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TARTALOM

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SYNOPSES OF THE PAPERS IN THIS ISSUE

Some erroneous parts in the theory of corrosion
by L. Krivián

The thermodynamic and kinetic theories of corrosion are based on the false chemical notions of reversibility and equilibrium. The model (Fe–H_2O) is incorrect, because without corrosion agent it is not suitable for description of corrosion process. The supposed chemical reactions do not proceed in the proposed model, consequently the model is far from reality. The kinetic theory also involves the false notions. So these theories are not applicable even to the uniform corrosion. The mathematical rules had been violated in the construction of diagrams.

Action-mechanism of furfural and furfuryl alcohol additives on electrodeposition of metals. III. Furfural and furfuryl alcohol additives in alkaline electrolytes
by I. Rusu, P. Átyim, E. Grünwald, Cs. Várhelyi and Cs. Várhelyi jr.

The brightening effect of furfural and furfuryl alcohol in acidic and alkaline electrolyte were tested. In this part of the paper cyanide copper-electrolytes moreover polyphosphate-based and cyanide zinc electrolytes are treated. Substituting furfural by its reduction product furfuryl alcohol the metal coating brighter in all cases. The electrolytes containing furfuryl alcohol are more stable. The potential of cathode decreases by 40–70 mV in this electrolyte.

Why do waterpipes perforate prematurely?
by M. Horvátth and V. Zanathy

The premature corrosion is described in the case of hot-water heating system in which steel, Zn-coated and copper pipes are installed together. Deposition of copper causes corrosion damage when the installation is made in contrary with the regulation. The Zn-coating may cause also corrosion damage. Originally it was used against atmospheric corrosion. In hot water system its corrosion potential may change (at a higher temperature) cathodic to the steel pipe thus forming a corrosion cell.

Comments on the paper of S. Szabó and I. Bakos titled Corrosion and chemical equilibrium (in Korróziós Figyelő, 2002. 42. (5) 146–151.)
by Z. Lukács jr.

The authors of the cited paper have applied the potential–pH equilibrium diagram to non-equilibrium corrosion system and made conclusions. Uncritically accepting Pourbaix's views, they have tried to explain the phenomena of electrochemical corrosion and cathodic protection in terms of thermodynamic considerations. In this Comment it was pointed out that the application of thermodynamics is insufficient for the interpretation of corrosion phenomena which are par excellence of kinetic nature. It was also pointed to that the empirical criteria of cathodic protection can hardly be verified by thermodynamic calculations.

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SYNOPSES OF THE PAPERS IN THIS ISSUE

Zero-condition – the starting point for the appraisement of industrial equipments
by A. Bacskai and K. Csáky-Csekő

The zero-condition is the condition of equipment before the start of operation. The aim of appraisement is the utilization of optimal machine life considering the safety regulations. If the residual life time is to be determined the knowledge of zero condition is indispensable. In absence of zero-condition data the first revision is a proper occasion for supplementing the necessary data. The circumstances of the zero-condition determining the reliability of appraisal in the case of legal dispute are outlined.

Non-destructive testing of pipelines and tanks
by Zs. Rónafalvi

The operation of pipelines and tanks advancing in years needs reliable appraisal of condition. CORROCONT Ltd has developed a computerized method based on electromagnetic induction of low frequency. The method can be applied for testing of painted and coated pipes and tanks. The measuring appliance consists of the measuring head, the controlling electronics, and the computer. Hundred meter pipeline can be checked daily. The bottom plate of a tank (D = 30 m) can be tested in two days. The measuring appliance completes the report of test and the true to scale drawings.

Accelerated corrosion testing of coatings with water diluted binder
by B. Lengyel and É. Fekete-Dániel

The coatings formed from one component water-soluble paint were qualified by accelerated corrosion tests and the results were unfavourable. It was proposed that the coating may improve by the time elapsed after painting and the accelerated tests reflect the quality of coating only for a short period after painting. So the results may be worse than it could be for a longer period. The aim of the present research work was the verification of this concept. Relation was sought between the results of accelerated and exposure tests. It was established that the test in humid-warm atmosphere and the salt spray test may be valuable testing method if the probes are properly preconditioned. The correlation between the results of accelerated and exposure test will be further studied.

Galvanization of components made from iron powder by shrinkage using pulsating direct current
by E. Grünwald, Cs. Várhelyi and P. Átyim

The following conclusions were derived from the experiments performed:

The throwing power of Zn electrolytes containing chloride ions is more powerful and the thickness of the deposited layer more uniform. The layer deposited from electrolyte of low concentration by pulsating current as the basis of bright Zn coating improves the corrosion resistance. The sequence of rinsing is important. It should be started by hot water and followed by cold water. According to the process No 6. the component coated in electrolyte of low concentration should be transferred into the brightening bath without rinsing. The components made from iron powder should not be treated in alkaline electrolyte because the traces of electrolyte remain in the pores. Filling of galvanised and chromated surface improves the corrosion resistance by 15–20%. At the last rinsing the application of dehydrating solution is advisable.

