

ELECTROCHEMICAL OBTAINING OF COMPOSITE NICKEL LAYERS WITH INCORPORATED MULTI-WALL CARBON NANOTUBES

ЕЛЕКТРОХИМИЧНО ПОЛУЧАВАНЕ НА КОМПОЗИТНИ НИКЕЛОВИ СЛОЕВЕ С ВГРАДЕНИ МНОГОСТЕННИ ВЪГЛЕРОДНИ НАНОТРЪБИЧКИ

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Abstract: Electrolytically obtained nickel nanocomposite coatings distinguish with good physical-mechanical properties, decorative appearance and well expressed corrosion resistance. The present investigation shows the possibility to obtain stable electrolyte composition the latter including suspended multiwalled carbon nanotubes (MWCNTs). The electrodeposition conditions for receiving of bright and semi-bright nickel coatings and their composites are determined. Protective properties and decorative appearance of these layers are analyzed depending on the concentration, distribution and type of the used MWCNTs. Their influence on the cathodic and anodic behavior is investigated by using of cyclic voltammetry (CVA method). Scanning electron microscopy (SEM) demonstrates the shape and sizes of MWCNTs and the surface morphology peculiarities of the obtained coatings. Corrosion characterization in selected model medium is realized using potentiodynamic polarization curves.

Keywords: NICKEL COMPOSITES, CARBON NANOTUBES, ELECTROCHEMICAL CHARACTERIZATION

1. Introduction

In the last decade the carbon nanotubes (CNTs) are object of increased scientific and technological interest which follows from their unique chemical and physical properties first of all described by Iijima [1]. These nanotubes consist of similar carbon atom networks but demonstrate different characteristics due to their size, shape and other characteristic parameters. Some scientists investigated selected physical parameters of CNTs like bending stiffness [2], Young's modulus [3] etc. The discovery of CNTs led to their practical application in various devices the latter being characterized also with nano-sized dimensions – for example nanodiodes, nanotransistors etc [4,5]. It has been determined that the multiwalled CNTs – MWCNTs - are stiffest among this group of materials and they can be used for example in different atomic imaging instruments. CNTs have been also applied as reinforcements like fibers and for producing of nano-composites [6-8]. However, the data about their corrosion behavior in different aggressive media are relative scarce.

The aim of the present work is to obtain Ni-based composite coatings with incorporated MWCNTs from stable electrolytes and to characterize their corrosion behavior in a model acidic medium.

2. Experimental procedures

2.1. Nickel coatings

Nickel coatings are electrodeposited from a starting electrolyte (SE) containing $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ – 250 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – 60 g/l, H_3BO_3 – 30 g/l, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5,5 \text{H}_2\text{O}$ – 4 g/l, special selected surfactant benzylidimethylacryl (BZL) – 0,16 g/l at operating conditions as follows: temperature of 50 °C, current density values of 3 and 5 A/dm² respectively, circulation (700 rpm) of the electrolyte, Ni anodes, pH was adjusted to 4. Two additives are also used: saccharin – 1 g/l and butindiol – 0,2 g/l. The coatings with an average thickness of about 10 µm are electrodeposited on iron substrates the latter being plates with sizes 2 x 1 x 0,1 cm (whole working area of about 4 cm²).

2.2. Multi-wall CNTs (MWCNTs)

Commercially available MWCNTs with different sizes have been used during the investigations. Their characteristic dimensions are presented below:

MWCNTs of the type “A” have lengths in the range of 0,5 – 2 µm and diameters of about 20-30 nm.

MWCNTs of the type “B” distinguish with lengths in the range of 10 – 30 µm and diameters of 20-30 nm.

Both types MWCNTs are added to SE as powders in different concentrations (0,15 – 0,3 – 0,5 g/l, respectively) in order to find the optimal one.

2.3. Nickel composite coatings

Nickel composite coatings are obtained from SE with addition of the MWCNTs types described above. Both latter have been added after preliminary treatment with the special selected surfactant – BZL - aiming the wetting the MWCNTs, ensuring their stability in SE and also more uniform incorporation in the metal matrix. In addition, SE was treated in ultrasonic bath during 10 minutes before the electrodeposition of the composites. It was previously established that the direct mixing of both carbon nanotubes' types with SE led to their fast agglomeration, precipitation and sticking on the walls of the cell.

