increase in current) on a cyclic polarization curve at potentials 0.4 -0.6V. High-carbon steel45 is weak in these conditions.

Conclusions. 1. Regression equations were obtained as a result of processing the data presented in STATGRAPHICS, its variance and graphical analysis were performed.

2. The possibility of using cyclic voltammetric curves to study the stability of different steel samples under conditions of local corrosion is shown.

1. Korkhaus J. Application of corrosion-resistant steels in chemical industry / Korkhaus J. // Mater. of the Conf. “Stainless Steel World 99”. KCL Publishing BV. – 1999. – P. 27 –41.

CORROSION RESISTANCE OF NEW AUSTENITIC-FERRITE STEELS IN THE COKE&CHEMICAL PLANT

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The corrosion resistance of DKS SAF 2507, 254 SMO duplex steels was studied in the most aggressive sulfuric acid environments of the recovery shops - mother liquors of sulfate compartments, aggressive environments of arsenic-soda desulfurization and coke shop environments (quenching car, quenching tower). Gravimetric tests were performed according to GOST 9.908-85. The studies were carried out both in coke plants and in laboratory conditions. Based on gravimetric tests, as well as studies of cyclic voltammetry, it has been shown that these materials are highly resistant to pitting and crevice corrosion in technological environments of sulfate compartments, aggressive environments of arsenic-soda desulfurization, and coke shop environments (quenching car, quenching tower), which are caused by the presence corrosion activators (H2S, HCN, HCNS, Cl^-). This statement is confirmed by the significant resistance of passive films of molybdenum-containing steels [1].

The essence of the technique is the use of cyclic voltammetry to assess the tendency of stainless steels to pitting in a standard medium of iron chloride (6% ferric solution at 50 ° C). The medium is similar to ASTM G-48.

The results showed that Russian-made steel 12X18H10T, 10X17H13M2T, 0X23H28M3D3T undergoes pitting corrosion in an iron chloride solution (50 ° C) with a free corrosion potential, since the difference between the pitting repassivation potential ($\varphi_{рп}$) and the free corrosion potential ($\varphi_{sw.c.}$).

Is less 0.05V ($\Delta\varphi = \varphi_{рп} - \varphi_{sw.k.} < 0.05V$). X25H7AM4 steel is not subject to pitting corrosion under similar conditions, since the difference between the pitting repassivation potential (φрп) and the free corrosion potential ($\varphi_{sw.k}$). Is significantly greater than 0.05V. The potential values were calculated from cyclic voltammograms.

During the experiment, when taking cyclic voltammograms, the presence of pitting was detected on samples from steels produced by RF-0X23H28M3D3T, 10X17H13M2T, 12X18H10T. No pits were found on X25H7AM4 and Avesta 254SMO steels. This circumstance fully confirms the high corrosion resistance of duplex steels against local types of corrosion.

Based on studies using the developed methodology, it was shown that duplex steels X25H7AM4 and Avesta 254SMO are highly resistant to pitting and crevice corrosion and are superior to conventional steels 0X23H28M3D3T, 10X17H13M2T, 12X18H10T used for the production of heat-exchange equipment.

1. Korkhaus J. Application of corrosion-resistant steels in chemical industry / Korkhaus J. // Mater. of the Conf. “Stainless Steel World 99”. KCL Publishing BV. – 1999. – P. 27 −41.

REDUCING CORROSION LEVEL: USING OF AUSTENITIC STEEL – RESISTANCE TO HARD SEAWATER CONDITIONS

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The recently ratified IMO (International Maritime Organization) Ballast Water Management Convention (BWM) is a mandatory requirement ("strict condition") for ships to have the appropriate innovative ballast water management systems, requiring the latest type approval certificate. The procedure for evaluating such systems has been developed since the adoption of the BWM Convention in 2004. Certificates issued by independent, authorized organizations today include a more detailed test approach, as well as issues related to operational limitations of ballast water systems, salinity, temperature and UV transmission.

Oddly enough, most ballast water treatment systems have moved out of the land-based potable water treatment industry.

Thus, the technologies used in them are only adapted for use in marine conditions in an attempt to fulfill all the requirements, respectively, were not originally intended for this. Land ultraviolet water treatment systems are based on less complex water environment. Safety on board is a priority. UV-based systems are safer than chemical-based systems, but for any system, safety is of utmost importance to prevent serious equipment damage. [1, 2].