Comments on the paper of L. Krivián titled Some erroneous parts in the theory of corrosion [in Korróziós Figyelő, 2003. 43. (1) 3–7.]
by Gy. Inzelt

The article is series of misunderstanding and misinterpretation. The author's thesis that "every chemical reaction is irreversible in thermodynamic way" is based on misunderstanding the notion of reversibility–irreversibility, equilibrium electrode and equilibrium.

The statement that "there is no chemical equilibrium in thermodynamic sense" is wrong. The working or able to work galvanic cell is not in a state of equilibrium, however, equilibrium may exist at the phase boundaries except at the liquid–liquid interface. The ΔS as defined by the author can be positive and negative too. The fact that the chemical energy is not utilized totally, does not touch the essence of things. The thermodynamic calculations can be used for definition of maximum reachable efficiency. The theory that only one electrode reaction can take place on one electrode is false. Nobody claims that the corrosion is an equilibrium process. The Pourbaix-diagrams only give a certain point of reference, since the real processes are indeed more complicated than that the diagrams show. The usage of the quantity calculus form is mathematically well established.

Remarks on a misleading publication
by L. Kiss

The author of the article criticizes the domain and competence of thermodynamics, interpreting some of its concepts in a peculiar way, or not having full knowledge of the field. He ignores the fact that large-scale industrial processes are based on the neglected chemical equilibrium.

On the basis of equilibriums, and by utilising thermodynamic data it is possible to decide if the given processes do or do not take place in the course of metallic corrosion.

The statements laid down concerning the kinetic theory of corrosion are totally contrasting with the results of laboratory tests.

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Corrosion investigation of the heat exchangers in the Hungarian nuclear power plant. Part I. General corrosion state and morphology

by K. Varga, Z. Németh, A. Szabó, K. Radó, D. Oravetz, P. Tilky and J. Schunk

Systematic corrosion investigations of the heat exchanger tubes from 16 different steam generators of the Hungarian power plant were performed. The passivity of the stainless steel tube specimens was studied on the inside surface by voltammetry. The morphology and chemical composition of the oxide-layer formed on the surface were analysed by SEM-EDX methods. On the basis of the measured corrosion characteristics (corrosion rate, thickness and chemical composition of the protective oxide-layer) the steel tube samples can be classified into three groups. Presumably the chemical decontamination of the heat exchanger tubes, performed by the AP-CITROX process, exerts detrimental effect on the corrosion state of the steel tubes.

Corrosion investigation of the heat exchangers in the Hungarian nuclear power plant. Part II. Chemical composition and structure of tube surfaces

by Z. Homonnay, E. Kuzmann, S. Stichleutner, Mrs. K. É. Makó, K. Varga, Z. Németh, A. Szabó, K. Radó, P. Tilky, J. Schunk, and G. Patek

Within the frame of a project dealing with the comprehensive study of the corrosion state of the steam generators the surface properties (chemical and phase compositions) of the heat exchanger tubes supplied by the power plant were studied by X-ray Diffraction (XRD) and Mössbauer Spectroscopy (CEMS) methods. Comparative analysis of chemical structure on the outer and inner surfaces has revealed that the main constituents of the protective oxide layer are magnetite, hematite as well as amorphous $Fe(OH)_3$. The relative amount of these constituents is decisively related to the corrosion state. In the case of those samples which have undergone $\gamma \rightarrow \alpha$ phase transition, no adequate relationship between the presence (and extent) of the phase transition and the corrosion state could be established.

Corrosion state of the primary and secondary side of steam generators

by O. Nagy, J. Ősz, T. Salamon, A. Cserháti, T. Pintér, J. Schunk, P. Tilky and G. Patek

Steam generators contain boiler tubes of thin wall-thickness. The perfect condition of these pipes is very important. The corrosive effect on the surface in contact with steam is higher so they were primarily tested. The copper condensers and the steel preheaters were substituted by alloyed steel ones. In consequence the operation of the system needed further changes. The steam generators had to be cleaned from copper. The effect of decontamination of the machinery was also tested. The results are summarized and the necessary modification improving the security of operation are determined.

