The energy approach to electrochemical corrosion studies of nano-copper coatings

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Properties

ABSTRACT

Purpose: The paper presents research results on energy impacts and effects of corrosion of electrodeposited nano- and microcrystalline copper surface layers and involve activation energy and mass transfer effects.

Design/methodology/approach: The activation energy and mass transfer effects indicate effectiveness of one-period energy approach in the control of the corrosion resistance of copper deposits. Properties of coatings are examined.

Findings: Loops of one-period energy dissipated during the corrosion of electrodeposits were determined. Non-sinusoidal periodic excitations of the corrosion cell and integrations of response waveforms were taken into account. The corrosion energy is expressed by the area of the loop on the energy phase plane. The influences of supplying voltage on the topography, morphology and surface roughness of the electrodeposits were examined.

Research limitations/implications: The approach is suitable for system operating under non-sinusoidal periodic conditions. The main feature lies in the elimination of the frequency analysis and gives significant simplifications of the corrosion rate measurements realized with a computer processing system or function generator and digital oscilloscope.

Practical implications: The important implications consist in complete eliminations of Fourier series analysis and direct exhibitions of susceptibilities of the studied material to corrosion through evaluations of one-period energy loops. The approach involves more physically exact insights on non-sinusoidal influences of environments.

Originality/value: The original value consists on introduction of the energy state variables and representing the absorbed energy during the corrosion tests by the area of one-period energy loops. The novelty lies on the identification of various crystalline structures susceptibility on corrosion destructions.

Keywords: One-period energy; Electrochemical copper surface layers; Corrosion resistance; Morphology and topography

1. Introduction

Electrodeposition is a versatile technique for producing nanocrystalline materials. It is a technologically and economically viable production route to metals, alloys and metal matrix composites, both in bulk form and as coatings. Nanotechnology offers a unique possibility to manipulate the properties through the fabrication of materials using the nano-objects as building blocks. It is therefore considered as an enabling technology by which existing materials, virtually all man-made materials, can acquire novel properties and functionalities making them suitable

for numerous novel applications as materials tailored for a great variety of special applications varying from structural and functional to advanced biomedical purposes [1-3]. While, materials properties are determined by their atomic and molecular constituents and structure, their functionalities emerge when the microstructure of these early ensembles is in the nanometer regime. The properties and functionalities of these ensembles may be different as their size grows from the nano- to micron-regimes and bulk structures. It is now evident that the nanotechnology has the potential for revolutionizing the ways in which materials and products are created and the range as well as the nature of functionalities that can be accessed. Improvements in environmental impact can be achieved utilizing nanostructure particulates in coatings and eliminating the requirement of toxic solvents.

Nanocrystalline copper and surface composite electrodeposits with grain sizes smaller than 100 nm have attracted extensive interest due to their improved electrochemical, mechanical and physical properties. Properties of nano-structured electrodeposits such as hardness, wear resistance, electrical resistivity and corrosion protection are strongly grain size dependent. Corrosion behavior of nanocrystalline copper and composite electrodeposits has been assessed by several techniques in various environments [4].

Recently, several methods have been proposed to evaluate the susceptibility of various metals coatings to electrochemical corrosion. This research direction has quite important significance since no single technique can be employed in all practical situations. The development of numerous techniques for the study of the mechanisms of corrosion and corrosion protection has, on one side, brought quite satisfactory results and, at the same time, there have been a lot of critical remarks on the interpretation of the differences between various physical models [1-6]. Even simple models are the cause of some controversy in the literature [7, 8]. Among the various electrochemical methods suitable for the measurements of the corrosion rate of metals, the harmonic current analysis method is quite useful because in the method the corrosion current can be obtained without the use of Tafel constants at corrosion potential. Significant advances in the study of the mechanisms of corrosion and corrosion protection have been achieved since the development of the impedance measurements. The measurements have been extended to the study of mass transport and stress corrosion cracking, as well as to the noise analysis used to study the localized corrosion, stress corrosion cracking and blistering of coatings [9-15]. In particular, the impedance measurements have been adopted to separate the different elementary steps involved in overall process, and receiving a better knowledge of mechanisms and progress of corrosion, as well as of possible means for the corrosion protection [16-23].

In this paper we extend the results of [9-11,14,15] for the corrosion measurements and analyze them in the context of the activation energy and mass transfer effects. Section 2 is devoted to presentation of the quantitative results of the one-period measurements for the micro-crystalline technical copper thin-layer coatings. They are considered from point of view of indications how this approach may be used to control the corrosion resistance. Several interesting properties of those coatings are examined in the context of various dissipative mechanisms involved. Section 3 presents the experimental results obtained for corrosion resistance of electrodeposited nano- and microcrystalline copper thin layers. Discussion and review of established facts are included into Section 4. Section 5 follows with the conclusions.

2. The one-period energy approach

It is well known that the electrochemical corrosion takes place when two different metals come into contact with a conductive liquid - usually impure water or soil moisture - resulting in a flow of direct current electricity. The current always flows away from the anodic metal (anode), and the anode is corroded. The current flows through the electrolyte to the cathodic metal (cathode), but the cathode is not corroded. The potential that causes the current to flow is always due to some kind of difference between the anode and the cathode, such as a difference in the two metals, concentration of the conductive liquid, a difference in temperatures, a difference in the amount of oxygen present, or some other difference in operation conditions.

A uniform attack of corrosion process environment is normally characterized by chemical and electrochemical reactions that proceeded uniformly over the whole exposed surface and over a large area of the sample. The products of corrosion may be dissolved species or solid corrosion products. In either case, the energy of the system is lowered as the metal converts to a lower-energy form. The change in the internal energy of the material is the driving force for the corrosion process and is a subject of thermodynamic principles.

Early identification of signs of corrosion, especially in hard to reach locations where visual inspection is impossible, helps prevent or slow down the onset of serious corrosion. The same approach works for evaluating protective coatings under real-world conditions. While excellent electrochemical kinetic models have been available for decades, each one is system specific and almost all apply only to dilute solutions and were developed to address specific questions. Thus, a more general model of corrosion rate in mixed solvent process environments is indispensable to predict component activities and transport properties of the bulk (aqueous, nonaqueous or mixed) phase that is in contact with the metal. In a number of respects the impedance spectroscopy is the method of choice for characterizing the electrical behavior of corrosion systems in which the overall system behavior is determined by a number of strongly coupled processes, each proceeding at a different rate. However, such type of corrosion investigations can be carried out in the conditions of stability, causality and linearity of the tested electrochemical system. In a general case electrochemical systems are non-linear systems. For the above mentioned insufficiencies and limitations of the up-to-date methods being in using for identifications of corrosion processes an elaboration of a more accurate approach to the subject problems is indispensable. When being developed it must exhibit abilities for prediction the stability of multicomponent alloys as well as thermodynamic equilibriums, transport properties and rates of general corrosion as a result of existing electrochemical and chemical processes. An accomplishment of these goals is possible by an expansion and modifications of existing thermodynamic and kinetic modeling tools [11,21,22-29].