The scientists of DI NU "OMA" (Izmail) have developed and properly designed a ballast water treatment system, multi-functional, designed specifically for operation not only in real marine conditions, but also for appropriate decontamination and wastewater treatment of industrial enterprises [3].

One of the nodes developed by the experimental setup is a block of ultraviolet radiation. In the manufacture of a UV reactor, which is filled with sea water during operation, from 316L steel, corrosion is possible in it after 5 years of operation, which leads to the need for its replacement.

The key component in our UV radiation unit is resistant to harsh conditions of sea water – steel AISI 304 – austenitic, low carbon, able to withstand corrosion. Therefore, such components can be used much longer, the service life of up to 20 years or more is possible.

In addition, a necessary condition in our system is the capture of a sea water stream with a wide spectrum of wavelengths parallel to the stream (thereby reducing the resistance to fluid movement) and a higher level of UV illumination is provided for the disinfection of invasive alien species in water ballast [4, 5].

1. Ballast Water Management Systems (BWMS). – [Electronic resource]. – Access mode: http://www.marconost.ru/index.php?id=87
2. GloBallast Programme. – [Electronic resource]. – Access mode: http://www.imo.org/en/OurWork/Environment/MajorProjects/Pages/GloBallast-Programme.aspx.
3. Danilyan A. A new approach to the localization of invasive aliens in the ballast waters of ships / A. Danilyan, N. Bykovets, N. Tiron-Vorobiova // Proceedings of the VIII International Scientific and Practical Conference: International Trends in Science and Technology (December 25, 2018). – Warsaw (Poland)ю – P. 10–15.
4. Global invasive species database. – [Electronic resource]. – Access mode: http://www.iucngisd.org/gisd/species.php?sc=38.
5. European Strategy on Invasive Alien Species. – [Electronic resource]. – Access mode: https://ec.europa.eu/environment/nature/invasivealien/index_en.htm

ANALYSIS OF THE INFLUENCE OF CONSERVATION CONDITIONS AND THE LONG-TERM RESERVE OF GAS AND COAL-FIRED POWER UNITS ON THE RELIABILITY OF AUSTENITIC HEATING SURFACES.

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As is well known, the superheaters of coal-fired ultra-supercritical pressure (USP) boilers made of austenitic steels of type 12Cr18Ni10Ti (12Cr18Ni12Ti) are one of the most thermally stressed elements.

Experience in the operation of USP boilers indicates that among the most numerous and dangerous failures of these heating surfaces are the damages of pipes by intercrystalline corrosion (ICC) .

The occurrence and course of the ICC is determined by many factors, which significantly complicates or makes it impossible to determine the residual service life of austenitic heating surface, especially given the lack of reliable methodologies in the regulatory documentation. Diagnosis, in oder to determine the state of the metal, is also complicated by the need to use destructive control methods.

Rigorous environmental regulations (in accordance with European directives) and economic factors of high cost of fuel (gas, coal) lead to the transfer of a large number of Ukrainian power units to a long-term reserve. At the same time, the conservation methods specified in the industry regulations do not provide full protection of the austenitic heating surfaces of USP boilers.

Studies indicate that such long-term reserves have a particularly negative impact on the residual term of superheaters, significantly intensifying ICC.

Under above-mentioned conditions, careful selection of parameters and planning of equipment conservation measures are very important, from the point of view of the reliability criteria of the USP boilers and prevention of the appearance of the ICC. It is necessary (for ICC prevention) to revise the existing regulatory documentation for the conservation of equipment of thermal power plants. Another way is to redesign the superheaters in order to use new grades of steels and material classes to prevent the appearance of the ICC.

The mechanisms of the ICC are widely covered in literature [1].

These ICC theories are considered mainly under long-term exposure of samples to the critical temperature range [2-3], favorable for the chromium carbides formation and diffusion, but do not fully take into account the processes occurring below the specified interval in terms of equipment reserve.

Monitoring of the state of the austenitic heating surface metal over a long period of time, which resulted in a variety of studies with the involvement of research institutes, made it possible to become more fully aware of the risks and consequences of the ICC, and more importantly to determine the ways and directions for its prevention.

