

ABSTRACTS OF THE MAIN REZULTS

1). Phosphating of mild steels by zinc and modifying zinc-phosphate solutions

(Articles: Index 7 – No 1, 2, 7, 9; Index 8 – No10)

The formation of crystal phosphate coatings on mild steels by novel concentrates containing zinc and modifying by nickel, calcium or manganese in different ratios have been studied. By gravimetric, chemical, electrochemical and physical methods are determined the characteristics of preparations (density, pH, conductivity, total and free acidity) and those of the produced coatings (thickness, phase and chemical compositions, structure, protection ability). The concentration range has been varied from 5 to 20% vol., while the temperature effects have been studied in the range from 20 to 80°C.

It is proved that Ni- phosphate presence increases the coating thickness and formation rate for all working solution concentrations (5 – 20%) and temperatures (20 – 80°C). Under the same conditions, Ca-phosphate has a minor effect while the manganese one decreases the deposition rate and coating thickness. The results obtained indicate that the coatings developed in zinc and manganese baths contain the following phases: hopeite, phosphophyllite, hureaulite, quasihopeite, strunzite and mixtures of them.

The effect of P_2O_5 and NO_3^- ratio on the thickness/mass of the produced coatings, their phase composition and structure are carried out in 15 % by volume solutions of the phosphating composition and $P_2O_5:NO_3^-$ ratios 1:1.80; 1:3.12 and 1:7.06, respectively.

All coatings formed in phosphate concentrates possess a good resistance in a model 3.5 % NaCl corrosion solution.

2). Amorphous phosphating of mild steel, zinc and aluminum surfaces

(Articles: Index 7 – No 3, 5; Index 8 – No 11)

The effect of different factors on formation, composition and morphology of coatings obtained by treatment of aluminum (Al – 99.5 %) and low carbon steel surfaces in solutions containing ammonium and sodium phosphates, MoO_4^{2-} promoting ions, buffers, softeners, inorganic activators, as well as surfactants, have been investigated.

Gravimetric and electrochemical methods, optical microscopy, transmission and scanning electron microscopy with EDX-analysis, X-ray photoelectron spectroscopy and atomic force microscopy have been used to determine the effect of concentration (2.0÷11 vol. %), pH (2-6),

temperature conditions (20-80°C) and agitation rate (0-2000 rev min⁻¹) on the process of phosphating. The thickness of coatings on zinc surfaces increases by increasing the cathode current density under other equal conditions.

The coating contents include phosphorus, oxygen, molybdenum and nickel, and consequently a conjecture about probable chemical compounds.

3). Corrosion of different materials

(Articles: Index 4 – No 1, 3; Index 7 – No 4, 6, 8; Index 8 – No 12)

The effect of the cold plastic deformation (0÷80 %) on the main mechanical characteristics, microstructure and the residual stresses of low-alloyed (Cr~2 %) carbon steel have been investigated. The results revealed that with increase in the degree of deformation there was significant enhance in the ultimate tensile strength, the yield strength and the hardness of the steel tested. The relative elongation reduces at about one order of magnitude. The model aqueous solutions of sulfuric acid allow observing the effect of the plastic deformation on the corrosion behavior of the steel: It was established that the highest corrosion rates corresponded to deformation range 40-50 %.

A comparative study concerning corrosion behaviors of two steels suggested as construction materials in mining industries have been carried out. Samples of widely used carbon steel st.25 and the new conceived, low-alloyed, steel KP-355 (0.96 % Cr, 0.36 % Cu) have been tested. The tests have been held in model media containing the main aggressive components appearing in real mining waste waters. It has been estimated that the steel KP-355 exhibited better mechanical strength behavior and higher corrosion resistance in all media used in the tests.

The relation between the film composition and the susceptibility of mild steel (0.17% C) to stress corrosion cracking (SCC) in ammonium nitrate solutions at different potentials has been studied. The susceptibility to SCC is evaluated by constant slow strain rate tests under potentiostatic conditions (-0.5 V – 1.5 V, SCE). The composition of the surface film is identified by Mossbauer spectroscopy. It is found that in the region of the highest susceptibility to SCC (0.0 V – 0.8 V, SCE) the film is composed mainly of fine particles of FeOOH as well as some quantity of γ -Fe₂O₃. However, at potentials outside this region, where the resistance of the steel to SCC increases considerably, exclusively oxides with a spinel structure Fe₃O₄ and γ -Fe₂O₃ compose the film. It is suggested that the conditions, which favour the formation of a spinel structure film, may lead to an increased resistance of the steel to SCC.

The results from investigations on the corrosion behavior of mild steel (0.17 % C) in water solutions of liquid fertilizer at different concentrations (0.2, 0.4, 0.6 1.0 % vol. and concentrate) and temperatures (20, 40, 60°C) have been obtained by means of gravimetric and electrochemical methods. The steel could be recommended as good and comparatively cheap construction material for manufacturing of installations, equipment, tanks and other machinery used for handling and operation with this fertilizer.

Corrosion of implants is included in the topic of biocompatibility because it is a determining factor in their sustainability and seamless fulfillment of their functional purpose. The work presents the results obtained in the comparative study of two austenitic stainless steels (Cr18Ni9 and Cr18Mn12N) in two models of artificial saliva, accepted as environments for testing the corrosion behavior of materials for these aims. The nature of the corrosion attack, the composition of the corrosion products at 37°C and the pH 5.5 and pH 6.75 of the model media were determined using physical methods such as SEM and EDX of investigation and analysis. It was found that Cr18Mn12N steel (0.61 % N), exhibits higher corrosion resistance.

