
Nanomaterials Produced by Electrocrystallization Method

6

Maria Trzaska and Zdzislaw Trzaska

Contents

Introduction.....	136
Fundamentals of Electrocrystallization Processes.....	138
Electrocrystallization of Nanostructured Copper.....	141
Control of Nanocrystalline Copper by Current Waveforms.....	141
Control of Nanocrystalline Copper Structures by Compositions of Electrolyte Solutions.....	144
Electrocrystallization of Nanostructured Nickel.....	151
Electrocrystallization of Nanostructured Composites.....	154
Nanocrystalline Composites with Nickel Matrix.....	155
Nanocrystalline Composites with Nickel Matrix and Disperse Phases Built from Carbon.....	159
Nanocrystalline Composites with Copper Matrix.....	163
Summary and Conclusions.....	165
References.....	166

Abstract

This chapter presents the possibility of forming nanocrystalline structure and design properties of materials by electrocrystallization method. The basis of the electrocrystallization process and factors determining the result of the processes under considerations are presented. The electrocrystallization method was used for producing metal materials Cu and Ni and nanocrystalline structure of the nanocrystalline composite materials with matrix Cu, Ni, and nanosized particles

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M. Aliofkhaezei, A.S.H. Makhlof (eds.), *Handbook of Nanoelectrochemistry*,

DOI 10.1007/978-3-319-15266-0_16

135

of the disperse phase in the form of Al_2O_3 , Si_3N_4 , and CNTs. Methods of X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were applied for the complete characterizations of the dispersion phases and the structure of the produced materials. The results of these studies are presented in the form of the corresponding images and graphs.

Keywords

Electrocrystallization • Nanomaterials • Nanocrystalline composites • Nanocrystalline surface layers • Doped graphene nanocrystalline layers

Introduction

The rapid development of technology and the increasing requirements of the final products force researchers not only to new designs of appliance's structures but also to the search for new materials with improved performance characteristics. Tasks posed for materials used presently in the practice are becoming more and more expressive in terms of better adapting them to the special technological characteristics and reducing their wear and tear. Thus, the basis for rapid technological progress are intensive studies aimed on the development of new materials, which should be characterized by much better performance parameters compared with those being currently in use. Progress in science and engineering at the nanoscale appears now as a critical factor for society's security, prosperity of the economy, and enhancement of the quality of life. Nanotechnology is focusing on the formation of purposeful materials, devices, and systems through the management of matter on the nanometer scale and the utilization of new occurrences and attributes at that scale. Rapid and continued advancement in the field of nanotechnology has accelerated the demand for specific professional knowledge and skill. Recently determined research and development for targeted nanoscience and nanotechnology have resulted in discovery and application now culminating in marketable products and new commercial applications, among other things, graphene. Because such products, for instance, sunscreens, cosmetics, clothing, upholstery, paint, bodywork of vehicles, and computer components, utilize nanotechnologies, it is not strange at present as well as in the near future that nanotechnology will infiltrate consumer products holistically.

The enormous potential for use in the development of new properties of the material lies in the possibility of conscious control of its structure at the nanometric scale. Presently, it is well known, that material properties, both mechanical, electrical, thermal, and chemical, are the result of the phenomena occurring in structures of nanometric size. Nanometric structure materials have particularly advantageous properties and are an effective alternative to conventional materials. Material engineers have just started to produce complex nanomaterials, and there is still a long way to go to reach the natural "best practice" examples in terms of precision, functionality, and efficiency of production. Therefore, a solution-based approach to

innovation in material research seems to be more rewarding and beneficial, for the companies as well as for the scientists and engineers who develop and produce such materials on the prototype level. Diverse range of nanomaterials is extensive and includes, among other things, functional materials, hierarchical materials, functional gradient materials, responsive materials, materials with an expiration date (i.e., they only work for a certain amount of time), and biodegradable materials [14]. A short summary of previous works in the subject is given in Table 1.