In this work an attempt is put on description of a new method which takes into account the activation energy and mass transfer

effects. It is based on non-sinusoidal periodic excitations of the corrosion cell and integrations of the measured response waveforms. This is done through the use of time-periodic signals of suitable amplitudes, and it is recommended not to introduce a DC potential difference across the system, which can induce further electrochemical activity. Using the small periodic non-sinusoidal excitation, and assuming that the system's time response is also periodic we can evaluate energy absorbed during the corrosion process [2-4,17,24]. The block diagram of the experimental setup is shown in Fig. 1.
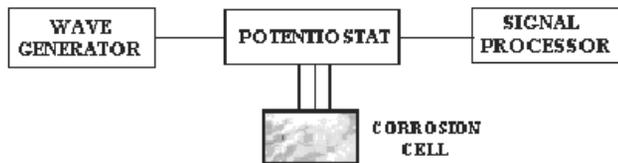
Fig. 1. Block diagram of the experimental setup

The wave generator can supply a controlled amplitude time-periodic voltage wave of specific frequency and form. Such excitation is potentiostatically impressed to the corrosion cell using an elaborated electrochemical system and the current response of the corrosion cell is analyzed by a dynamic signal analyzer. An integrator of a measured signal is also applied. The samples of electrochemically produced copper thin layers and investigated in the corrosion cell are subject to an appropriate corrosion environment (usually 0.5M NaCl solution). The important novelty of the present approach is exhibited by employing the energy state variables (time functions), to determine the susceptibility of a given material to corrosion. The main feature of this method is the complete elimination of the frequency analysis what leads to significant simplifications in the corrosion rate measurement process. The second important feature is that that the method is based on the analysis of appropriate loops on the energy phase plane leading to an easy estimation of the corrosion process through the evaluation of the loop's area. The presented methodology leads to easily interpretable physical results, with robust properties.

Thus to identify the effect of active species that are responsible for corrosion of the investigated samples we can construct an equivalent electric model of the corrosion process basing on knowledge of the physical properties and the electrochemical processes that occur as corrosion results. The general scheme of such a situation is shown in Fig. 2a.

The steady state energy $W(\Delta t)$ delivered by the source v(t) to the corrosion system during the time interval $\Delta t = nT$, (T is the period, $n >> 0$ is a positive integer) is expressed by

$$W(\Delta t) = n \cdot W_T \qquad (1)$$

where W_T denotes the one-period energy delivered by the source. Thus, in the periodic state it is sufficient to evaluate W_T and by multiplying it by n we obtain the energy absorbed by a corrosion element during the given time interval Δt.

The derivation of the corresponding expression for W_T leads to

$$W_T = \int_0^T v(t)i(t)dt = \int_0^T v(t)\frac{d}{dt}\left(\int i(\tau)d\tau\right)dt = \int_{q(0)}^{q(T)} v(t)dq(t) = \int_{\psi(0)}^{\psi(T)} i(t)d\psi(t) \quad (2)$$

where

$$q(t) = \int i(t)dt \qquad \text{and} \qquad \psi(t) = \int v(t)dt \qquad (3)$$

denote the electric charge and quantity representing the integral of the source voltage $v(t)$, respectively.

a)
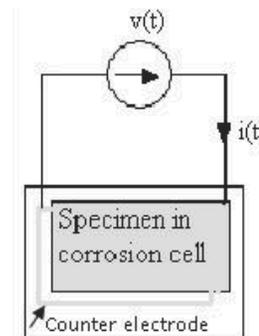
b)
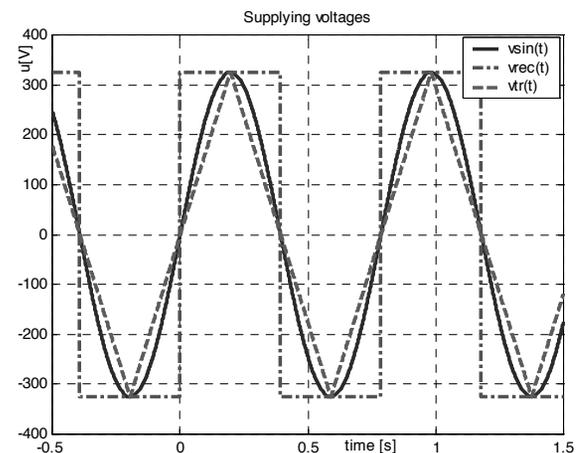
Fig. 2. Corrosion species in the periodic steady states: a) electric system scheme, b) waveforms of supplying voltage

It follows from (2) and (3) that the area enclosed by a one-period loop on the energy phase plane with coordinates $(v(t), q(t))$ or, equivalently, $(\psi(t), i(t))$ determines the one-period energy W_T delivered to the controlled element operating under periodic non-harmonic conditions [25-30]. The above approach can also be applied when a given system operates at a permanent sinusoidal input excitation as well as in a non-linear condition.

We emphasize that it does no matter which energy phase plane we choose to determine W_T. In some cases it is easier to evaluate the phase variable $q(t)$ and in other ones the phase variable $\psi(t)$ should be used. Thus, for any corrosion specimen

operating under periodic non-sinusoidal conditions it is possible to directly determine the one-period energy W_T without using the power or the Fourier series approach [24,29,31-34].

The second important feature of the one period energy approach is an easy way of evaluating the area enclosed by the loop in the energy phase plane. In most applications we have the preliminary knowledge concerning the forms of the physical system response on the given input. This allows choosing a priori the most appropriate energy phase plane calculations. Moreover, the results of calculations can be easily interpreted and have robust properties. The usefulness of the proposed technique has been examined for microcrystalline and nanocrystalline copper surface layers deposited on a polycrystalline substrate by the electro-crystallization method. The quantitative results obtained from the measurements of the one-period energy loops are applied to control the corrosion resistances of the micro- and nano-copper thin-layer coatings. Several experiments performed on real testing specimens verified the efficiency of the method in electro-chemical corrosion analysis of many practical systems.