2.4. Sample characterization

2.4.1. A scanning electron microscope JEOL JSM-6390, Japan is used for the investigation of the surface morphology of both pure and composite nickel electrodeposits as well as for registering of the distribution, shape and sizes of the incorporated MWCNTs.

2.4.2. Cyclic voltammetry (VersaStat 4, Ametek PAR device) is applied to investigate the influence of the suspended MWCNTs and of the additives on the cathodic and anodic processes.

2.4.3. Potentiodynamic polarization curves

Potentiodynamic polarization investigations (linear sweep polarization) for both nickel and its composites are carried out using VersaStat 4 device by applying polarization steps of 1 mV/s in three electrode cell with Luggin capillary, platinum plate as a counter and saturated calomel electrode (SCE) as a reference electrode.

2.5. Corrosion medium

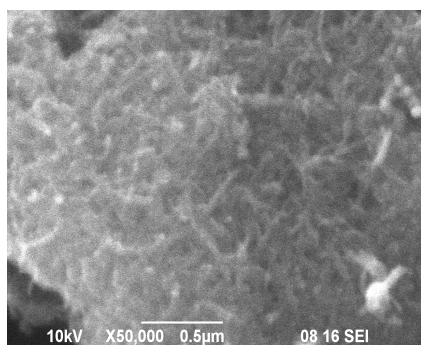
A free aerated model corrosion medium consisting of 0,5M Na_2SO_4 and 0,5M H_3BO_3 at pH 2 at ambient temperature of about 20 °C was used for the investigations.

3. Results and discussion

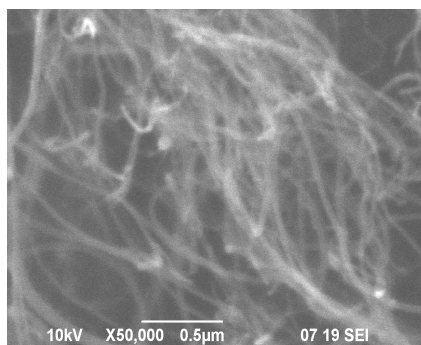
3.1. SEM studies

The results obtained from the SEM investigations of powdered probes are presented in Fig. 1. It is clearly evidenced that the

applied MWCNTs types are interwoven (especially in the case of the type “A”) and it is difficult to separate them.



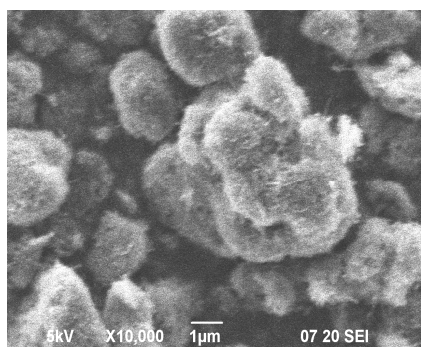
Type “A”



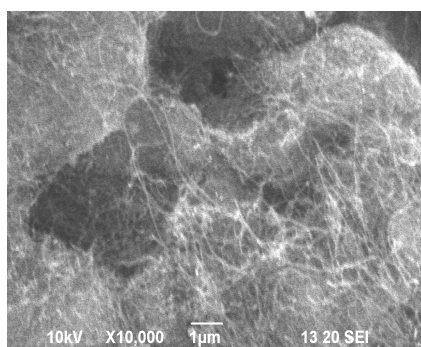
Type “B”

Figure 1. SEM images of powdered MWCNTs

It must be noted that if the preliminary treatment with the surfactant BZL of the powdered nanotubes is not applied the electrodeposition conditions are indefinite. In such a case the MWCNTs concentration in the electrolyte decreases since part of them stick on the walls, agglomerate or precipitate on the bottom.



