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The continuous measurement of the potential during the process of the electrochemical copper setting

Abstract. The article presents usefulness of the computer modelling support through the remote measurements in the electrochemical technologies. Modelling of the electrolytic covers demands problem solution connected with current distribution in the electrolyte, electrodes shape and composition of the electrochemical environment in which the process takes place. The adapted methodology is used in the potential analysis and its influence on the covered layer structure and its topology. Classification of methods properties makes possibility of its evaluation concerning elasticity, usefulness in the galvanic process and its use in practice.

Streszczenie. W artykule przedstawiona zostanie przydatność komputerowego wspomagania modelowania poprzez przeprowadzanie zdalnych pomiarów w technologiach elektrochemicznych. Modelowanie powłok elektrolitycznych wymaga rozwiązania problemów związanych między innymi z rozkładem prądu w elektrolicie, kształtem elektrod i składem elektrochemicznym środowiska, w którym zachodzi proces. Zastosowaną metodologię wykorzystuje się do analizy potencjału i jego późniejszego wpływu na strukturę osadzonej powłoki i jej topologię. Klasyfikacja własności tej metody umożliwi jej ocenę pod względem elastyczności i przydatności w procesie galwanizacji oraz możliwość późniejszego zastosowania w praktyce. (Ciągły pomiar potencjału podczas procesu elektrochemicznego osadzania miedzi)

Keywords: electrocrystallization, electrode processes, copper surface layer, additive electrodes.
Słowa kluczowe: elektrokrystalizacja, procesy elektrodowe, powierzchniowa warstwa miedzi, elektrody dodatkowe.

Introduction

Contemporary engineering increasingly focuses its attention on covering non-metallic surface, such as ceramic, plastic or wood materials, with metallic coatings. This is connected with customers needs concerning more aesthetic and resistant external structure of products. This can be achieved through conducting certain technological processes in which an item can be covered with metallic layer during electrolyze. Nowadays, copper layers are of great interest. They are used for producing negative forms of injection moulding machines. The forms, filled with plastic in the production process, are used to produce numerous kinds of spare parts of domestic equipment. The moulding forms are used many times, therefore they should have high thermal and mechanical resistance. The crucial factor in this situation is the evenness of the metallic layer covering an item.

Electrocrystallization is an effective method used in modelling the covering layer. It enables making layers of pure metals, their alloys, composite or multilayer structures. Moreover, there is a possibility of creating crystalline structure of a different size of crystals: from micro- to nanometre. The electrocrystallization method enables us to influence the electrochemical process in a way which makes it possible to achieve good quality of the covering layer.

The objective of the research presented here was to show the influence of the electric factors on the achieved effects of the electrochemical process of copper coating. The research aimed at pointing the correlation between the crystalline structure of metal and particular components of the electrolyte solution. Moreover, the research concerned the potential distribution on the surface of the samples. This will allow to form the electric field intensity around the cathode by using appropriate screens. As a result, a regular metallic layer on a non-metallic object will be achieved.

Process of the electrochemical copper setting

Copper surface layers are made during the electrocrystallization process. This process is conducted in the composition which consists of electrolyser tilled with multicomponent solution. The basic component of this solution is the acid which includes the copper ions. Two electrodes – anode and cathode – are sunk in the solution. First of them – the anode, is made of the same metal as the setting layer (copper). The item whose surface is covered participate in the process as the cathode. An external power supply extorts the potential difference between electrodes and the current flow in the electrolytic environment. Well ordered movement of independent ions initiates a chemical process and a physical process. During the electrochemical process of the copper setting on the cathode, the reduction reaction of the two-positive copper ions to the atomic shape takes place [1]:

$$(1) \qquad Cu^{2+} + 2e \rightarrow Cu^0$$

On the other hand, opposite process occurs on the anode surface – reaction of the copper ions oxygenation to the two-positive ions as shown below [1]:

$$(2) \qquad Cu^0 - 2e \rightarrow Cu^{2+}$$

Both the above reactions take place with the same velocity, causing the dynamic equilibrium state, and constant content of the copper ions in the electrolyte solution is kept. The anode dissolution and copper setting on the cathode takes place during the electrocrystallization process. The thickness of the cathode is determined due to the following dependence (3):

$$(3) \qquad d = \propto \frac{MIt}{zF\rho A}$$

where: M – mol mass of the setting metal, z – number of the electrons which take part during the electrode processes (reduction and oxygenation), F=96485 C/mol – Faraday's constant, I – current between the electrodes, t – time of the surface setting, ρ – density of the material which sets on the cathode surface, A – field of the active cathode surface, α – dimensionless coefficient (cathode performance) [2].

The electrocrystallization is a process where, as a result of two processes – reduction and oxygenation taking place on the electrodes, metal sets on the cathode surface. This process consists of the following stages [2]:
- transport of the metal ions from the solution to the cathode surface,
- metal ions reduction on the cathode to the atomic shape,

- creation of the crystalline centres called crystalline embryos and their growth.

