MODELING OF THE FORMATION PROCESSES OF NANOCOMPOSITE COATINGS BY THE ELECTROCODEPOSITION

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Abstract. The coupled mathematical model of electrocodeposition process on the rotating cylinder electrode is presented. Low Reynolds k-ε model with Abe-Kondoh-Nagano damping functions is used to describe mass transport of electrolyte. The cathodic and anodic processes are described by the tertiary current distribution theory. Mass transfer of electrolyte ions is described by diffusion-convection equation and is studied throughout the volume of the electrolyte cell. The simulation of electrocodeposition of Cu-Al₂O₃ nanoparticles on rotating cylinder electrode of are presented. It is found that the unsteady diffusion layer is formed close to the rotating electrode surface. Also it was found that the sign of the zeta potential of nanoparticles has a decisive influence on the possibility of forming the composite coatings. The results of mathematical modelling are in good agreement with the experimental data.

1 Introduction

The metal matrix composite electrochemical coatings (MMEC) with improved and unique operational characteristics, such as wear resistance, cracking resistance, anti-friction properties, corrosion resistance, radiation resistance and high adhesion to the substrate can be produced by electrocodeposition (ECD) technics [1-5].

The MMEC are prepared from the suspensions, representing electrolyte solutions with additives of certain quantity of a superfine powder. The particles are adsorbed onto cathode surface in combination with metal ions during ECD process and the metal matrix composite coating is formed. MMEC consists of galvanic metal (dispersion phase) and particles (dispersed phase).

The particles of synthetic diamond, ceramic or organic materials can be used as dispersed phase [4]. The particles of metals that can't be electrodeposited from aqueous electrolyte also can be used as dispersed phase. Usually, the particles with diameter from 4 to 800 nanometers are used in ECD process. The concentration of suspended particles in electrolyte bath usually ranges from 2 up to 200 g/l, which is producing composites coating with 10±1 vol. % of embedded particles [1-5].

The metals as Cu, Ni, Co, Cr, Zn, Ag, Fe, Au, As and their alloys can be employed as metal matrix of composite coating. The particles of oxides Al₂O₃, ZrO₂, TiO₂, SiO₂ and Cr₂O₃, carbides SiC, WC, TiC, various allotropic form C, nitrides Si₃N₄, polymers polystyrene, PTFE and several various materials can be used as dispersed phase.

The advantages of EPD process are the lowering of waste material in contrast with spraying or dipping

technologies, the composite coating homogeneity of thickness and chemical composition even if the covered detail have a complex shape, the low-level of environment pollution [1]. The ECD process are not required the high operation temperature or pressure, vacuum or atmosphere of shielding gas. The ECD process realized at relatively low temperatures (in vicinity of ambient temperature), which is reduced to a minimum the undesirable chemical reactions or inter diffusion [5]. The thickness of coating can be accurately controlled by adjusting of applied current density. Nevertheless, there are several difficulties for example the agglomeration or sedimentation of nanoparticles and the nonuniformity on the nanoparticles concentration in the electrolyte.

The number of particles in the MMEC is a key factor which largely determines the properties of the composite coating. To produce the MMEC with specified physical and chemical properties it is necessary to define the main relation between the parameters of the ECD process and the properties of the MMEC. The determination of such empirical relationships, in addition to its purely practical significance, will allow developing the general production methods of the MMEC with required properties and the more accurately mathematical model.

It was found that there are several parameters that directly or indirectly effect on the properties of the MMEC. These parameters may be classified into three main categories (Table 1)

However, in practice it is difficult to reliably determine the influence of any single parameter on the particles content in the MMEC, since the influence of

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various parameters are often interconnected with each other.

Table 1. The system parameters.

Electrolyte parameters:	The particle parameters:	Parameters of electrodeposition:
<ul style="list-style-type: none"> • chemical composition; • pH value; • pollutants or additives; • life time of electrolyte. 	<ul style="list-style-type: none"> • particle material; • particle size; • shape of the particles. 	<ul style="list-style-type: none"> • concentration of the electrolyte; • current density; • electrolyte mixing; • temperature of the electrolyte.

Also, unfortunately, there are no experimental studies dedicated to determination the impact on the ECD process a series of above mentioned parameters.

2 ECD models

Historically the ECD process as an independent processing procedure was proposed in 1962 by Whithers [2]. Also, he made a first attempt to explain the mechanism of ECD process. He suggested that the particles suspended in the electrolyte solution may have a positive charge. Consequently, such particles are attracted to the negatively charged electrode (cathode) by electrophoretic forces.