In situ radiotracer study of the formation of surface ad-layers on polycrystalline gold in aqueous solutions containing Cr(VI) ions

by R. Marczona, L. Gáncs, I. Szalóki and K. Varga

Results of in situ radiotracer and voltammetric studies on the formation of surface ad-layers in the course of Cr(VI) reduction on gold electrode, and a novel detection and calculation method for the quantitative evaluation of the surface excess of radio labelled Cr species via measurement of the intensity of low energy X-rays (E = 4.90 keV) emitted by ^{51}Cr are presented. From the experimental results can be concluded:

- The electro-reduction of Cr(VI) particles presumably proceeds via a ce (chemical-electron-transfer) mechanism and yield a gold surface covered with intermediate surface ad-layer containing Cr(VI) species and added anions (HSO_4^-/SO_4^{2-}, ClO_4^-).
- The extent and mechanism of ad-layer formation are affected by the pH of solution.
- The maximum surface excess of Cr-containing species ($\Gamma_{pH=0} = 1{,}2\times10^{-9}$ mol·cm^{-2}, $\Gamma_{pH=2,0} = 1{,}6\times10^{-9}$ mol·cm^{-2}), as well as the molar ratio between the Cr species and HSO_4^-/SO_4^{2-} ions ($m_{pH=0} \approx 6$ at E = 0,80 V, $m_{pH=2,0} \approx 2$ at E = 0.05 V) attest that the coverage of the gold surface with intermediate complexes does not exceed one mono layer.

Chalcones as corrosion inhibitors for nickel in HCl and H_2SO_4 solutions

by A. S. Fouda, H. S. Gadow and A. A. El-Shafei

Potentiostatic polarization and polarization resistance studies show that some chalcones act as an effective inhibitors for nickel corrosion in 1 M HCl and 0.5 M H_2SO_4. They are predominately cathodic inhibitors in both acids. Corrosion rate depends on the concentration and nature of the medium. Adsorption occurs according to the Frumkin isotherm. Thermodynamic parameters for adsorption process are calculated and discussed. The order of efficiency in both acids is: 4-chlorobenzal acetophenone 4-bromobenzal acetophenone anisal acetophenone benzal 3-nitroacetophenone benzal acetophenone.

Response to the objections on the paper "Some erroneous part in theory of corrosion"

by L. Krivián

Two critical paper have been presented in the "Korróziós Figyelő" on the principal chemical notions discussed in the quoted paper. The objections are analysed in the response. In the objections the logical rules are violated with the aim of affirmation of obsolete notions. The inconsistent argumentation is clarified. The concept of electrode potential is explained on the basis of physical notions. The ununderstanded parts are reaffirmed by new argumantation. The annuciations without argumentation are neglected.

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Hot-dip Zn coating and economic efficiency
by Á. Antal

The aim of this paper is the increase of economic efficiency of hot-dip coatings. The analysis of the process can lead to rationalization. The partners of the production have to cooperate in the selection of the possibilities. Attention has to pay to the selection of steel quality, the shape of the product, and the hot-dip process.

Testing of duplex coatings
by V. Zanathy and M. Horvátth

The duplex (hot-dip Zn coating and paint coating) coatings embrace the advantages of the different coatings increasing the protective power by 50%. Laboratory tests were performed using salt spray (2500 h), humidity cabinet (2500 h) and immersion in water (8500 h) exposures. The efficiency of corrosion protection was evaluated by visual examination, dry coating thickness, adhesion of coating, and deep drawing of the probes. The results are compiled in tables. The proper coating can be selected on the basis of results considering the actual circumstances.

Painting of hot-dip Zn coating soon after dipping
by L. Szabó

It is advisable to paint hot-dip Zn coating after 3–6 months of exposure. In consequence of this fact steel structures were painted after installation causing manifold difficulties. Nowadays the painting can be executed in the workshop after grit blasting the new Zn coating decreasing its thickness by 5–10 μm. This technology and the workshop are described.

Experiences with the in situ painting of Zn coated truss-girder
by L. Szabó

The task of the company is the maintenance of the electric distribution network. The data of the network are summarized in graphs. The corrosion protection methods, the insurance and control of quality are detailed. The most favorable solution of corrosion protection is the application of duplex coating.

Corrosion protection of Zn alloys
I. Zinc alloys and their properties
by G. Felecan, Á. Kún, E. Grünwald, Cs. Várhelyi, and X. Pop

In the first part of the paper consisting of three parts the compositions of those Zn alloys are reviewed which are used in the mass-production. The most important alloying elements are Al and Cu. The effects of these elements in the production and employment are summarized. The beneficial properties of cast Zn alloys are reviewed.