The correlation between the time duration of several stages has the influence on topology and morphology of the created metallic layer. Electrocrystallization process could be steered by many factors. Every factor will influence the stages of the new phase creation in a different way. We could reckon among: current density, electrolyte composition, electrolyte stiffness, solution temperature, solution stirring, process time. Current density and solution temperature cause electrosetting of the metal atoms on the surface. The electrolyte influences the coat creation with the suitable physical and mechanical proprieties. Individual components of the galvanic solution have different influence on the embryos creation and crystal growth. Submissive ions unload on the cathode and then result in the faster growth of crystal embryos – coarse-grained layer. Too fast acceleration of the reaction will cause the decrease in ion stiffness around the cathode. This will further result in worse quality of the achieved layers. Excrescences are directed to the electrolyte and, in consequence, the layers are rough and spongy. As the result of suitable stabilization of the reaction, the created layers are fine-grained. This type of layer is the most desired and applied in the industry [3].

Research procedure and achieved results

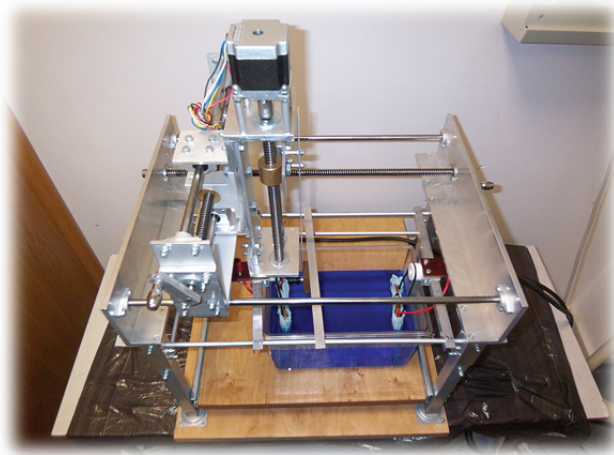In order to do the experimental part of the research, a laboratory stand was prepared (Fig.1).

Fig.1. General view of the electrolytic bath and a measuring arm steered by step motors

The stand consisted of bath tubs filled with 4 litres of liquid. To produce electrochemical layers of copper, two types of liquid electrolyte were used. First of them was the basic electrolyte of the following composition [1]:
- copper sulphate ($CuSO_4 \cdot 5H_2O$) – 200 g/litre,
- sulphuric acid (H_2SO_4) – 50 g/litre,
- hydrochloric acid (HCl) – 30 g/litre.

The second liquid was modified in relation to the first one by reduction by 10% the share in the composition of copper sulphate bath.

Three electrodes were immersed in the bath. Two anodes with dimensions of 100×90×10 mm and a cathode (a coated electrode) with dimensions of 60x40x8 mm (Fig.2). The anodes were located at a distance of 240 mm from each other, while the cathode was located in the middle of them. Two kinds of experiments were conducted. They concerned electrochemical setting by different value of current density 5 A/dm^2 and 2.5 A/dm^2.
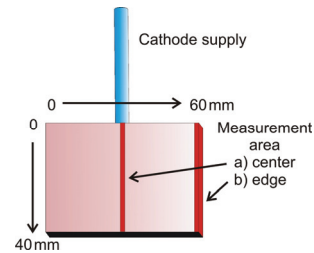

Fig.2. The way of dimension assigning and measuring places of the cathode.

The research was done with the use of data acquisition and specialized electrochemical process control system [4]. In addition the system was equipped with a carrying device of a potential probe. The device was built as an independent arm steered by step motors controlled by the microcontroller (Fig.3).
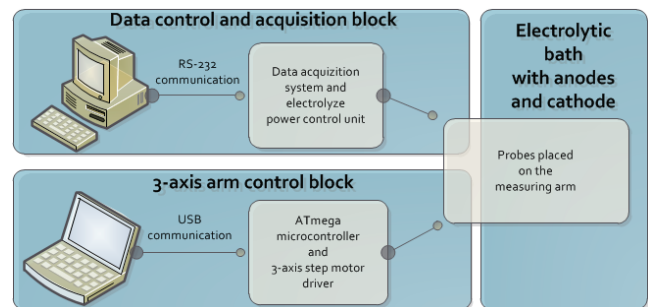

Fig.3. Block diagram of the computers controlling the electrolyze process.

The research was done with the measuring step of 1 mm of the potential on the cathode surface. The potential was measured in the vertical orientation, in the middle part and on the edge of the cathode (Fig.2).
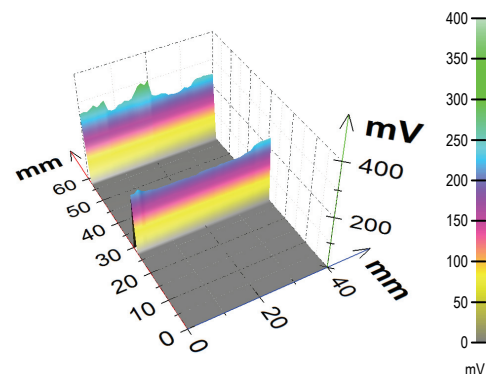

Fig.4. Potential distribution on the surface of the cathode in the case of supply of 2.5 A/dm^2 and with the enriched composition of the electrolyte.