In 1964 Martin and Williams [3] suggested that the particles move throughout electrolyte volume to the cathode surface due to the convective flow caused by agitation of the electrolyte. And then particles, located close to cathode surface, are mechanically entrapped by growing coating.

In 1967 Brands and Goldthorpe [4] suggested that van der Waals attraction force acts on the particles which were adsorbed on the electrode surface. This force keeps the particles on the surface during the time necessary for covering particles by metal matrix.

In 1972 Buzzard and Boden [5] suggested that the mechanism of ECD process can be divided into a series of sequential steps. On the first step the particles mass transfer to cathode surface occurs by the convection of electrolyte. After that the particles collides with the electrode surface and absorbs on it. Then the adsorbed particles are covered by the growing metal matrix.

In 1972 Guglielmi [6] proposed the mathematical model. The two successive steps were laid in the basis of this model. These steps were called weak and strong adsorption. The Guglielmi mechanism of MMEC formation is schematically shown in Figure 1.

During the first step there is only weak physical adsorption of the particles that have reached the electrode surface. On the surface of such particles there is a thin layer of adsorbed electrolyte ions which inhibits chemical reactions between the particles and the cathode surface.

The second step has an electrochemical nature. During this step the external electric field is applied to electrodes of electrochemical cell. The ions of the electric

Figure 1. Guglielmi mechanism of ECD process.

double layer around the particles are reduced on the cathode by the influence of electric field and metal matrix is growing around weakly adsorbed particles.

Guglielmi model was experimentally verified on various electrochemical systems like Ni-SiC, Ni-TiO₂, Cu-Al₂O₃, Cr-C, Ag-Al₂O₃, Cu-SiC и Cu-P.

In 1974 Kariapper and Foster [7] based on experimental data suggested that the ions adsorbed on the surface of the particles have a dual role in the process. On the one hand, they define the zeta potential of particles and thus effect on particles electrophoretic mobility and on the other hand they physically links particles with cathode surface by ion reduction at the cathode. Kariapper and Foster divided the process mechanism on the two consecutive steps as well as Guglielmi. The first step is the physical adsorption, the second step has an electrochemical nature. On this step the ions adsorbed on the particle surface are reduced to metal atom. The mechanism of MMEC formation according to the Kariapper and Foster model is schematically shown in Figure 2.

Figure 2. Kariapper and Foster mechanism of ECD process.

In 1983 Celis, Roos and Buelens [8] proposed the mathematical model that allows determining the amount of the embedded particles for electrochemical systems with a rotating disk electrode. Their model took into account the particle transport mechanism from the bulk electrolyte to the electrode surface. They mechanism of the ECD process is suggested to consist of 5 consecutive steps which are shown schematically in Figure 3.

Figure 3. The scheme of the ECD process by Celisa.

On the first step electrolyte ions are adsorbed onto surfaces of particles suspended in the electrolyte. Therefore, the electric double layer is formed around each particle. On the second step the particles are transferred to Nernst diffusion layer due to the electrolyte convective flows caused by electrolyte mixing. Further, on the third step the particles reach the electrode surface through diffusion mass transfer. On the fourth step the particles surrounded by double electrical layer of electrolyte ions are weakly adsorbed on the electrode surface. On the last fifth stage the weakly adsorbed particles are covered by a layer of growing metal matrix due to reduction of the metal ions located near at the cathode surface and adsorbed at surface of particles.

In 1987 Valdes suggested the model [9], which takes into account the mass transfer of the particles in the electrolyte by diffusion, convection and migration. Valdes suggested that the intensity of particles adsorption process related to the intensity of reduction of electrolyte ions adsorbed on the particle surfaces.

In 1988 Guo [10] proposed the mathematical model allowed to describe the particles mass transfer by using the similarity criterions, which are dimensionless values. The Sherwood similarity criterion was upgraded by the Guo to describe the mass transfer process of particles:

$$Sh' = Co Re^c Dm^d Sx^e Gq^f \quad (1)$$

where Sh' is the modified Sherwood number, Re is the Reynolds number of hydrodynamic system, Dm , Sx and Gq are the dimensionless numbers that characterize the parameters of the particle electrical double layer, the particle concentration in the bath, the incorporation process of the particles in the metal matrix, Co , c , d , e and f are the empirical coefficients which are used to fit the model to the experimental data.