An efficient method of preparation of nanocrystalline materials is the electrochemical method using electrocrystallization processes stemming from reactions of oxidation and electrochemical reduction. Electrocrystallization method gives the ability to control the structure of the gauge area, which is a great potential for use in the development of new material properties [15]. This method is exceptionally suitable for preparations of specific materials, mainly the protective layers, and in the near future may be more effective than previously involved methods in surface

Table 1 Topics in electrochemical manufacturing at the nanoscale

Topics	Area of study	References
Nanostructures in electrochemistry	Metal clusters, wires, functionalized layers	[1, 2]
Electrocrystallization technology	Processes stemming from reactions of oxidation and electrochemical reduction, development of new material properties, preparations of specific materials, conscious control of the structures in the nanometric areas, expensive equipment not required	[3–6]
Precision through electrochemistry	Precision sensing and ultrasensitive sensors, control at nanoscale, transparent electronics	[7–9]
Nanoartifacts	Fuel cells, batteries, photovoltaic generation, electronic and computing devices, lighter parts for transport vehicles	[2, 10, 11]
Scanning electron microscopy techniques	Characterization of local structures and properties of surfaces and interfaces, modification on the micro- to subnanoscale	[1, 6, 12, 13]
Potentiometric investigations	Light-addressable potentiometric sensors, cytosensor microphysiometers, integrated biosensors, potential Donnan sensors	[14, 15, 28]
Biomedical applications	Fluorescent biological labels, drug and gene delivery, biodetection of pathogens, cancer therapy, detection of proteins, probing of DNA structure, phagokinetic studies	[15, 16]
Modeling and computer simulations	Large molecules of technological interest, supramolecular structures in interaction or adsorbed at surfaces, and bulk systems for which nanostructural units can be clearly identified, self-assembly and self-recognition of nanoscale objects, understand and characterize the behavior of nanostructures	[17, 18, 29, 31]

modification technologies of known materials, as well as newly produced materials.

These layers can be used together with their grounds or separated from them. Taking into account the specificity of materials electrolytically produced, it is possible that the formation of such a structure of the material and its properties cannot be obtained by other technologies. The possibility of conscious control of the structures in the nanometric areas leads to the production of useful materials with new properties and overcomes previously insurmountable barriers to the development of technology. Understanding of biological processes on the nanoscale level is a strong driving force behind the development of nanotechnology.

This chapter aims at mapping new frontiers in emerging and developing technology areas in nanomaterial research and innovation. Section “[Fundamentals of Electrocrystallization Processes](#)” is devoted to the presentation of fundamentals of electrocrystallization processes and parameters influenced by the final quality of the resulting products. In section “[Electrocrystallization of Nanostructured Copper](#),” essential problems concerning the electrocrystallization process of nanostructured copper products are presented. Section “[Electrocrystallization of Nanostructured Nickel](#)” is aimed on descriptions of electrocrystallization processes of nanostructured nickel products. Problems involving the application of the electrocrystallization method for producing nanostructured composites are included in section “[Electrocrystallization of Nanostructured Composites](#).” Conclusions and final remarks are presented in section “[Summary and Conclusions](#).”

Fundamentals of Electrocrystallization Processes

Electrocrystallization method offers ample opportunities to shape the structure and properties of materials so produced (Table 1). It is currently the most efficient method of producing nanocrystalline materials. The attractiveness of the method for the electrocrystallization of materials is, among other things, in the fact that it does not require expensive equipment. It eliminates a dilemma, whether to master technologies of materials using expensive and complicated equipment or cheap, not demanding financial outlays, but only appropriate knowledge of the physical and chemical processes. Recently, much interest in electrocrystallization of nanocrystalline materials has evolved due to (i) the low temperatures involved; (ii) the ability to coat geometrically complex or non-line-of-sight surfaces of porous products; (iii) the ability to control the thickness, composition, and microstructure of the final product; (iv) the possible improvement of the substrate/coating bond strength; and (v) the availability and low cost of equipments [3].