During the electrochemical process the measurements of the potential on the sample surface were conducted (Fig. 4, 5, 6), with the use of the chloride-silver Ag/AgCl$_2$ electrode which was connected to the electrochemical process control device [4]. In addition to the potential measure probe in the electrolytic bath also contained probes to measure temperature and electrochemical factor K. Thanks to that it was possible to use the probe to measure and register values of the potential, the temperature coefficient, electrochemical coefficient and the current on the PC computer at the same time [4]. It is worth stressing that during measurement the potential meter functions as a voltmeter with high input resistance of the

order of 1012 Ω, potential range of ±2000 mV and accuracy of ±0.5 mV. Temperature readings were made with the accuracy of ±0.01°C. The conductance was measured with the use of the conductivity sensor with a fixed sensor of 0.5 cm^{-1} and the measuring range of 1 mS/cm to 100 mS/cm [4].
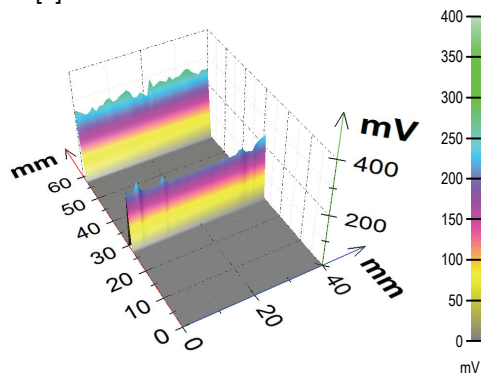

Fig.5. Potential distribution on the surface of the cathode in the case of supply of 2.5 A/dm^2 and with the basic composition of the electrolyte.
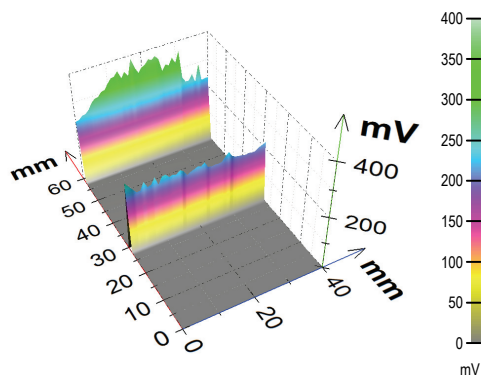

Fig.6. Potential distribution on the surface of the cathode in the case of supply of 5 A/dm^2 and with the basic composition of the electrolyte.
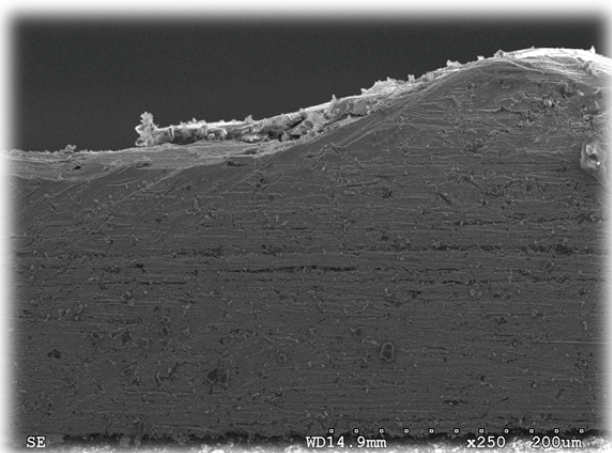

Fig.7. The scanning electron microscope Hitachi S-3000N view of the cathode cross-section. The sample was obtained from a cathode which was cut next to the measured edge.

The proximity of the edge has a direct connection with the different values of the potential. Visible roughness near the edge of the cathode confirms the theoretical foundation. As it can be observed in figure 7, the copper (darker colour) surface was distorted during the electrolyzing process. This was caused by the irregular potential distribution next to the cathode.

Conclusions

Measurements of the potential value next to the cathode can give us information about expected copper settings. As it can be observed in figures 4, 5, 6, the values of the potential are more irregular on the edges than in the centre of the samples. In cases presented in figures 4 and 5, the shapes of the potential distribution are comparable. In figure 6 the bigger value of current supply during electrolyzing process influenced the potential on the edge of the sample. This fact affected the final surface shape. During the research, the straight relationship of the potential value to the setting layer regularity was proven. Mutual correlation between potential gradient and the setting layer was confirmed. Violent changes of the potential value reduced the quality of the probe surface.

The following research will be focused on placing the appropriate screen, which can be useful for reducing potential in the places whose values are too high. The other way of working on the improvement of the electrolyzing process will be creating a fully automatic system of the electrochemical measurement connected with the screen movements.

Acknowledgements

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