Type “A”

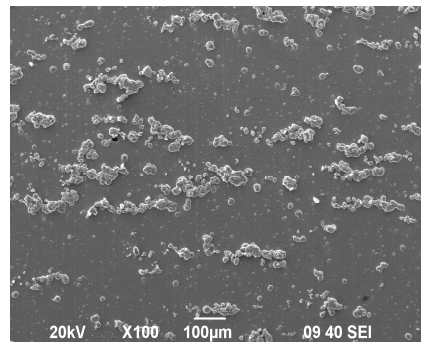


Type “B”

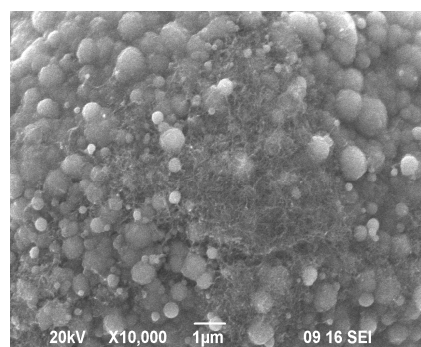
Figure 2. SEM images of MWCNTs from evaporated solution after treatment with BZL

The SEM images (after evaporation of the solutions) of the nanotubes treated with BZL and then suspended in SE are shown in Fig. 2. The shorter MWCNTs are still interwoven (although not in the same degree like the powdered probes) which will lead to their uneven distribution in the electrolyte. It can be supposed that they will be incorporated in the metal matrix predominantly in agglomerated form.

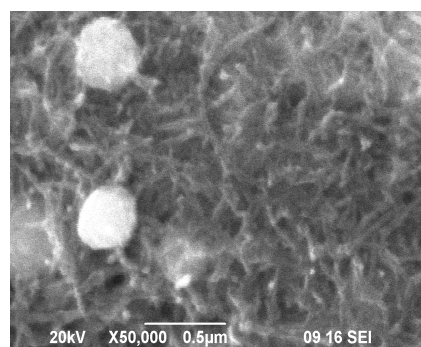
Contrary to this the longer MWCNTs of the type “B” seem to be separated to a definite degree (similar to the powdered probe) which will ensure more even distribution in SE and in the metal.



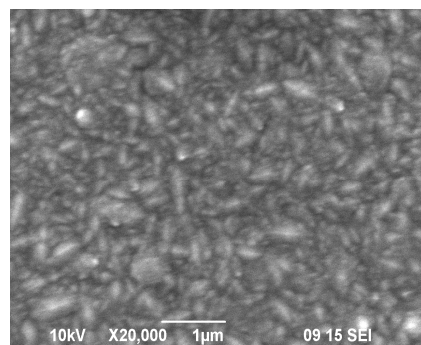
A



B



C



D

Figure 3. Surface morphology of the nickel composites at different magnifications

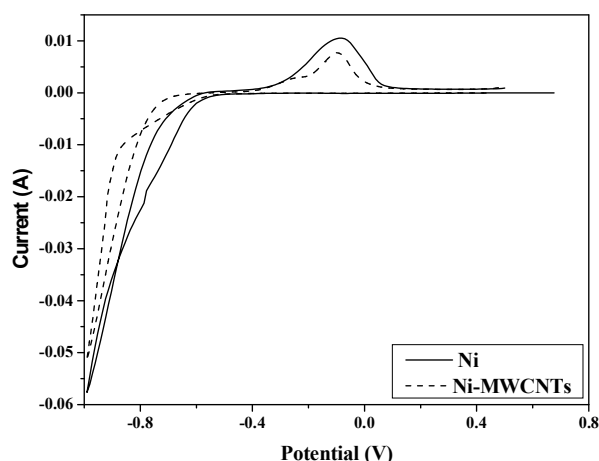
The surface morphology at different magnifications of the obtained pure Ni and composite coatings can be observed from Fig. 3. In general, it is evidenced that different zones appear – some of them include MWCNTs (mainly in the form of interpenetrating net – Fig. 3B and 3C) while the rest seem to be pure metallic parts – Fig. 3D). This unhomogeneity of the surface is better demonstrated at lower magnifications – Fig. 3A.