To illustrate the main feature of the one-period energy approach a series of experiments have been performed and analyzed. In all cases a three-electrode 'flat-cell' arrangement was used exposing $1\,cm^2$ of working electrode made from polycrystalline technical copper plates. A large area platinum foil and a saturated calomel electrode were used as the auxiliary and reference electrodes, respectively. Quiescent 0.5M NaCl (pH=6) solution was used for electrochemical corrosion testing. Three different voltages supplied by the wave generator were taken into consideration successively, namely, clean sinusoidal $v_{sin}(t)$, rectangular $v_{rec}(t)$ and triangular $u_{tr}(t)$ waveforms changing in time with the same period T, and exhibiting the same magnitude values $/V_{max}/ = 10mV$. The graphs of the supplying voltage waveforms are shown in Fig. 2b.

The processes were monitored by measuring the current $i(t)$ during 30 min intervals. Each of these voltage excites in the corrosion cell corresponding currents $i_{sin}(t)$, $i_{rec}(t)$, and $i_{tr}(t)$, respectively, exhibiting variations in time more or less different with respect to supplying voltages. The excited currents were measured and then suitably processed in the context of the activation energy and mass transfer effects.

Plots of the current waveforms corresponding to particular voltages shown in Fig. 2b are presented in Fig. 3a. It is easily seen that all currents as time functions take similar forms but their magnitudes differ importantly. Taking into account the input voltages shown in Fig. 2b we can measure the one-period energy absorbed by the samples on energy-phase plane (q(t), v(t)) in accord to expression (2).

The corresponding one-period energy loops are presented in Fig. 3b. Since both the input voltages and output charges contain many harmonics with different spectra the one-period energy loops have different shapes and surfaces. It is possible to arrange the energies absorbed by the investigated samples into the following inequalities

$$W_{Trec} > W_{T\sin} > W_{Ttr} \qquad (4)$$

This means that the input voltage of rectangular waveform exhibiting most rich spectrum of harmonic components makes better allowances for corrosion tests than other waveforms of the excitation voltage. It is easily seen from the Fourier series for the

rectangular and triangular waves with period T, phase offset 0, and magnitude A which leads to

$$f_{rec}(t) = \frac{4A}{\pi} \sum_{n=1,2,5,...}^{\infty} \frac{1}{n} \sin(\frac{2n\pi t}{T})$$

$$f_{tr}(t) = \frac{8A}{\pi^2} \sum_{n=1,2,5,...}^{\infty} \frac{(-1)^{(n-1)/2}}{n^2} \sin(\frac{2n\pi t}{T}) \qquad (5)$$

a)

b)
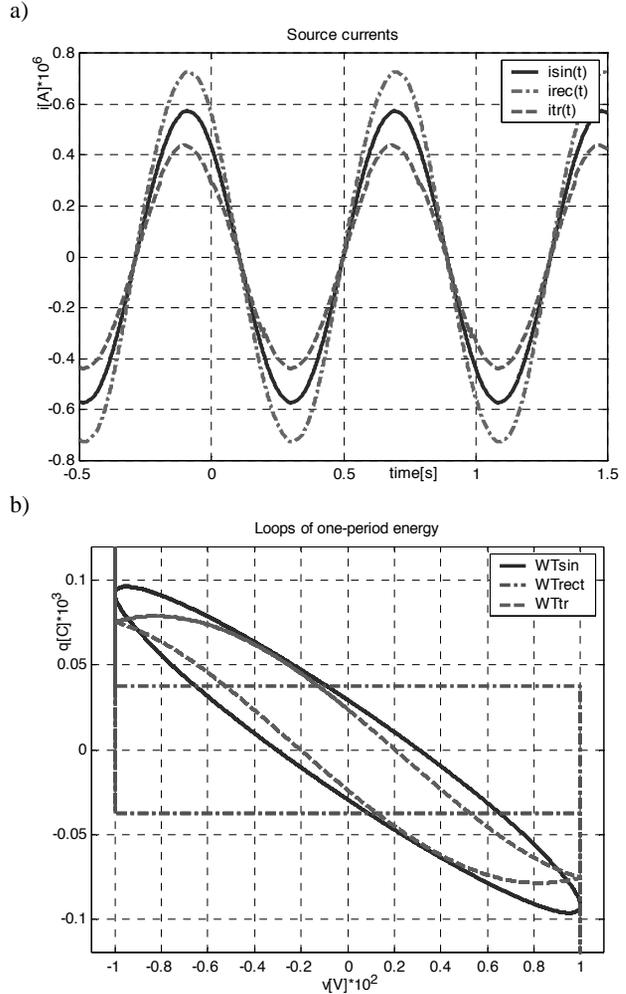
Fig. 3. Output values of the corroded samples: a) current waveforms, b) loops of one-period energy

