Electrochemical methods for evaluation of the protective ability of electroplated coatings and conversion films

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One of the main functions of electroplated coatings and conversion films is corrosion protection. For evaluation of their corrosion protective ability (CPA) different types of tests – natural conditions, artificial media and electrochemical methods – have been applied.

The natural tests are limited because of their long duration. This is the reason for the application of accelerated tests being in a good correlation with natural ones. At present, different electrochemical methods for accelerated optimization of the CPA are applied.

The multilayer Ni/Cr and Cu/Ni/Cr coatings, developed for severe corrosion media, consist of several Ni layers and a microdiscontinued Cr layer on the top. The realization of a high CPA in these coatings requires a control of the microdiscontinuity of Cr; the polarity, potential differences and thicknesses of the Ni layers, and the thickness of the Cu layer. This control is possible to be fulfilled effectively and fast by using of electrochemical methods.

The corrosion protection of electrodeposited coatings with a large application – such as Zn, Zn-Fe, Zn-Ni, Zn-Co and others – is realized by chromate conversion films. The express evaluation of their protective ability is possible to be performed by the electrochemical method and apparatus developed in IPC based on an approved correlation between the values of the anodic potential maxima under galvanostatic polarization and the results from the accelerated tests in a neutral salt spray chamber. The replacement of Cr(VI), according to EU Regulations, requires the development of environmental friendly conversion coatings and methods for their test.

Key words: electrodeposited coatings, conversion films, corrosion methods.

INTRODUCTION

Metals and alloys in many practical applications (as iron, zinc, copper, magnesium, aluminium, silver and their alloys) are oxidized very easy. Some of the above metals are thermodynamically unstable (magnesium, aluminium, zinc and iron), and others are preferably oxidized in a specific corrosion medium (for example, silver and copper in a sulphide medium). Oxidized by one or other way they lose their decorative appearance, and especially – their functionality.

For keeping the initial properties and main functions of the above-mentioned metals and alloys different finishing treatments as electroplating of metals, formation of conversion films and other types of protection layers have been applied [1–6].

Development and application of different types of coatings requires also suitable methods for control of their properties and not finally of their CPA. The most reliable are the studies in natural dynamic and/or static working conditions, but they are with the longest duration. There are different accelerated tests as a neutral salt spray (NSS) [7], acetic-acid salt spray (ASS) [8], Corrodkote test [8], SO₂ test [9], etc. Their effectivity for a particular corrosion medium in a large number of investigations is approved and some of them are accepted also as international standardization documents (ISO) for testing of the conversion coatings [10–13]. The test duration by accelerated methods depends on the type of the coating and the base metal and in many cases several days and nights or some times several weeks are necessary. The contemporary requirements and the accelerated development of new more environmental friendly processes for production of electrodeposited and conversion coatings together with the harmonization of the relevant standards have to be connected with simpler methods for express evaluation of CPA of the coatings not only during the investigation stage, but also in their practical realization.

The electrochemical technique gives such a possibility. By using of different regimes (galvanostatic, potentiostatic, linear polarization resistance...
(LPR), impedance, etc. in different electrolytic media, the correlations between the electrochemically determined parameters of the samples and the results from accelerated corrosion tests by ISO methods have been established.

**ELECTROCHEMICAL ASSESSMENT METHODS**

One of the universal electrochemical ways for calculation of the corrosion rate of metals, alloys and different type of coatings is LPR technique determination. The theoretical basis of the LPR technique was founded in a publication dating back to 1957 [14]. According to this publication, the following assumptions are necessary: an uniform corrosion damage of the sample; an activation control (simple, kinetic model) for both the anodic and cathodic reactions; a single reaction (anodic or cathodic); known values of the Tafel constants; solution of relatively high conductivity (a negligible solution resistance) and a stable free corrosion potential. In the LPR technique a small value of potential (10–20 mV) is applied and current response is measured. The relationship E/I is linear (kinetic model by Tafel) and the calculated polarization resistance is inversely related to the uniform corrosion rate.