The nickel composites obtained from SE with MWCNTs concentration of 0,5 g/l are rough and with insufficient good decorative appearance especially when the shorter nanotubes are incorporated in the metal matrix. The coatings obtained at cathodic current density value of 3 A/dm² are smoother compared to the composites obtained at 5 A/dm².

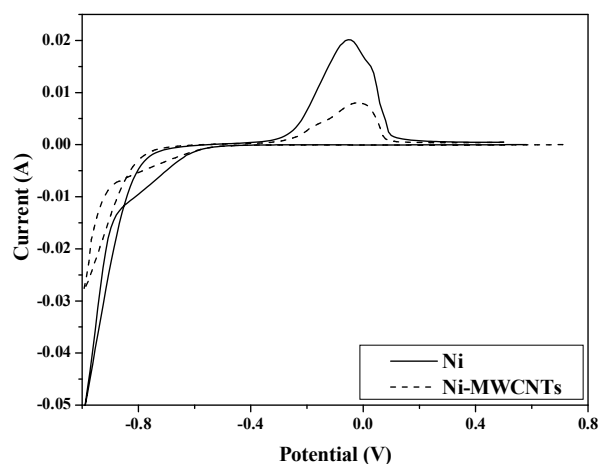
When saccharin and butindiol are added to SE the coatings obtained become bright and with very good decorative appearance but some of them (obtained at MWCNTs concentration of 0,5 g/l) are still rough and uneven. This was to reason to continue further investigations mainly with SE containing 0,3 g/l of the carbon nanotubes. The EDX analysis of the coatings reveal that the carbon concentration on different surface areas is very irregular - in the wide range between 0 and 17 wt.%.

3.2. CVA investigations

The results obtained about the influence of MWCNTs on the cathodic and anodic behavior using cyclic voltammetry tests are presented in Fig. 4(A, B).



A



B

Figure 4. Influence of MWCNTs on the anodic and cathodic processes: A – SE; B – SE with saccharin and butindiol

Figure 4(A) shows the results concerning the starting electrolytes for Ni and Ni-composite (MWCNTs – 0,3 g/l). It can be registered that the addition of MWCNTs strongly polarizes the cathodic process with about 250-300 mV. This phenomenon follows most probably from the blocking of the surface by the carbon nanotubes and the follow-up difficulties in the electrodeposition process. Additionally, the conductivity values of the metal and MWCNTs are also different.

In the anodic part of the curve it can be observed that both peaks (of the pure metal and of the composite one) are placed practically at one and the same potential value. This means that no changes in their structure (fcc) appear after the incorporation of the nanotubes. However, the peak of the composite coating is weaker expressed which is a sign that the electrodeposition process is hampered to a certain degree – the deposition rate in that case is lower compared to the pure metallic coating. It can be supposed that MWCNTs being in general insoluble in that medium tear of and fall in the solution without any direct participation in the dissolution process.

Figure 4(B) presents the CVA investigations in the starting electrolytes containing saccharin and butindiol. The influence of MWCNTs on the cathodic process is qualitatively the same as in the previous case (Fig. 4A). The presence of saccharin and butindiol also leads to increase of the overvoltage of deposition process in the cathodic region.

It can be concluded that MWCNTs polarize the cathodic processes of both starting electrolytes. This effect is stronger expressed in the case when saccharin and butindiol do not present in the solution. Both additives also polarize the electrodeposition process in the absence of MWCNTs due to their adsorption on the surface but their influence is weaker compared to this of the nanotubes. The influence of both additives in SEs with suspended MWCNTs is not very significant compared to the case when the carbon nanotubes do not present in the electrolyte.

3.3. Potentiodynamic investigations

The peculiarities of the electrochemical and anodic behavior of the pure nickel and nickel composite electrodeposits in the model corrosion medium used are presented in Figures 5 and 6.