It is worth noting that although both waveforms contain infinitely many harmonic components the rectangular one is much better convenient for corrosion studies because its all harmonic components have greater and positive magnitudes with respect to triangle wave. Thus supplying the corrosion cell by the source with rectangular waveform voltage we can eliminate inconveniences of the electrochemical impedance spectroscopy approaches. Moreover, such type of supplying voltage leads to a simple form of the one-period energy loops having the form of a rectangle on the (q(t), v(t)) plane.
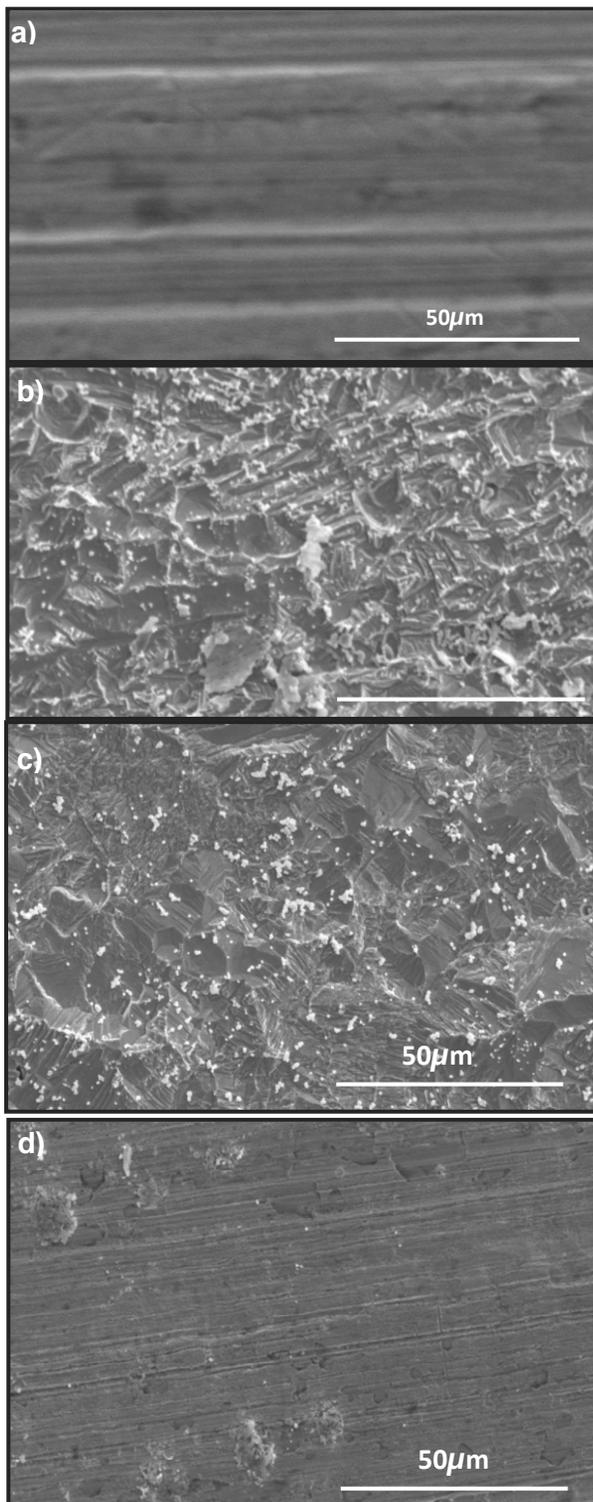
The one-period energy absorbed by the specimens can be easily evaluated to be WTrec = 1.6 µJ so that during the whole test time Δt = 30 min. we get W(Δt)≈ 3.667 mJ. In the case of two remaining supplying voltage waveforms the absorbed energies are appropriately smaller.

Under corrosion cell conditions the applied voltage acts in the double layer immediately after the supplying source is connected. The resulting current response contains the different parts of current, like double-layer charging due to the voltage step, adsorption, and condensation more or less distinguishable according to the cell and kinetic parameters. For the experimental conditions this means that the entire electrode process, including the above-mentioned processes, takes place with a variable local double-layer potential.

Dependent on the cell resistance, the transients change their shape. The one-period energy loop expresses the steady state energy consumed by the tested sample. This means that the potential energy which is stored in the capacitance of the double-layer is responsible for its charging. It has any influence on the energy losses in the sample being under corrosion investigation in the steady state.

Images of the surface morphologies of the investigated samples before and after the corrosion tests are presented in Fig. 4. The results of this study show that the corrosion tests performed with the voltage of rectangular waveform reveal much more details in the morphology of sample destroyed surfaces than the other waveforms of the supplying voltage. It is worth mentioning that, although computers can easily provide results up to four or more digits, care must be taken to ensure that the overall system remains linear. Moreover, the corrosion rate also depends on the material microstructure and such factors as the crystallographic texture, porosity, impurities and triple junctions.

3. Experimental part

When the electrodes in corrosion cell are polarized by a periodic pulse voltage source, under stable conditions, the corrosion current also has a periodic waveform but, in a general case, its shape differs significantly from that of the excitation voltage. The voltage periodic waveform distorted from the sinusoid better describes the conditions that exist in practice. By perturbing a corroding system with a distorted periodic nonsinusoidal signal of low amplitude we do not need to perform a harmonic analysis. Moreover, electrochemical corrosion processes are non-linear in their nature. Polarization characteristic representing the complexity of electrochemical phenomena during the corrosion is given in Fig. 5a. The use of relatively high amplitude input nonsinusoidal signal and the determination of the total response signal which is excited at the output of the tested system allows its full corrosion characteristics. The suitability of the absorbed energy appears as a good base for the complex characterisation of the tested system.

The approach presented in Section 2 can be applied even in a nonlinear case when a given system operates under permanent periodic conditions. Controlling the output of the wave generator at the voltage waveform shown in Fig. 5b we can measure the one-period energy absorbed by the investigated sample. A direct comparison of the absorbed energies appears as a main factor determining the corrosion resistance of a given material. In this

Fig. 4. SEM images of the copper surface morphology of the investigated samples: a) before corrosion test, b) after corrosion test with $v_{rec}(t)$, c) after corrosion test with $v_{sin}(t)$, d) after corrosion test with $v_{tr}(t)$

new approach the analysis of each harmonic component is completely eliminated and only the absorbed energy during the corrosion test determines the material quality.

a)

b)
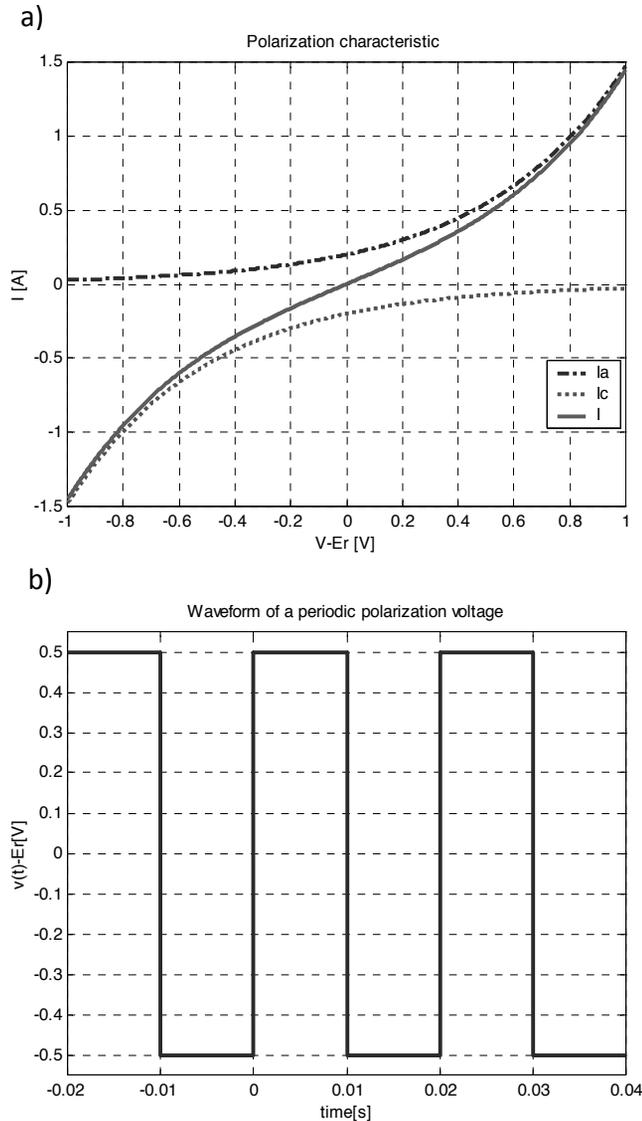
Fig. 5. a) Typical polarization characteristic of electrochemical corrosion system, b) waveform of the pulse voltage applied for corrosion tests