Recovery of Ag from wash-water
by K. Molnár-Lambertus and Gy. Vértes

In the thrifty washer at low concentration (3–5 g/l Ag ion and 10–15 g/l potassium cyanide) the recovery of metal produces solid metal coating only at low current density. Although the increase of the concentration of cyanide ion up to ten times higher level improves the recovery, the flow rate in front of the cathode has to be increased to 2–8 cm/s to achieve significant improvement. Under condition of a workshop Ag was depleted at a rate of 15 g/l by 0,25–0,30 A/dm^2. So the recovery can reach a level of 10%. This process ensures the requirements needed to take out a permit for the utilization of environment.

Response to the critique of Z. Lukács jr. entitled "Objections"
by S. Szabó

The author rejects the critique thoroughly expounding his arguments which are divided in four topic. These are:
- Homage to prof. M. Pourbaix
- Significance of electrochemical reaction kinetics
- Chemical equilibrium
- Thermodynamical immunity of Fe.

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SYNOPSES OF THE PAPERS IN THIS ISSUE

Corrosion protection of Zn alloys II. Chemical and electrochemical treatment of Zn alloy components before electroplating or painting
by E. Grünwald, Cs. Várhelyi, X. Pop, A. Kún and G. Felecan

Degreasing treatments (including electrochemical ones) which are applied after mechanical treatment (polishing, glazing) of Zn alloy components are reviewed. Degreasing is usually followed by rinsing in diluted acid solution. Phosphate treatment is necessary to increase the adhesion of paint coating. Chromate treatment improves the corrosion resistance. Phosphate and chromate baths are described in tables.

Interpretation of remote potential in the diagnostics of cathodic protection
by Z. Lukács jr.

Although the concept of remote potential (sometimes called ”remote earth”) has been applied in cathodic protection diagnostics for a long time, no general agreement is achieved in the interpretation and use of the phenomenon. The definition of the physical content of the remote potential determines also the conditions of the correct measurement. The modern methods of cathodic protection diagnostics (CIPS, DCVG) have opened new prospects in the application of the remote potential, but in some methods it is not exploited or its application is not quite correct. The comparison of the remote potentials with the close ones offers a basis to classify the critical sections of the pipelines.

The importance of insulating flanges mounted in gas lines and the problems with them
by P. Janitor and K. Koóš

The improper knowledge of the application of insulating flanges can cause significant problem for the constructor and the operator of pipelines. The faulty insulating flange may prevent the proper operation of electrochemical protection. The failure of insulating flange may cause damage and increased operation costs too.

Practical experiences referring to measurement of stray currents
by M. Horvátth and I. Kondor

In situ corrosion tests were performed in a case of corrosion failure of a pipeline. General review is given on stray current corrosion and its basic notions. The results of the measurements are summarized in tables and interpreted in sentences.

Interaction of insulating coating for protection of underground tanks and pipelines and the biological feature of soil
by D. Rónay

On the basis of experiments and experience the hindrance of sulphide-formation with respect to corrosion prevention is useful. It can be achieved by prevention of anaerobic conditions. Practical possibilities are:
– Use of loose and well-aired soil around the structure
– Increase the pH of the filling earth
– Apply cathodic polarization to the structure
– Apply biocide additive in the coating material

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Corrosion protection of Zn alloys
III. Electrodeposition of metal coatings on Zn alloys
by E. Grünwald, Cs. Várhelyi, X. Pop,
A. Kún and G. Felecan

Almost any metal can be deposited on the surface of Zn alloys. The most favoured metals are: copper, nickel, chromium and brass. But silver, gold, and zinc may be also deposited. These metal coatings are described in detail.

Cast iron materials of water mains and their damage
by I. Artinger and Á. Németh

The cast iron is generally a proper material for water mains. Unfavourable circumstances may cause damage within 30 years. In acidic soil coating is necessary to prevent the contact between cast iron and soil. Graphitic corrosion also reduces the durability. The prevention of corrosion effect caused by stray current is also advisable. The mechanical load may cause the fracture of water mains.

Deposition corrosion and its prevention in cooling systems
by E. Péter

The problems emerging in the operation of cooling systems are: formation of scale, corrosion, sedimentation, bio-fouling. Bio-fouling is good isolator but promotes the formation crystalline deposits and collects suspended material. The causes of deposition and the corrosion under the depositions have been analysed. The methods of prevention are summarized.

Experiences of the corrosion investigation performed on the water-side of boiler tubes
by A. Majoros and Zs. Rózsavölgyi

The aim of the investigation was to help the planning of the preventive maintenance and the valuation of the technical state of boilers. The materials and the methods of operation are summarized. The destructive and the non-destructive tests are described. The principles and the requirements used in the valuation of the state of boilers are touched.