1. F.F. Khimushin. Stainless steel. 2nd ed., // M .: Metallurgy. –1967– P. 800
2. ASM HandBook. Vol. 13 of the 9th Edition Metals Handbook – Corrosion, –1987.– P. 263-267
3. VladimiR Cihal Irena Kasova. Relation between carbide precipitation and intercrystalline corrosion of stainless steels. // Cor. Scien. –1970.–Vol.10. Iss. 12. P. 875 – 881

BORING THE INNER SURFACE OF THE PIPELINE TURN CVD STEAM GENERATOR

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The cavitation wear of the switching pipelines of the circuits of the steam generators leads to serious localized destruction of the structural materials. Especially often such accidents occur in the bend zones of pipelines [1, 2]. The solution of the problem is possible by protecting the bend zone of the pipelines with protective coatings based on iron borides, which will slow down the cavitation processes of wear. Boron steels have a fairly high wear resistance compared to cemented or nitro-cemented steels due to the formation of solid iron borides.

One of the progressive directions in modern materials science is the development and development of gas-phase methods of material deposition [3]. The obtained condensates are characterized by high, close to theoretical density, low impurity content, metal alloys and various refractory compounds in the form of borides, nitrides, carbides, silicides, oxides can be obtained in the deposition processes. This makes it possible to apply protective, separation, corrosion, wear-resistant coatings on parts of complex shape.

According to the results of thermodynamic calculations of hydrogen reduction of boron trichloride, gas dynamics of the gas-vapor mixture BCl_3: H_2, studying the kinetics of the growth rate of coatings based on iron boride, certain parameters of gas-phase deposition of coatings on austenitic steel. X-ray diffraction studies showed that the coating has only 1 phase of Fe_2B. The lattice parameters of this phase are a = 5.117 Å; c = 4.243Å. The coating contains (100) texture, that is, Fe2B iron boride grains, which are predominantly oriented crystallographic {100} plane parallel to the sample surface, Fig. 1.

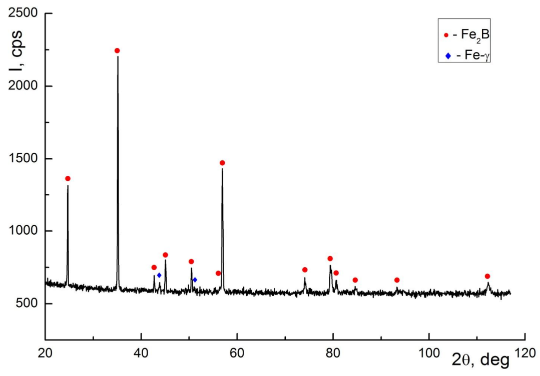

Fig. 1. X-ray studies of boron steel

1. L. Ozhigov, A. Mitrofanov, E. Kraineuk. Operational wear of the pipelines of the second circuit of VVER-1000 units. Bulletin of Ternopil National Technical University. 2013.– Vol. 69. No. 1. – P.55–62.
2. W. Kastner, M. Erve, N. Henzel, B. Stellwag. Erosion corrosion in power plant piping systems-calculation code for predicting wall thinning International Atomic Energy Agency, Vienna (Austria). International Working Group on Reliability of Reactor Pressure Components. – 1990. – P. 49–59.
3. K. Powell, D. Oxley, and D. Blocher. Gas phase deposition. M.: Atomizdat, 1970.

CORROSION RESISTANCE OF STEEL FOR FRAME OF BOOM SPRAYERS IN ENVIRONMENT OF LIQUID AGROCHEMICALS

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For increasing the corrosion resistance of agricultural machinery components to liquid mineral fertilizers and plant protection agents, inhibitors, or substances that reduce their corrosion activity are added. Nevertheless, corrosion does a great deal of damage to these machines and units [1, 2]. The critical factor in this situation is the chemical reactions or other physicochemical interactions that result in the formation of corrosive-active substances such as ammonia, hydrogen sulfide, or where the ions of chlorine, potassium, ammonium, and others are present.

The object of study was the steel Ст3пс for frame of boom sprayers with nominal chemical composition (in weight %): 0,14…0,22 C; 0,05…0,15 Si; 0,4…0,65 Mn; < 0,04 P; < 0,05 S; < 0,3 Cr; < 0,008 N; < 0,3 Cu; < 0,08 As; remainder Fe. The specimens were cut from the real frame. For corrosion tests, three environments were used, namely: the demineralized water (as a model of condensate or rainwater); the saturated solution of the Nurell D (as an insecticide), and the saturated solution of the UN-32 (as a liquid complex fertilizer).