The use of the one-period energy approach in evaluation of the micro- and nano-crystalline copper thin-layers and their interactions with various corrosive environments are illustrated by the SEM images shown in Fig. 6. The layers used in this study were deposited by the electrocrystallization method on polycrystalline copper substrates. Pure copper thin-layer electrodes with effective area of 1 cm^2 were used as the working electrodes. The corrosion tests have been carried out by using the

set of apparatus shown in Fig. 1. Taking into account the voltage input shown in Fig. 5b the one-period energies absorbed by the samples have been measured. In order to do a comparison of obtained results the corrosion test measurements were repeated with sinusoidal voltage of the same amplitude and frequency as that rectangular one. In each case the working electrode was polished with 1/0, 2/0, 3/0 and 4/0 emery papers degreased with trichloroethylene. The solutions were made using analar grade

a)

b)
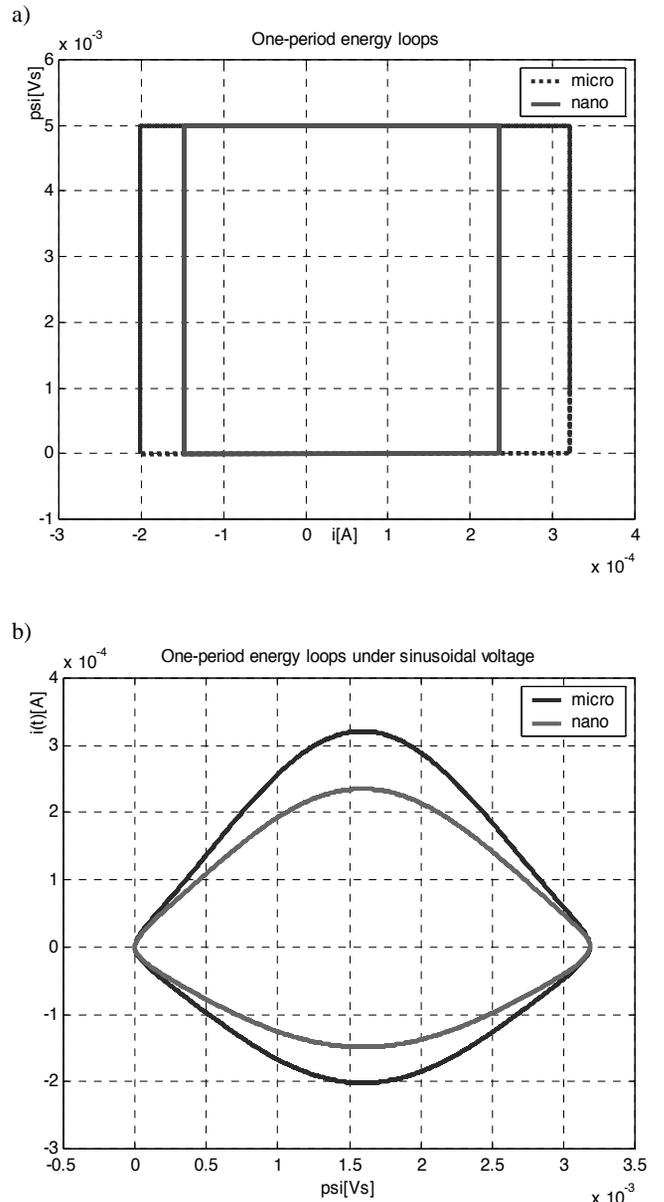
Fig. 6. SEM images of surface structure of the copper layers: a) microcrystalline – A) before and after corrosion, B) enlarged fragment of the corroded area, b) nanocrystalline – A) before and after corrosion, B) enlarged fragment of the corroded area chemicals with triple distilled water

a)

b)
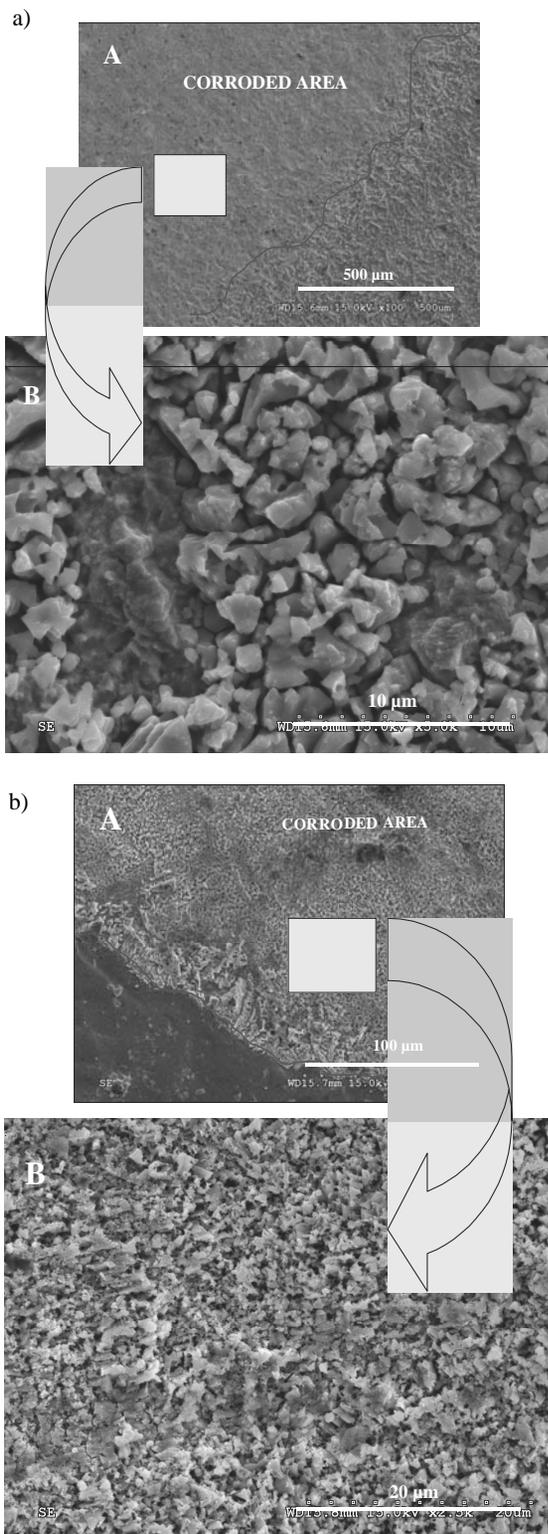
Fig. 7. One-period energy loops for copper thin layers obtained with input voltage of waveform: a) rectangular, b) sinusoidal

The quantitative results obtained from the measurements of the one-period energy loops were used for controlling the corrosion resistance of the micro- and nano-copper thin layer coatings. The obtained loops of one-period energy for non-sinusoidal periodic voltage excitation as well as sinusoidal one are presented in Fig. 7.