In 1991 Eng upgraded the Valdes's model for a description of the ECD process on a rotating cylindrical electrode (RCE). In the Eng model the influence of the hydrodynamics was considered only by the thickness of the diffusion layer near the surface of the cathode, which is determined in accordance with the empirical expression:

$$\delta = 1.61 \cdot D^{1/3} \cdot \Omega^{-1/2} \nu^{1/6} \quad (2)$$

where δ is the thickness of diffusion layer, D is the diffusion coefficient, Ω is the angular velocity of rotating electrode and ν is kinematic viscosity of electrolyte.

In 1992 Fransaer proposed mathematical model [11] to describe the ECD process on a rotating disc electrode of non-Brownian particles, i.e. particles with dispersion is less than 10^6 m^{-1} . This model is based on a trajectory analysis of particles, including convection and gravity, electrophoretic, Coulomb and inertial forces. The codeposition process was separated into two steps: the reduction of metal ions and the coincident deposition of particles. The probability of particles codeposition depends on the balance of forces acting on a particle near the electrode surface (Figure 4). Fransaer thought that if the interaction force between the particle and the surface of the cathode, $F_{adhesion}$, is more than the total shear force, F_{shift} , then particle codeposited into metal matrix otherwise particle leave the cathode surface.

Figure 4. The forces acting on a particle near the electrode surface.

In 1993 Hwang and Hwang [12] proposed the more universal model than Celis model. They also suggested that the particle codeposition process is caused by reduction of electrolyte ions adsorbed on the particles. The intensity of which is determined by the parameters of the convective diffusion. In Hwang and Hwang model the mass transfer of particles and electrolyte ions are described by diffusion-convection equations and the calculated area is limited by the thickness of diffusion layer, within which the influence of convection is not considered.

In 2000 Vereecken proposed the mathematical model [13] to describe the ECD process of nanoparticles on a rotating disc electrode. The movement of the particles and the residence time with the electrode surface are considered in this model. The author investigated the mass transport of nanoparticles in the ECD process within the diffusion layer with convective diffusion equation. As in previous works Vereecken realize the mathematical simulation only within the Nernst diffusion layer.

In 2006 Huerta [14] proposed a mathematical model that describes the deposition of copper from sulfuric acid electrolyte with and without presence of chlorine anions and additives of polyethylene glycol nanoparticles. Author considered the adsorption process of polyethylene glycol nanoparticles and the reduction process of copper

ions on the electrode as the multistep reactions during which intermediate compounds are formed. To describe this process author used the diffusion-convection equation and the equation of conservation of mass, as well as electroneutrality condition of the electrolyte. However, author performed the mathematical modeling within computational domain only at 3 times greater than thickness of the diffusion layer. Simulation was made in a one-dimensional scale. The influence of hydrodynamics on the mass transport of nanoparticles and electrolyte ion within computational domain was not accounted.

In 2007 Lee and Talbot [15] based on models of Celis and Vereecken developed a mathematical model describing the ECD process of alumina Al_2O_3 nanoparticles with copper matrix on a rotating cylindrical electrode. Authors have changed the basic model algorithm Vereecken to describe the ECD process at RCE. However, as in the previous models the computational domain was a narrow region near the cathode surface with the thickness of diffusion layer.

In 2013 Eroglu published a paper [16] on the modeling of ECD process of MMEC of Ni-SiC on a rotating cylindrical electrode. Eroglu proposed a new mechanism for description of nanoparticles adsorption. But as in previous models the effect of electrolyte hydrodynamics on mass transfer of nanoparticles and ions was taken into account only by the thickness of diffusion layer.

In 2015 [17,18] authors of this paper proposed a new mathematical model of ECD process. The proposed coupled mathematical model of ECD process on the rotating cylinder electrode is presented. The model takes into account the electrolyte turbulent flow. Low Reynolds k- ϵ model with Abe-Kondoh-Nagano damping functions is used to describe mass transport of electrolyte. The cathodic and anodic processes are described based on the tertiary current distribution. Mass transfer of electrolyte ions is described by diffusion-convection equation and is studied throughout the volume of the electrolyte cell.

The results of hydrodynamic mathematical modeling of Cu- Al_2O_3 nanoparticles electrocodeposition on rotating cylinder electrode of are presented. For the first time ever, it is found that near the RCE surface the unsteady diffusion layer is formed by the electrolyte turbulent flow. Also, it is found that when the current density achieves their limit value the nonstationary diffusion layer with the variable thickness is formed near the electrode surface by the electrolyte turbulent flow.