The corrosion studies were realized with the application of the standard three-electrode electrochemical cell where the dynamic electrochemical laboratory VoltaLab40 has been used. The potentiodynamic polarization curves for steel Ст3пс were received under the potential range from –1000 mV to +1000 mV. Here, the potential scan rate was 1 mV/s for all conducted tests. The comparative assessment of the corrosion behavior of Ст3пс steel in these three environments had to lead to the following findings.

It has been shown that in the environment of demineralized water the process of general corrosion of the steel surface dominates. This result is consistent with data from the works [3, 4].

In the environment of the insecticide solution, along with the general corrosion process, a localized process of pitting corrosion is partially realized.

In the environment of liquid mineral fertilizer, the metal surface is passive due to the presence of phosphorus-containing corrosion inhibitors, which leads to inhibition of the general corrosion process.

Finally, it should be noted that in the case of a local damaging of the passivity of the metal surface, the process of intensive formation of corrosion pits might have occurred. This can be considered as dangerous [5] for their possible further development and nucleation of crack-like defects in the structure. For clarification on this question, the further corrosion fatigue study is required.

1. Oki M., Anawe P.A.L. A Review of Corrosion in Agricultural Industries. Physical Science International Journal. – 2015. – 5. Iss. 4. – P. 216–222.
2. Eker B., Yuksel E. Solutions to corrosion caused by agricultural chemicals. Trakia Journal of Sciences. – 2005. – Vol. 3. No 7. – P. 1–6.
3. Popovych P.V., Mahlatyuk L.A. & Kupovych R.B. Influence of Organic Fertilizers on the Corrosion-Electrochemical Characteristics of Low-Carbon Steels. Materials Science. – 2014. – Vol. 50. No 2. – P. 284–289.
4. Popovych P.V., Slobodyan Z.V. Corrosion and Electrochemical Behaviors of 20 Steel and St.3 Steel in Ammonium Sulfate and Nitrophoska. Materials Science. – 2014. – Vol. 49. No 6. – P. 819–826.
5. Akid R., Dmytrakh I.M., Gonzalez-Sanchez J. Fatigue damage accumulation: the role of corrosion on the early stages of crack development. Corrosion Engineering, Science and Technology. – 2006. – Vol. 41. Iss. 4. – P. 328–335.

RESEARCH ON THE EFFICIENCY OF THE DESULFURIZATION OF LIQUEFIED PETROLEUM GAS

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Liquefied petroleum gas, called (LPG), is the most popular alternative fuel in Ukraine [1]. Contaminants present in the liquefied gas can cause corrosion of structural materials in contact with this fuel, such as fuel system equipment, transmission pipes.

Solid products of corrosion processes are mechanical pollution, which, penetrating together with the fuel into the vehicle's gas supply system, can cause damage to system components [1]. A standard corrosion test for liquefied gas is copper corrosion test (ASTM D-1838). In this test, a polished copper strip is immersed in a product sample for one hour at 100 ° F (38 ° C). The test strip is then evaluated against the four-color classifications of ASTM standards. Specifications for liquefied gas specify that the product should not exceed strip number 1, which indicates a product that does not cause corrosion [2].

The conditions of desulfurization of liquefied petroleum gas (LPG) under the operating conditions of the existing installation of JSC "Ukrgasdobycha" are considered. Studies have been conducted to develop recommendations for the purification of liquefied gas from mercaptans and hydrogen sulfide when using alkaline washing (NaOH solution).

It is shown that the composition of the liquefied gas is not constant and sometimes it contains carbonyl sulfide COS, there is always the presence of CS_2. In addition, there is a significant presence of CO_2 and H_2S in the gas. The amount of CO_2 reaches 3.4-3.6 g / kg. Mercaptans in liquefied gas are in the amount of 0.60 - 0.70% of the mass. The presence of diethyl sulfoxide and thiacyclan in the liquefied gas is proved.

Washing with 10 -20% alkali (NaOH) leads to a significant decrease in the mass of sulfur-containing compounds in the liquefied gas. It is recommended to intensify the mixing of alkali and liquefied gas using the developed static mixer. It is recommended to design a module mono-ethanolamine plant to reduce the carbon dioxide content of the liquefied gas and the reliable operation of the washing plant for reducing the amount of alkali loss.