The one-period energy approach is based on the supplying of the corrosion cell by the voltage source of appropriate waveform. In such a situation when the voltage amplitude is constant the energy absorbed by the investigated sample is inverse proportional to its electrical resistance. Nano-crystalline copper layers exhibit much higher resistance to the current flow because the developed grain boundaries which may occupy as much as 50% of the material volume contain some additives originated from the bath, as for instance, trace quantities of sulfur. This results in much lower internal energy of the nano-crystalline corroded sample and then absorbed energy is smaller in respect to the micro-crystalline copper layers.

4. Results and discussion

The performed corrosion investigations have showed that by the method of electrochemical reduction it is possible to produce copper layers with micro- and nano-meter sizes of grains. The decrease of the size of the material grains influences the change of the morphology and topography of the produced copper surface layers as well as it increases the rate of the corrosion. Surface topographies of technical copper and microcrystalline copper surface layer examined by atomic force microscopy (AFM) are presented in Fig. 8a and Fig. 8b, respectively. Surface roughness of copper layers was also examined but quantitative results can appear to be quite different depending on the scale which one investigates it. Illustration results relating to geometric profiles of the investigated materials are shown in Fig. 8c and Fig. 8d. The surface roughness was calculated as root mean square (rms) of heights by STM analyzer with different scales. The corresponding values are: $R_{aT} = 30$ nm and $R_{a\mu} = 82$ nm .

These results offer the important information for the process design of copper layer manufacturing in three-dimensional integration applications. This is due because the surface roughness is one of the most important properties of copper thin surface layers that affects many other behaviors of them like adhesion, friction, electrical properties, reflection or scattering and adsorption and etc.

We have also performed a series of experiments with using electrochemical impedance spectroscopy (EIS) and potentiodynamical investigations in quite equal corrosive conditions and obtained results are comparable with these acquired by the one-period energy technique.

Height fluctuations and surface roughnesses of nano- and micro-crystalline copper thin-layer electrodeposits on polycrystalline substrate have been investigated and illustration results are shown in Fig. 9. Variation of roughness against copper layer thickness exhibited an exponential growth and rises of thickness cause an increase of roughness and then start to saturate. Although rms values $R_{an} = 200$ nm and $R_{a\mu} = 1230$ nm of the nano-crystalline and microcrystalline copper layers, respectively,

differ by the rate equal six there is no direct physical relationship between surface roughness and coating parameters. Moreover, the corrosion resistance of nanocrystalline copper surface layers is smaller than that of microcrystalline copper layers. This phenomenon can be understood as follows: in the nanocrystalline layer grain boundaries are the regions of few atomic distances in thickness that isolate grains of different orientations and more molecules of additive substance contained in the bath during the layer electrodeposition cover the copper grains and the inhibition effect is worse. Atoms located in the grain boundary regions have higher energies. These regions are also prone to easier diffusion and segregation of foreign atoms and impurities. In result, it is easier for corrosive chloride ions to attack the copper grains through the interspaces between the tail groups of the adsorbed molecules and damage layers on their surfaces.

It is well known that there are several ways for analyzing randomly rough surfaces. We often need a statistical approach to determine some set of representative quantities. It is worth noticing that the AFM data are usually collected as line scans along the x and y coordinates that are concatenated together to form the two-dimensional image. The surface area can be estimated by the following approach. Let f_i for $i = 1, 2, 3, 4$ be values of the surface heights in four neighboring points (pixel centers), and g_x and g_y pixel dimensions along corresponding axes. We assume that the sampling interval is the same in both the x and y direction. Moreover, we also assume that the surface height at a given point (x, y) can be described by a random function $\xi(x, y)$ that has given statistical properties. If an additional point is placed in the centre of the rectangle which corresponds to the common corner of the four pixels (using the mean value of the pixels), four triangles are formed and the rough surface area can be approximated by summing their areas. This leads to the following formulas for the area of one triangle

$$S_{mn} = \frac{g_x g_y}{4} \sqrt{1 + \left(\frac{f_m - f_n}{g_x}\right)^2 + \left(\frac{f_m + f_n - 2\bar{f}}{g_y}\right)^2},$$

$$m, n = 1,2,3,4, \; m \neq n \tag{6}$$

wher $\bar{f}$ denotes the value of the surface height in the pixel center.

The surface area of one pixel (k) is determined by

$$S_{(k)} = S_{(k)_{1,2}} + S_{(k)_{2,3}} + S_{(k)_{3,4}} + S_{(k)_{4,1}} \tag{7}$$

By counting in the area that lies inside each pixel, the total area is defined also for grains and masked areas.

The geometric size of the area is determined by $L_x \times L_y$ where L_x and L_y are the sizes of the sample along x and y axes, respectively. The rate η_S of surface roughness is defined by