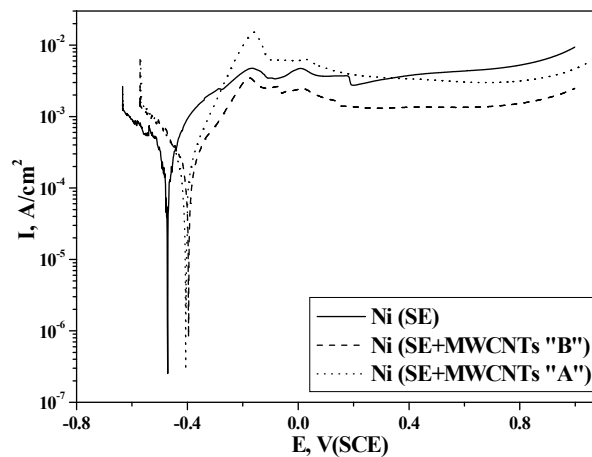


Figure 5. Potentiodynamic curves of pure nickel and its composites (obtained from SE) in model corrosion medium

Figure 5 shows that the pure nickel coating from SE without additives (only the surfactant BZL presents in the solution in that case) has corrosion potential more negative than the composite ones – the difference is about 70 mV. This means that the incorporated MWCNTs make the layer more noble ensuring better protective characteristics. In the anodic part of the potentiodynamic curve the composite with incorporated nanotubes of the type “B” demonstrates current density values from 1,5 up to 3 times lower

than these of the pure metal. This behavior and increased protective ability is observed during wide potential area – from about -170 mV up to 995 mV. Most probably, this phenomenon follows from the combined protective action of the metallic nickel and MWCNTs the latter being practically insoluble in the model corrosion medium used.

The other applied carbon nanotubes of the type “A” show similar results although their anodic current density values are greater compared to these registered for the coating with MWCNTs of the type “B”. In addition, there is a zone of potentials (from about -280 up to 320 mV) where this coating dissolves more active under anodic polarization than the pure nickel. The most probable reason for this could be the more intensive tearing off the agglomerated nanotubes during the corrosion attack which leads to opening of new fresh metallic parts and increase of the rate of the dissolution process.

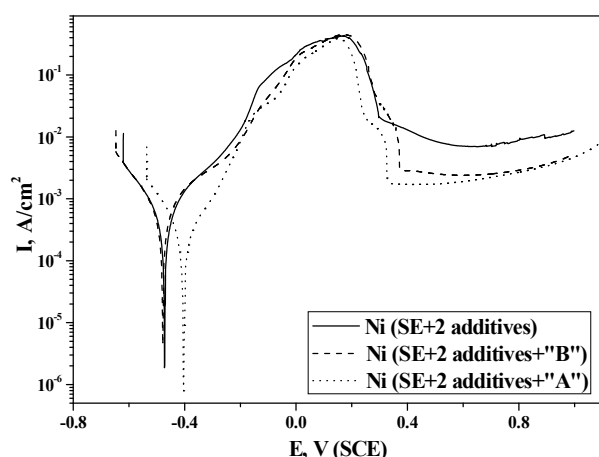


Figure 6. Potentiodynamic curves of pure nickel and its composites (obtained from SE and both additives) in model corrosion medium

Figure 6 demonstrates the potentiodynamic curves of nickel based coatings obtained from SE with the two applied additives – saccharin and butindiol – and MWCNTs (concentration 0,3 g/l). In that case the anodic processes are more intensive compared to the previous case which is related to the sulphur containing additive saccharin the latter ensuring in general better decorative appearance of the layer but lower protective ability.

In addition, the coatings with incorporated carbon nanotubes of the type “A” have to a certain degree better characteristics in that case – their corrosion potential is shifted to positive direction with about 70 mV which means it is more noble. All the coatings investigated present a passive zone in the potential area between 300 and 950 mV which is a sign that they are susceptible for passivation at these conditions. This zone is better expressed in the case of the composites most probably as a result of the embedded MWCNTs.

4. Conclusions

The investigations of nickel and nickel based composite coatings with embedded carbon nanotubes demonstrated that the latter lead to increase of the corrosion resistance and protective ability in acidic model medium at conditions of external polarization.

These characteristic parameters deteriorate when saccharin and butindiol are added to SE most probably as a result of the sulfur presenting in saccharin. Nevertheless, these coating types can be used as individual protecting layers but also as underlayer in multilayer systems.

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