1. Dzioba OG Analysis of potential resource base for diversification of sources and ways of natural gas supply to Ukraine / OG. Beetle // Scientific Bulletin of the Ivano-Frankivsk National Technical University of Oil and Gas. – 2009. – No. 2 (20). – P. 12–23
2. Wendy C. Andersen, Aziz I. Abdulagatov, and Thomas J. Bruno The ASTM Copper Strip Corrosion Test: Application to Propane with Carbonyl Sulfide and Hydrogen Sulfide Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305-3328 Received July 3. – 2002.

IMPROVING OF OPERATIONAL RELIABILITY BY MEANS OF USING OF SUBSTRUCTURALLY STRENGTHENED PIPES

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One of the main causes of emergency shutdowns of high unit capacity power units is damage of the boiler heating surfaces pipes. Thus, superheater pipes shutdowns, caused by metal overheating and accelerated by formation of creep flow, or typical damages of screen system connected with the emerging of corrosion-thermal fatigue and gas corrosion, occur after 10-15 thousand hours of work. The crucial task of ensuring the operation reliability of the pipes of heating surfaces of supercritical pressure boilers units is solved by using of steel 12Kh1MF pipes strengthened by mechanical heat treatment (MHT).

The MHT method is one of the most effective ways of substructural steels strengthening of pearlite class [1,2] due to deformation of 10-15% of pipes of pre-finished size after standard heat treatment [3] and subsequent polygonizational annealing at 700-720^{0}C. In this case, the structure is fragmented, the dislocation walls are ordered, the polygonal substructure is created and that gives the effect of strengthening.

As a result of the MHT, the strength of the steel at normal and operating temperatures increases on 27-9%, the yield stress increases on 58-12% (respectively) while maintaining the required level of plasticity. On trials for long-term strength time to shutdown of MHT pipes is 2-4 times higher than the standard. The research paper presents the results of the long-term industrial operation of substructure- strengthened pipes on the panels of the lower radiation part (LRP) of gas-oil boilers of TGMP-314 units with capacity 300 MW.

45% of panels made of MHT pipes were installed on two boilers of the indicated type. The total amount of installed bent and straight MHT pipe elements is 3079 units. Working service of MHT pipes on the panels of the Lower Radiation Part of TGMP-314 boilers is 96-104 thousand hours. Pipes operation runs, practically, without damages. Isolated cases of LRP pipe damages in the burner zone were observed only in one of the TGMP -314 boilers (less than 0.1% of the number of installed pipes), which was connected with unsatisfactory operation of the boiler's burner.

During the operation, temporal systematic observations of the metal pipes condition were made on places and on the control cuttings. It showed that in the process of operation the microstructure of the pipes metal consistently deteriorates, but the dislocation polygonal substructure of the steel remains stable. Correspondingly, any significant changes in the mechanical properties of steel are not observed. Unacceptable reduction in metal thickness of the pipe wall due to external corrosion is not observed. Welded joints of MHT pipes made by contact and manual welding are in satisfactory condition.

The positive experience of long-term industrial operation of strengthened MHT pipes made of steel 12Kh1MF on heating surfaces of supercritical pressure units testifies technical and economic reasonability of using such pipes in heat power engineering, which provides an increase of the longevity of the responsible power-equipment units more than in 5-6 times.

1. V.S. Ivanova, L.K. Gordienko. New ways to increase the strength of metals – Nauka: – 1964.
2. V.S. Ivanova, L.K. Gordienko, V.I. Geminov, P.V. Zubarev, Z.G. Fridman, Yu.P. Liberov, V.F. Terentev, N.A. Vorobev, V.G. Kudryashev. The role of dislocations in strengthening and breaking metals. – Nauka: – 1965.
3. Tehnicheskie usloviya TU 14-3-460: 2009/TU U 27.2-05757883-207:2009. Technical specifications TU 14-3-460: 2009 / TU U 27.2-05757883-207: 2009. Seamless steel pipes for steam boilers and pipelines.