A simplified scheme of appliances being widely applied as electrochemical reactors and automated nanostructured materials' processing equipments is presented in Fig. 1. Charged electrodes being able to carry out chemical reactions are in use for realizations of electrocrystallization processes [13].

Current directions of research conducted on the process for producing nanostructured materials by crystallization concentrate on the manufacture of materials with

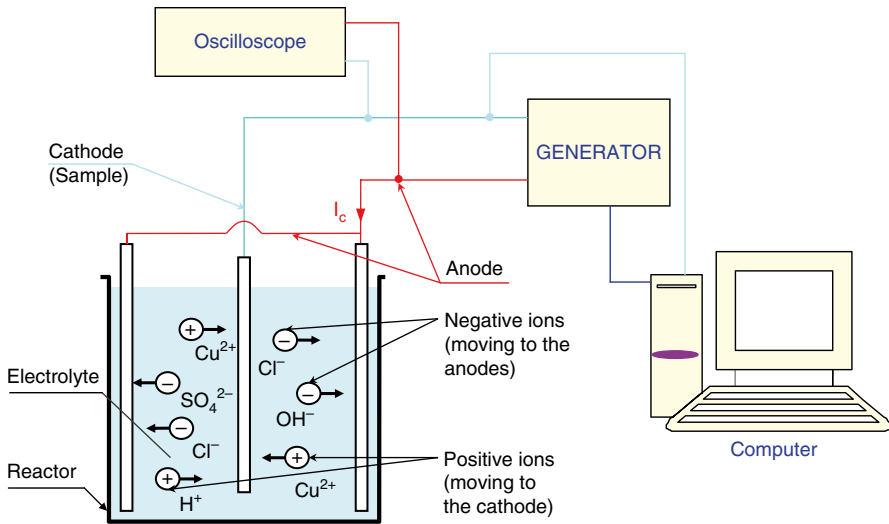


Fig. 1 Simplified scheme of appliances for electrocrystallization of nanocrystalline materials

different chemical and phase compositions and different structures which provide adjustment of their properties to the high demands on working conditions. By choosing the type and composition of the electrolyte solution, and the process parameters such as type and density of the current, temperature, and time duration of the process, can be designed a variety of materials meeting the features in the art.

Several application-specific types of electrocrystallization processing systems, each with its own specific requirements, have been produced up to date. Various waveforms of the current supplying the electrocrystallization reactor are shown in Fig. 2. All major process studies concentrate currently around the PPRC electrodeposition technology and the general metal finishing products (Fig. 2b–e). Pulse current electrocrystallization is able to produce layers with more uniform particle distribution and better surface morphology than those obtained under direct current [9].

By electrocrystallization method can be prepared a variety of metals, metal alloys, and composite materials. Especially great potential resides in shaping the properties of composite materials. Composite materials prepared by this method can be formed with a metal matrix, and a disperse phase may be constituted by different materials, for example, other metal (W), ceramics (Al_2O_3 , Cr_2O_3 , Si_3N_4), polymer (PFE), or carbon (graphite, nanotubes, graphene). The combination of two different materials, disperse phase and matrix metal, allows the control of produced material properties in a fairly wide range, which enables the formation of a material satisfying efficiently various functions in practice [5, 10, 19].

Realization's efficiency of simultaneous deposition of metal and nonmetallic disperse phase in the same process and the electrochemical reduction of the quality of the material will depend on such factors such as the nature and composition of the electrolyte solution, the process parameters (concentration, pH, temperature,