The other universal electrochemical way for a long time was the coulometric technique. It is used for measurement of the thickness of the coatings which are one of the main parameter for their CPA. It is based on the local anodic dissolution (for metal coatings) [15] or cathodic reduction of oxides, sulphides or similar films on non-noble metallic coatings [16] in a suitable medium depending on the type of the coating and the substrate. A review on the coulometric methods for determination of the most used electroplated metal, multilayer, intermetallic and alloy coatings as well as of different types of conversion coatings (especially oxides and sulphides) has been made by D. R. Gabe [17].

During development and practical realization of Ni multilayer coatings, as a part of the multilayer system Ni/Cr or Cu/Ni/Cr, the coulometric technique for identification of the separate Ni layers by their potential differences due to their different electrochemical activity has been found useful again. From the data for polarity, potential differences and thickness of the Ni layers achieved in one measurement it was possible to make conclusions about their contribution to the CPA of the system [18, 19]. The above exact, fast and economical method has been accepted as a STEP-test standard [20].

The CPA of multilayer Ni/Cr and Cu/Ni/Cr coatings depends on the microdiscontinuity (micro-porosity or microcrackness) of the Cr layer. The microdiscontinuity of the Cr layer is determined by an electrochemical method, known as Dubpernell-test [21, 22]. It is based on the treatment of the Cr layer (in case that the samples are fully covered with Cr) in acid copper sulphate electrolyte at low cathodic current density or low voltage. Under these conditions, copper is deposited onto the Ni through the pores or cracks of the Cr layer. A modification of this method for local nondestructive determination of the microdiscontinuity of Cr layer both on laboratory samples, as well as on complicated products with partial Cr plating is also known [23].

A large number of electrochemical investigations are dedicated to CPA of the conversion coatings on electrodeposited Zn and Zn-alloy coatings. The minimum thickness of the Zn coatings for the application in different practical conditions is prescribed in international standards [24].

W. Paatsch [25] has published a method for CPA estimation of the conversion films on Zn coatings on the base of stationary polarization investigations. He compared the results from the polarization studies with the corrosion resistance in neutral salt spray for different type conversion films onto Zn coatings with different thickness.

R. L. Zeller and R. F. Savinell [26] reported an impedance method for prediction of CPA of chromated Zn coatings on steel. Their method is based on the analysis of the experimental data from the impedance measurements by using a nonlinear mathematical model.

Kalantary [27] developed a method for isopotential contour mapping when studying the CPA of Zn-alloy coatings. By this method the potential difference between two points from the surface of the sample in suitable medium (NaCl or NH₄Cl solution) is measured using two reference Ag/AgCl microelectrodes and one of them is scanned on the surface according to a determined program. The obtained signals, after amplifying, have been used for plotting the potential contour maps of the surface. The comparisons of the results from the tests of the chromated Zn-Ni alloy coatings in a neutral salt spray for 1000 hours with the measurements by the above-mentioned method have shown a good coincidence.

In the paper of D. Gilroy et al. [28] the possibility for applying of different electrochemical methods (potentiodynamic, chronoammetric, polarization resistance) for comparison of CPA of chromated and non-chromated Zn coatings on steel has been shown.
S. C. Chung et al. [29] investigated by electrochemical impedance spectroscopy the corrosion resistance of Zn samples in artificial media.

G. Schmitt et al. [30] have offered a method for assessment of the CPA of chromated Zn coatings by measuring the exchange of electrical charge between two samples in 5% NaCl solution at pH = 5. The tests have been carried out in a Faraday’s cage. A good correlation with the results from neutral salt spray tests has been established.

B. I. Kudzene and G. D. Bikulchius [31] have developed a method for evaluation and prediction of the corrosion resistance of chromate films on Zn coatings by measurement of the break voltage (U_{fr}) through the films. The method is based on the Fritting effect, in accordance with a break voltage through some kind of a dielectric between two electrodes which occurred when electrical voltage of 10^6 V/cm was applied. A good correlation between corrosion resistance of chromated Zn coatings in neutral salt spray (NSS) and the break voltage (U_{fr}) has been established.