THE WORKABILITY OF DOMESTIC AND FOREIGN PIPE STEELS IN MINERALIZED ENVIRONMENTS WITH H_2S AND CO_2 IMPURITIES

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Corrosion damages of the tubing and of an industrial pipeline metal made of S-95 foreign steel, and domestic 20 steel after operation in the gas condensate field A: stratum pressure 70 MPa, H_2S and CO_2 content up to 25%, pH ≤ 5 5, chloride ion concentration of 135 g / l and at gas condensate field M (west region of Ukraine): H_2S concentration in the range 0.18 ... 0.28%, the average stratum pressure decreased during development from 5.25 to 1.1 MPa, the type of stratum water is calcium chloride, salinity – 500 mg / l, pH 6.8 ... 7.2 have been investigated. It is shown that on the surface of not inhibited tubes of C-95 steel there are corrosive ulcers that pass into cracks and superficial blistering. The corrosion rate of not inhibited pipes reaches 0.58… 0.88 mm / year, and the inhibited ones - 0.10… 0.16 mm / year. With a small tubing wall thickness (7.34 mm), such high corrosion rates of not inhibited pipes are unacceptable, since the time of reliable operation of the well will be very short. The actual period of operation of the wells was less than two years.

The inner surface of the 20 pipe steel is damaged by ulcers and blisters. The corrosion products are mainly found at the bottom of the pipe. The average value of the corrosion rate of the upper part of the pipeline does not exceed 0.02 mm / year and the lower one is ~ 0.11 mm / year, caused by moisture, abrasives, etc. Thus, during operation in the tubing and in the industrial pipeline of C-95 and 20 steels respektively , corrosive ulcers, corrosion cracks and hydrogen blisters are formed, that is, the steels exhibit a tendency for Sulfide Stress Corrosion Cracking (SSCC) and Hydrogen Induced Cracking (HIC).

The corrosion and corrosion-mechanical strength of the casing and tubing of the strength group D, K, L domestic pipe steels and foreign C-75 and P-105 steels were evaluated. Studies were performed in NACE solution and stratum water. It was established that the K strength group steel (domestic) and C-75 steel (foreign) are not subject to HIC and surface blistering, demonstrate high corrosion resistance, and their guaranteed resistance to SSCC in NACE solution is $\sigma_{ssc} \geq 0{,}8\sigma_{0,2}$, which meets the standard requirements of NACE MR-0175-99. Domestic D steel is somewhat inferior to the foreign C-75, and P-105 and L steels are extremely sensitive to SSCC.

It was revealed that the corrosiveness of stratum water is significantly lower than that of NACE solution. There is no surface blistering and HIC of pipe steels, and the general corrosion rate is 5 - 7 times lower.

Investigations of SSCC carried out in stratum water showed that the samples of C-75, K and D steels have gone through a full cycle of test for 720 hours without failure. Samples of P-105 and L steels were destroyed after 600 ... 670 and 520 ... 630 hours, respectively. So, domestic K, D steels and foreign C-75 steels have high workability in stratum water, and L and P -105 steels - unacceptably low workability.

Given that the load on the casing and tubing is small, since the depth of the gas wells of the Western region is up to 1400 m, it can be argued that the steel D is suitable for the construction of shallow gas wells with a low content of hydrogen sulfide in natural gas and in the presence of inhibitior protection.

In order to protect against possible corrosion destruction of gas equipment of Ukraine, the corrosion inhibitors of Naftohim-3, Naftohim-8 produced by the enterprise “Halychyna” (Ukraine) and German production Dodikor were investigated.

RESEARCH OF INFLUENCE OF LUBRICANTS ON WORKING AND OPERATING PROPERTIES OF CORROSION-STEEL STEELS

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Corrosion resistant steels are important structural materials. They find application in various fields of engineering: energy, industry, construction, medicine, etc. Lubricating and cooling liquids (LCL). Their main function is to reduce friction. Therefore, they can be used: 1) as process fluids intended to improve machining; 2) as process fluids designed to improve lubrication in tributary connections [1,2].

The effect of LCL friendly lubricating and cooling liquids (LCL) based on vegetable oils was investigated. It was found that LCL on the basis of sunflower (LCLs) and rapeseed oil (LCLr), compared with mineralized water. Petroleum-based (LCLn) was also examined for comparison.

Electrochemical studies of polished specimens in LCL and mineralized water were performed to determine the ability of the LCL to protect the surface of the machined parts from corrosion.

The character of curves for steel 12Kh18AG18Sh indicates the anode nature of the electrode processes. The time dependences of the electrode potentials for 12Kh18AG18Sh steel obtained after machining (cutting the sample surface with a cutter on a lathe) in LCL and water showed different electrochemical behavior. It is established that during stabilization of stationary potentials of steels with machined surfaces, repackivation of 12Kh18AG18Sh occurs (increase of potential values from -330… -340 mV to 40… 60 mV).