$$\eta_S = \frac{\sum\limits_{k=1}^{N} S_{(k)}}{L_x \times L_y} \tag{8}$$

where N denotes the number of pixels taken into account.
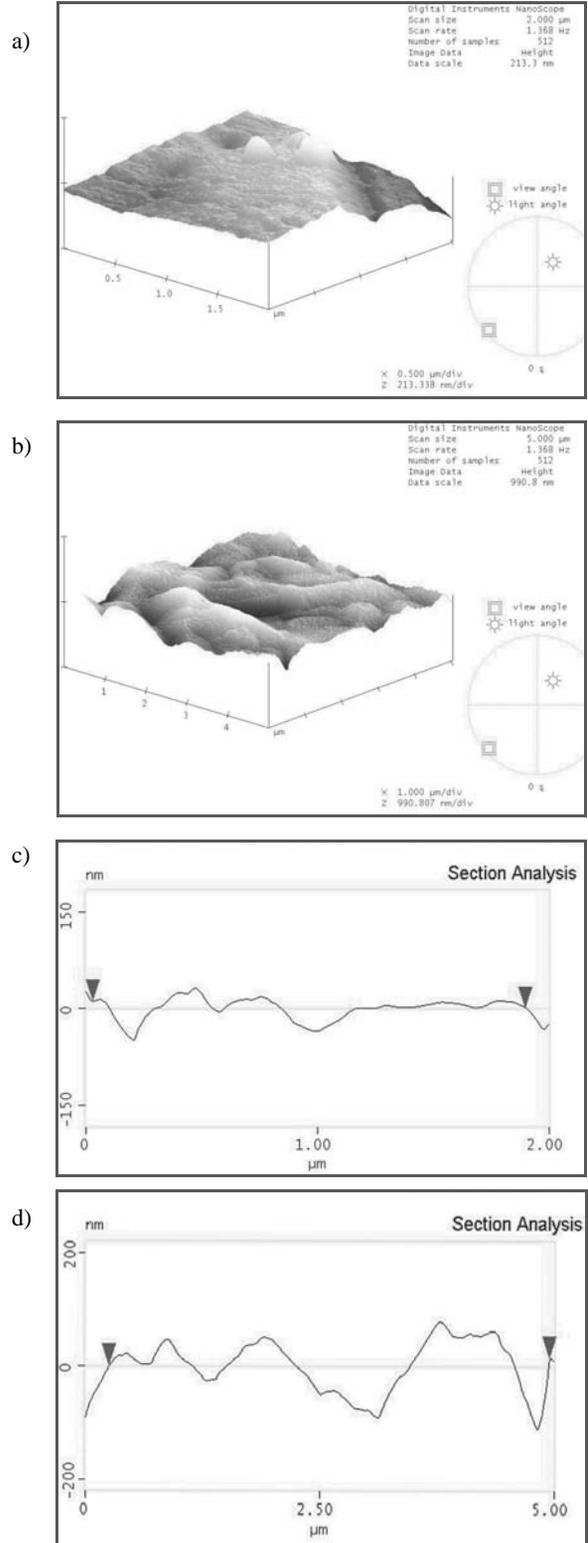
Fig. 8. AFM surface topography and geometric profiles: a), c) technical copper, b), d) microcrystalline surface copper layer
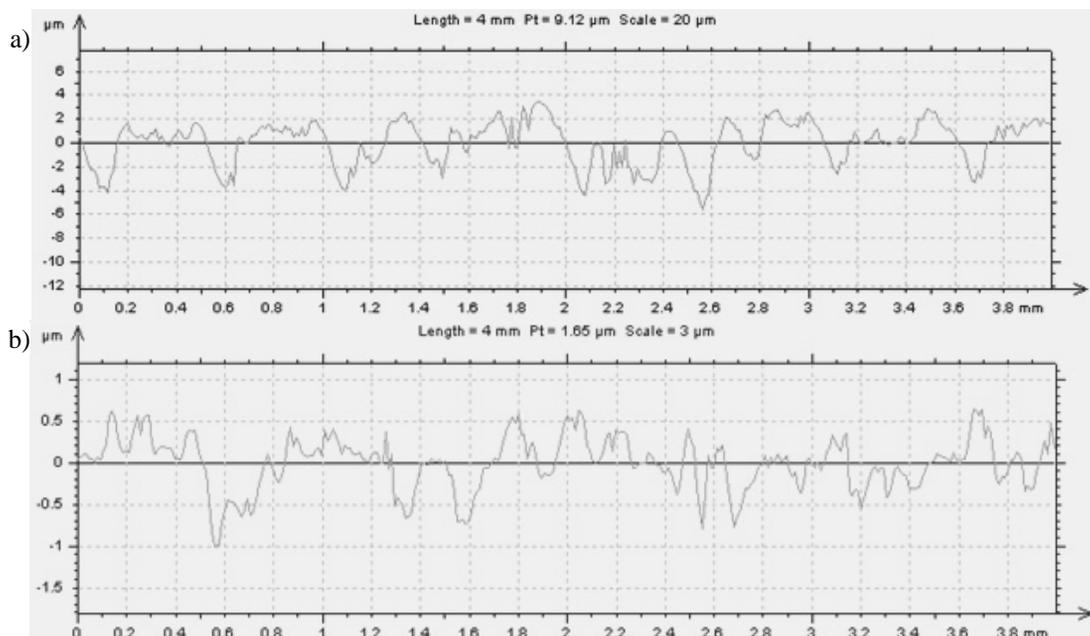
Fig. 9. Surface roughness of copper thin-layers: a) nano-crystalline, b) microcrystalline

The performed calculations using Digital Instrument Nanocope gave the following results: $\eta_{ST}=1.064$ for the technical copper and $\eta_{Su}=1.273$ for the micro-crystalline copper surface layer.

A determination of the quantitative correlation between absorbed energies and the surface roughness value is not a direct problem because it is dependent not only on surface roughness but also on the material structure and its chemical compositions (contaminations).

The quantitative results obtained from the measurements of the one-period energy loops are applied to control the corrosion resistances of the micro- and nano-copper thin-layer coatings. They were reported to the same conditions of the corrosion measurements but materials of these particular specimens of copper surface layers were characterized by different anodic and cathodic transfer coefficients. Fitting to experimental data the one-period energies absorbed by investigated samples can be a fairly straightforward task. It requires some knowledge of the corrosion cell being studied, its mechanism and a basic understanding of the behavior of cell elements. A good starting point for the development of the model is to compute the area of the one-period energy loop on the energy phase-plane (q(t), v(t)) or equivalently (ψ(t), i(t)). The corresponding surface integral denoted by W_T expresses the one-period energy absorbed by a given sample during the corrosion test. This method has the advantage that the prior knowledge of Tafel constants is not necessary and the calculation of the corrosion rate is accomplished within a very short time interval. Since both the input and output signals contain infinitely many harmonics, the one-period energy loops have different shapes that those obtained in the case of sinusoidal excitations. The method works very well both in linear as well nonlinear conditions. The applied methodology leads to easily interpretable physical results attesting the worst corrosion resistance of the nanocrystalline copper

surface layers with respect to microcrystalline copper layers even they were produced by the adequate electrodepositing processes under appropriate conditions. All studied materials were exposed to the same corrosive environment. The decrease of the size of the material grains influences the change of the morphology and topography of the produced copper surface layers as well as it increases the velocity of the layer corrosion

Different morphologies of the nanocrystalline copper and microcrystalline copper were observed in the SEM images presented in Fig. 6. The pitting corrosion failure on the surface of the microcrystalline copper is significant because of the smaller active intercrystalline area. This form of corrosion, however, is of great concern from the technical standpoint, because the life of equipment can be accurately estimated on the basis of the above comparatively simple tests. When localized corrosion phenomena occur, the characteristics of the fluctuations change dramatically, and these characteristics can be used to identify the most probable mode of attack. From a plant corrosion control perspective, this is important, since the technique provides an early warning of incipient localized corrosion [19].