The results of simulation were showed that the electrophoretic forces are considerably, and principal affected on nanoparticles content in composite coatings. Consequently, it is necessary not only takes they influence into account, but also utilized they influence on EPD process. The correct selection of the used electrolyte and surfactants can change the sign or value of the nanoparticles zeta potential.

The intensification of EPD process is occurred by changing parameters of hydrodynamic. The results of mathematical modeling are in good agreement with the experimental data.

3 Results of mathematical modeling

Simulation of copper electrodeposition with account of turbulent electrolyte flow was done at three studied rotational velocities (500, 1000, 1500 rpm).

The parameters of mathematical modeling corresponded to the experimental conditions [19]. While the simulation of electrocodeposition process of Cu- Al_2O_3 was done at three different concentrations of nanoparticles (39, 120 and 158 g/l) only at 1500 rpm. The computational time at all mathematical modeling was limited by 105 s. The voltage of electrochemical cell changes from the voltage of open circuit (+0.037mV vs SCE) to -0.5 V with a sweep rate of 5 mV/s during this time

The mathematical simulations of Cu electrodeposition confirmed that the hydrodynamics of electrolyte has a complex turbulent character at all studied rotation speed.

It is discovered that for all studied rotational speeds the concentration of Cu^{2+} ions close to surface of cathode is reduced to zero values when the cell voltage between the electrodes reaches -0.4 V relating to CRE. Therefore, at this cell voltage the applied current density is limited by the strong concentration polarization. Therefore, the diffusion mass transfer of Cu^{2+} ions to the cathode surface becomes the time-dependent step which determines the intensity of reaction of Cu^{2+} ions reduction at the cathode.

It is found for rotational velocity of RCE 500, 1000 and 1500 rpm that diffusion layer thicknesses are varied from 30 to 60, from 20 to 50, from 15 to 40 μm , respectively.

The rate of redox reaction achieves a limiting value because the diffusion mass transfer is limited. It should be noted that the oscillation of current density arise at all rotating speed of RCE when the diffusion mass transfer achieved a limiting value. The authors think that these oscillations can be explained by the turbulent flow near the cathode surface. The substitution by each other of zones with low (areas with blue color) or high speed (areas with red color) of electrolyte near the cathode surface leads to the appearance of current density oscillations (Figure 5). In more detail, the stagnant zones with small concentration of electrolyte ions are being appeared in some time point near to surface of cathode. Consequently, the diffusion layer with larger thickness is arisen too (Figure 6).

Figure 5. The substitution by each other of zones with low or high speed of electrolyte near the cathode surface

The simulation of ECD on the RCE was carried out. The results of modelling are presented on the figure 7. The results are point out that the flow of nanoparticles to the cathode linearly increases with increasing of applied current density. This means that the zeta potential of nanoparticles should be a positive.

Figure 6. The various diffusion layers at 1000 RPM.

Figure 7. The concentration of Al_2O_3 particles in the composite coating.

4 Conclusions

The EPD process is the advanced method for using in practice the nanotechnology to creation new materials and coatings with unique working characteristics. The mathematical modeling of EPD process is the significant and needful step in the way of explanation of composite coatings formation mechanism.

The experimental determination of hydrodynamic optimal parameters is the complex and time-consuming process. Consequently, it is necessary to simulate how the electrolyte hydrodynamic affects on the studied process before the start to produce it at real conditions.

The coupled mathematical model of electrocodeposition process of $\text{Cu-Al}_2\text{O}_3$ nanoparticles on the rotating cylinder electrode is presented. The mathematical model account the mass transfer of electrolyte ions and nanoparticles, electrode reactions, the adsorptions of nanoparticles and turbulent flow of electrolyte. Near the surface of the electrode the zones with a low velocity of the electrolyte are formed. Which

is significantly affected on the ions mass transfer to the electrodes surface.

It is found that the unsteady diffusion layer is formed near the electrode surface when the current density achieves the limited values.

The results of modeling confirm that the nanoparticles zeta-potential played the key role in the ability of composite coatings deposition. The sign of particles zeta-potential depends on the type of the crystal lattice of the particles (α or γ).

Next step of our works is the development the mathematical modeling of the ECD process using the methods of mesodynamics and molecular dynamics.

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