The chromate conversion coatings/films (CCC) are also applied in many cases on aluminium alloys both for corrosion protection and for improving the adhesion with the possible finishing polymer layer.

D. Gilroy et al. [32] have estimated the corrosion resistance of chromated aluminum by using different electrochemical methods - cyclic voltammetry (CVA), chronoamperometry and polarization resistance.

By electrochemical impedance spectroscopy and electrochemical sound method, it has been shown that the increasing in the aging temperature has changed the electrochemical properties of the chromated samples and their corrosion resistance [33].

D. Chidambaram et al. have investigated the influence of different types of surface treatments of an aluminum alloy AA2024-T3 on the composition and electrochemical behaviour of the oxide film [34] as well as on the composition and electrochemical parameters of the chromate conversion coatings (CCC) such as polarization relationships potential/current, corrosion current, polarization resistance, double layer capacitance, etc. [35]. They have established that the composition and the thickness of the formed surface film as well as the CPA of the CCC are influenced considerably by the type of the pretreatment of the aluminum surface.

P. Campestrini et al. [36] have studied the process of growth of chromate conversion coatings onto the surface of aluminium alloy AA2024 by means of modern microscopy methods (SEM, EDS and AMF). Especially they investigated the influence of intermetallic compounds and copper-rich smut (product of acid pickling as a result of prior treatment) on the alloy’s surface. According to these authors, intermetallics and copper deposits negatively affect the CCC morphology (formation of large defects) as well as they decrease the thickness and adherence of the film to the Al alloy.

The same authors in [37] by using electrochemical impedance spectroscopy (EIS) studied the corrosion resistance of the CCC formed on two different substrates (bare and clad) of aluminium alloy 2024. According to this paper, the EIS measurements enabled the correlation between the differences observed in the chromate film morphology and its corrosion protection. The authors concluded that the corrosion resistance is determined not only by CCC, but by the type of Al alloy as well as the process of prior pretreatments of its surface. A limited amount of intermetallics and copper-rich smut on the surface of the alloy leads to the formation of more protective CCC.

The estimation of the CPA is important not only for the chromate coatings. At the Symposium, held in Düsseldorf during 1997, on the phosphating problems with the participation of the producers of equipment and chemicals, the necessity of fast, economical and nondestructive methods for the production control of phosphate coatings has been discussed [38]. The conclusions gave a stimulus for the electrochemical investigations in this direction.

It is possible to establish the protective properties of different phosphate coatings on steel using electrochemical methods especially by cathodic polarization curves [39]. Shorter test times in relation to the standards reduce the investigation stage during development of similar processes. It is also possible to make conclusions about the optimization of the total process of metal treatment from the electrochemical results.

T. Badea et al. [40] have applied electrochemical methods – cathodic polarization curves and electrochemical impedance spectroscopy - for evaluation of the corrosion behaviour of phosphate coatings on steel.

G. Lendvay-Gyorik et al. [41] have offered a simple method of impedance measurements of the phosphate coatings on steel surfaces for quantitative assessment of their corrosion protection by applying appropriate frequency and recording the imagination impedance part. According to the authors, the above simple method may be applied in industry for estimation of the corrosion protection of phosphate coatings on steel surfaces.

B. Elsener and A. Rossi [42] have studied the passivity of the amorphous alloys Fe70Cr10X13C7 (X = P, B) by combination of X-ray photoelectron
spectroscopy (XPS) for surface analysis and electrochemical measurements. This is a new method for simultaneous evaluation of the thickness and composition of the surface films on the multicomponent alloy.

A. Müller et al. [43] have investigated the growth of thin passive films on Ti in 1 M NaOH and in 0.5 M H₂SO₄ by potentiostatic and galvanostatic techniques with simultaneous measurement of the sample weight on a microbalance. They carried out impedance studies, too. The results are compared with the data obtained by using other methods.