The results of the surface roughness evaluation of the 12X18AG18S steel samples after grinding in the above media obtained after processing the profilograms showed that the surface quality of the steel samples during grinding in LCLs improved by almost 1.5… 2.0 times compared to treatment in LCLn and without treatment fluid 12 times, which shows the prospect of using vegetable oil for LCL.

It has been shown that chips and corrosion products on its surface can be unique indicators that allow to analyze the performance of machining processes of a workpiece and material properties. It is reported that when increasing the machining speed to 500 rpm, chip breakage occurs without the use of chip breakers. This avoids the formation of long chips that can damage the work surface.

The use of LCL as a lubricant in tribo (steel 45 - high-nitrogen steel) in the conditions of rolling friction allowed us to establish that the intensity of wear (P = 500 N) in comparison with industrial oil I12A when using LCLs is lower by 45%, and at LCLr 35%.

1. Balyts'kyi, O.I., Kolesnikov, V.O., Eliasz, Y., Havrylyuk, M.R. Specific Features of the Fracture of Hydrogenated High-Nitrogen Manganese Steels Under Conditions of Rolling Friction. // Mater. Sci. – 2015 – Vol. 50. Iss. 4. – P. 604–611.
2. Balyts'kyi, O.I., Kolesnikov, V.O., Havrylyuk, M.R. Influence of Lubricating Liquid on the Formation of the Products of Cutting of 38KhN3MFA Steel. // Mater. Sci. – 2019 – Vol. 54. Iss. 5, 15. – P. 722–727.

CORROSION OF CONTACT WIRE OF ELECTRICAL TRANSPORT IN THE ATMOSPHERE CONTAINING SULFUR COMPOUNDS

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MF contact wires with a cross-sectional area of 100 mm^2 are mainly used for main roads of electric transport and 85,90 mm^2 for stationary roads made of copper and copper alloys. One of the operational characteristics of the wires is the wear due to friction and corrosion.

It is known that copper reacts very quickly with sulfur and its compounds. As a result, some compounds are formed on the surface of the wire, which significantly reduce its electrical conductivity and accelerate wear. Along with sulfur, it also affects the humidity and the content of various impurities. Conducted studies of the surface of the wire showed that the following components are present in the corrosion products, such as CuS, Cu_2S, CuO, Cu_2O and in a small amount of CuCl and $CuCl_2$. It is established that the presence in the atmosphere of sulfur and its compounds SO_2, H_2S, mercaptans, etc. is a rather aggressive and corrosive environment. The most active component is hydrogen sulfide. At high humidity, sulfur oxides also cause significant corrosion.

Investigations on the condition of the surface of the contact wire were conducted during operational tests at the section of the regional branch «Lviv Railway» of JSC «Ukrzaliznytsia». The appearance of its surface is presented in Fig. 1, which is made directly during operation.

Fig. 1. The appearance of the contact wire

In the process of making the contact wire, the condition of the surface and the oxide film thickness on its surface are monitored. Therefore the installation company of Confident Instruments, INC. Fort Wayne, Indiana, USA is used (Fig. 2).

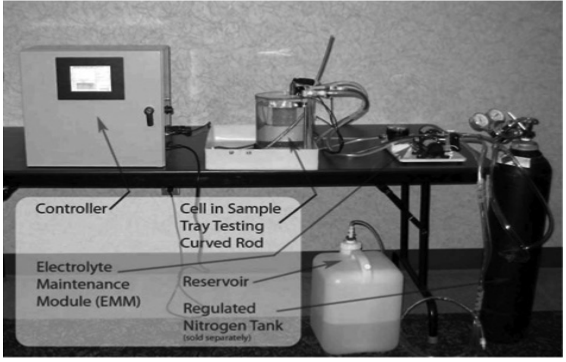

Fig. 2. Installation for determining the thickness of the oxide film

The Confident Instruments installation allows ещ determine the thickness of the oxide film relative to the permissible limits according to the standard. The studies have allowed to estimate a surface condition of a wire and influence of a surface film thickness on its technological and operational characteristics. Special process fluids are used to protect the rolled wire and contact wire at the production stage. Protective fluids of the ANTICORIT DFO 6301 and ANTICORIT RP 4107 brands of FUCHS PETROLUB AG company are characterized by high thixotropic properties, optimum stability of the protective film and corrosion protection of St 14O5 is about 1.5 g/m².

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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** (corrosion-fatigue 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).