Therefore, some concentrated active anode spots yielded serious pitting corrosion. Pitting results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pitting is one of the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size and because the pits are often covered with corrosion products. Pitting is particularly vicious because it is a localized and intense form of corrosion, and failures often occur with extreme suddenness. It is believed that during the initiation or early growth stages of a pit, conditions are rather unstable. Many new pits become inactive after a few minutes. It appears that pitting, though quite similar to crevice corrosion, deserves special

consideration since it is a self-initiating form of crevice corrosion, which does not require a crevice. It is also known that all systems that show pitting attack are particularly susceptible to crevice corrosion, but the reverse is not always true: many systems that show crevice attack do not suffer pitting on freely exposed surfaces. Stable passivation does not occur on the surface of conventional microcrystalline copper.

The results of this study show that the corrosion pits, likely formed on grain boundaries, impurities, triple junctions and surface defects, are significant on a microcrystalline surface and the uniform attack is present on nanocrystalline structured specimen, respectively. The above mentioned facts are illustrated by the one-period energy loops presented in Fig. 7. The energy absorbed by the tested specimens when supplied by rectangular voltages can be easily evaluated and they are: $W_{Tmicro} = 2.6437$ μJ, and $W_{Tnano} = 1.9013$ μJ, respectively. Analogous measurements performed for one-period energies absorbed by investigated samples when sinuosidal input voltages were applied give: $W_{Tsinmicro} = 0.8243$ μJ, and $W_{Tsinnano} = 0.6008$ μJ. A simple comparison of the determined energies leads to conclusion that during the corrosion tests the nanocrystalline copper layer absorbs about thirty per cent less energy than the microcrystalline copper layer. It can be also seen that the nanocrystaline copper layers exhibit worse corrosion resistance than the microcrystalline cooper layers, both being exposed to the same corrosive environment. This can be generally attributed to the unique microstructure of the nanocrystalline materials in which the grain boundaries may occupy as much as 50% of the material volume.
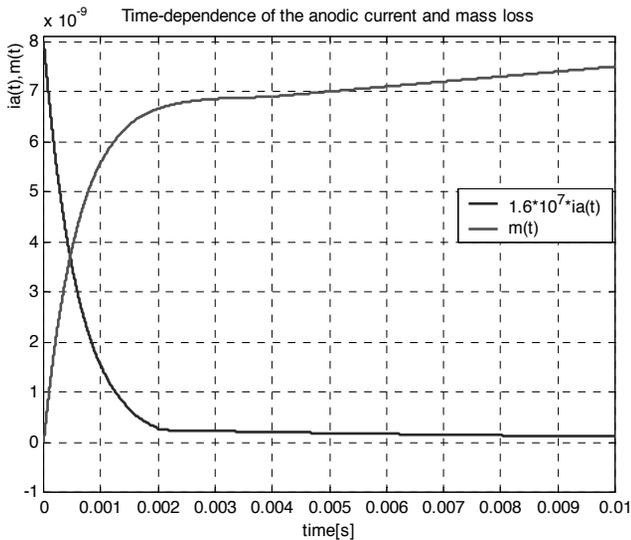
Fig. 10. Time dependences of the anodic current and mass loss of nanocrystalline copper thin-layers during the corrosion test

To estimate the corrosion rate, which is equal to

$$\chi = \frac{dm}{dt} = \frac{Ai_a}{zF} \tag{9}$$

where m is the weight loss of the metal, A is the atomic weight, i_a denotes the anodic current of the bath, z is the valence of the

electrolyte and F is the Faraday constant, we must measure the time-evolution of i_a. The plot of mass loss evolution of nanocrystalline copper thin-layers during the anodic time-interval of the corrosion test is presented in Fig. 10 where the instantaneous values of anodic current in significantly reduced scale are also shown. Taking into account (9) it is easily state that the changes in corrosion rate χ are proportional to that of the anodic current. The plots shown in Fig. 10 exhibit the dependence of the copper thin-layer corrosion on parabolic law of the mass loss with time run, namely

$$m^2 = k \cdot t \tag{10}$$

where k is a constant depending on microstructure of the corroded nanocrystalline copper layer and its thickness. The thicker the layer, the lower the mass loss. This appears as a fundamental aspect which governs the corrosion processes in nanocrystalline copper thin-layers produced by electrochemical method.

5. Conclusions

The presented considerations and measurements of the non-linear system representing corrosion processes of micro- and nano-crystalline copper surface thin-layers produced by electrochemical method are based on one-period energy approach. We have shown that the nanocrystalline copper layers exhibit inferior corrosion resistance compared to the microstalline copper layers even when both type of layers were produced by the same electrochemical process. The decrease of the size dimension of the material grains influences on the change of the morphology and topography of the produced copper surface layers as well as increases the velocity of the layer corrosion.

The one-period energy loops such that shown in Fig. 7 can provide new information which could not be obtained previously with traditional techniques such as measurement of the open circuit potential, the polarization resistance, recording of polarization curves and/or the electrochemical impedance spectroscopy [1-5]. It is evident that applying the above tools we can accurately predict all the factors that are responsible for corrosion. The corrosion behavior of nanocrystalline copper surface thin-electrodeposits in this investigation suggests that interactions of crystallites are modified by the presence of numerous grain boundaries and other structural defects that likely provide preferential attack sites upon exposure to a corrosive environment. By perturbing a corroding system with a distorted nonsinusoidal periodic voltage of suitable amplitude we do not need to perform a harmonic analysis of the current response.

The main feature of the present approach is the complete elimination of the harmonic analysis which in turn simplifies the appliances used to measure the corrosion rate. The method is based on the time-domain data only and there is no need to use the second domain of analysis such as, for example, the frequency domain used in the EIS method [1, 3, 17]. The use of the typical mathematical tools, such as the Fourier series and Fourier transforms [18] is avoided. This is very important result in this respect that copper surface layers manufacturers must continue to rise to the challenge by designing copper products with attributes that meet the more stringent requirements of the future.

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