It has been developed a method for an express complex assessment and prediction of the CPA of multilayer Ni/Cr and Cu/Ni/Cr coatings by subsequent determination in one apparatus – the micro-porosity of Cr layer, polarity, potential differences and thicknesses of Ni layers as well as the thickness of Cu sublayer [44–49].

Ways for comparison of the possibilities of different electrochemical methods for estimation of the CPA of conversion coatings have been searched [50]. On the base of the carried out large-scale corrosion investigations by accelerated standard test methods in salt spray chambers, conclusions about the possibilities of different electrochemical methods, such as the tri-point method of Barnardt, the method of polarization resistance, the comparative method of Paatsch, etc., for precise and stable assessment of the properties of conversion films, have been made [50].

A method for express evaluation of the CPA of conversion films on Zn and Zn-alloy coatings was developed [51, 52]. The existence of a very good correlation between the obtained information by the above method and the results from the standard tests of similar coatings in a salt spray chamber was shown [51, 52]. On the base of the method, a Bulgarian Patent was granted [53] and an apparatus has been developed and applied in measurements for express assessment of the CPA of conversion chromate films.

Subsequently the method was applied successfully for determination of the influence of the magnetic field on the CPA of conversion films formed on Zn and Zn-Co coatings [54, 55] as well as for estimation of the properties of “top coatings” on chromate films [56–58]. It was applied successfully for evaluation of the anticorrosion inhibitors’ efficiency of a thin organic film on the metal surface [59].

CONCLUSION

The above reviewed methods for evaluation of different types metal and non-metal coatings mainly are based on complicated and expensive equipment. The results from these methods are undisputed for scientific assessment of the CPA, but they use a very expensive and complicated technique for application in industrial conditions. The development and application of simpler, cheaper and reliable methods and apparatus, remain actual.

At present, the elimination of the Cr(VI) compounds according to the EU Regulations [60] puts for ward the necessity of development of new, environmental friendly electroplated coatings and conversion films as well as methods for their test.

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ЕЛЕКТРОХИМИЧНИ МЕТОДИ ЗА ОЦЕНКА НА ЗАЩИТНАТА СПОСОБНОСТ НА ГАЛВАНИЧНИ ПОКРИТИЯ И КОНВЕРСИОННИ ФИЛМИ

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(Резюме)

Защитата от корозия е едно от основните предназначения на галваничните покрития и конверсионни филми. За оценка на тяхната корозионно-защитна способност (КЗС) се прилагат различни видове изпитвания – в естествени условия, ускорени (в изкуствени среди) и електрохимични методи.

Изпитванията в естествени условия се прилагат ограничено, поради тяхната продължителност. Това е основанието за използването на ускорени методи, които са в добра корелация с натурните. Понастоящем се прилагат също и различни електрохимични методи за ускорено определение на КЗС на покритията.

Многослойните Ni/Cr и Cu/Ni/Cr покрития, разработeni за експлоатация в силно агресивен среди, състоят от няколко никелов слой и най-горен микропрекъснат хромов слой. Реализирането на висока КЗС при тези покрития изисква контрол на микропрекъснатостта на Cr, на поляритета, потенциалните разлики и дебелините на Ni слоеве и на дебелината на Cu слой. Този контрол може да се осъществява ефективно и бързо чрез използването на електрохимични методи.

Корозионната защита на електрохимичните покрития с масово приложение – като Zn, Zn-Fe, Zn-Ni, Zn-Co и други – се реализира с хроматни конверсионни филми. Експресна оценка на тяхната защитна способност е възможно да бъде извършена чрез използване на електрохимичния метод и апарат, разработени в ИФХ, базиращи се на установена корелация между стойностите на максимумите на анионния потенциал при галвансатична поляризация и резултатите от ускорените изпитвания в камера с солена мъгла.

Заместването на Cr(VI), съгласно препоръките на ЕС, изисква разработването на нови, екологически облагородени конверсионни покрития и методи за тяхното изпитване.