The hybrid inorganic-organic nanostructured sol-gel coatings were synthesized by sol-gel technology at room temperature using vinyltrimethoxysilane (VTMS) as silicon precursor and methylmethacrylate (MMA) or hydroxyethylmethacrylate (HEMA) as organic materials in different proportions. The coatings were deposited on mill steel substrates and thermally treated at 25 and 200°C. The composition and the structure of the hybrids were characterized by FTIRS, XRD, BET-analysis, EDS, SEM and AFM. The presence of strong chemical bonds (Si-C, Si-O-C, Si-CH₃) between inorganic and organic parts of the hybrid materials, which are in amorphous state was proved. The corrosion resistance of the coatings was studied using electrochemical potential-sweep technique and a model corrosive medium of 0.5 M Na₂SO₄ solution. It has been shown that the coating affects both partial corrosion reactions, but it decreases more strongly the anodic metal dissolution, thus decreasing the corrosion rate of the steel substrate more than an order of magnitude.

4). Synthesis of intermetallic nanoparticles

(Articles: Index 4 – No 4, 5, 6, 9, 10; Index 8 – No 13, 14, 15)

Intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles have been synthesized through a wet chemical reduction with NaBH₄ in aqueous solutions of the chloride salts of Co, Ni, and Sn (CoCl₂·6H₂O, NiCl₂·6H₂O and SnCl₂·2H₂O) at room temperature. In addition, nanocomposite materials have been obtained in-situ using the same nanoparticles synthesis method but applying a template technique and using carbon-based support. The ratio of the metallic components has been chosen according to the phase diagrams of the relevant binary (Co-Sn, Ni-Sn, Co-Ni) systems: Co: Sn=35:65, Ni: Sn=45:55, Co: Ni=50:50. Graphite and a carbon powder has been used as a support. To avoid the nanoparticle aggregation β-cyclodextrin has been added to the reaction solutions. Regardless of the elemental composition, the nanosized particles are characterized by a relatively high specific surface area (SSA). The Ni-Sn nanoparticle have the largest SSA (80 m²/g), while the Co-Sn particles have the lowest SSA (69 m²/g).

The morphology, specific surface area, elemental and phase composition of the synthesized intermetallic nanoparticles and their carbon-based nanocomposites have been investigated by the help of scanning electron microscopy (SEM), BET, energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) respectively. The distribution of the elements

on the surface (surface composition) and in the volume of the obtained nanopowders (the synthesized intermetallic nanoparticles and their carbon-based nanocomposites) is studied by EDS and XPS investigation methods. Maps for the distribution of each element are also taken. The prepared nanopowders (Co-Sn, Ni-Sn, Co-Ni) and their carbon-based nanocomposites have been studied also by FTIR spectroscopy in the mid-IR region from 4000 to 400 cm^{-1} . FTIR spectroscopy investigations carried out have established the atom /molecule groups formed in the Co-Ni nanoparticles and their carbon-containing nanocomposites.

The use of a carrier modifies the SSA of the resulting nanocomposites differently depending on the size and shape of the carrier's particles. The studies conducted on the intermetallic nanoparticles synthesized with various carriers demonstrate that the particle's morphology, size, and specific surface area for the different supports are suitable for use as catalysts, electrode materials in Li-ion batteries and as magnetic materials for biomedical applications.

5.) Others articles

(Articles: Index 4 – No 2, 7, 8)

Lithium manganese dioxide spinel combines high specific energy density – volumetric and gravimetric, high coulomb efficiency - close to the theoretical one, long cycle life. It is non-toxic, environmentally friendly and with low cost but possesses some disadvantages as low starting capacity and low stability at elevated temperatures. Optimizing the synthesis methods and elucidating the factors influencing the electrochemical stability, we have obtained manganese dioxide spinel, which is very attractive and prospective cathode material for large-scale application. Cathode materials based on manganese dioxide spinel with high coulomb efficiency close to 90%, discharge rates of 4C and cycle life up to 1000 cycles are presented.

Doped lithium cobaltates $\text{LiCo}_{1-y}\text{M}_y\text{O}_2$ ($\text{M} = \text{Mn}, \text{Ni}$, $y = 0.1, 0.3, 0.5$) have been prepared by low temperature solid-state reaction. The structure of the samples was characterized by X-ray diffraction (XRD). The specific surface area (SSA) of the materials was examined by B.E.T. method. The electrochemical performances of the compounds were studied by galvanostatic cell cycling in the high-voltage range between 3.0 and 4.8 V vs. Li/Li^+ electrode. It was shown that the type and the amount of the doping element greatly affect the structure, electrochemistry and cycle life characteristics of the investigated materials. $\text{LiCo}_{0.9}\text{Mn}_{0.1}\text{O}_2$ has shown better cycling results compared to all other compounds.

Investigations are carried out on the electrochemical formation of Zr, Ce and Y oxides from alcoholic solutions and are characterized by SEM and XPS. The possibility of using the oxide systems as cathodes in the hypochlorite preparation process is studied by volumetric determination of the currency efficiency with respect to hydrogen reaction in NaClO 6.8 g dm^{-3} containing chloride solutions. It is found that steel cathode with coating of 1-2 μm $\text{ZrO}_2\text{-CeO}_2\text{-Ce}_2\text{O}_3$ (after heat treatment at 650°C and duration 2 h) provides possibility for considerable improvement of the hypochlorite preparation process currency efficiency compared to pure steel

cathode. The experimental results present grounds to make conclusion that this fact is due to the decrease of the super-voltage of hydrogen evolution on the oxide.

Note: Numbering of the articles are in according to lists of Applications 6a and 6r.