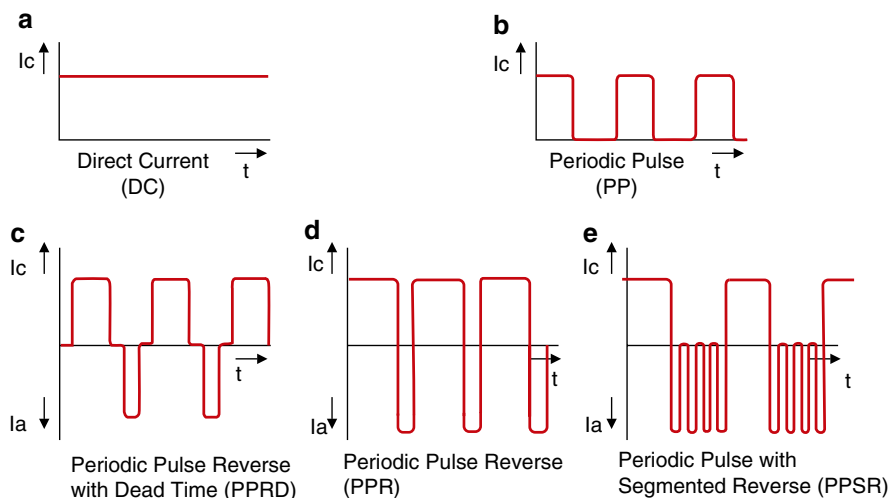


Fig. 2 Current waveforms for electrocrystallization processing

stirring, current conditions), and the chemical nature of the grain structure built in nonmetallic disperse phase, chemical nature, and content of various additives, as well as the quality of the substrate material and the condition of its surface. The low processing temperatures minimizes crystallite interdiffusion, while the high selectivity of electrocrystallization process allows uniform modification of surfaces and structures with complicated profiles. All of these factors must be taken into account when designing a composite material to be properly (i.e., as expected) working under determined conditions. Such a large number of parameters, which influenced the control of electrocrystallization processes and affected the quality of the manufactured material, give on one hand a great flexibility in its ability to modify constituted material but on the other hand present a big challenge for the proper and optimal choice of their selection. This requires a thorough diagnosis of the mechanisms of these complex processes, as well as their practical implementation of parameters. So, the set of the parameters of the implementation of such processes in the production environment and the relationships between these parameters and the structure and properties of the produced nanocrystalline material requires complex experimental research and in-depth analysis [1, 4, 20].

The parameters of the current supplying electrochemical reactor and its density limit the electrode redox processes on the surface of the electrodes. In contrast, the composition of the electrolyte solution can control the rates of the two competing processes of forming a new phase resulting from the electrocrystallization and decides on the size of grains of the deposited material.

While the applications of nanocrystalline materials are beginning to play a greater role not only on quantitative considerations as quality, electrocrystallization method could be competitive in relation to other methods. So far, the main obstacle in the application of electrocrystallization technology for receiving materials on a larger

scale was undoubtedly the complexity and synergistic influence of the preparation of raw materials in accord to the desired properties of final products. It seems, however, that in the era of modern techniques of analysis of processes during the material production, including electrocrystallization process, it will be possible to know precisely than ever the relationship between structure and properties of materials and their resulting parameters [7]. Applying the electrocrystallization method nanocrystalline materials from pure metals Cu, Ni, and Co and composite materials nanocrystalline Ni/Al₂O₃ and Ni/Si₃N₄ were prepared. Appropriate chemical composition of electrolyte solutions and process parameters of electrocrystallization process capable of producing nanocrystalline materials were established. Produced nanocrystalline materials exhibited crystallites with sizes ranging from 10 to 50 nm, depending on the nature and chemical composition of the electrolyte solution, temperature, degree of agitation, if used, and other parameters of electrocrystallization processes. Taking into account potential applications of nanocrystalline materials, the pursuit of deposit *uniformity*, especially thickness uniformity, has been a technical imperative for suitable controlling every produced nanocrystalline material [21, 27].

Studies of the properties of the produced materials including corrosion resistance and microhardness were performed using the mathematical modeling and scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

For comparative purposes, tests were also subjected to the same kind of materials with microcrystalline structure produced also by electrocrystallization method.

Electrocrystallization of Nanostructured Copper

In the present section, an effort has been made to examine various modes of nucleation and growth of nanostructured copper electrocrystallization with direct and pulse periodic currents. The performed studies focus on nanocrystalline bulk copper deposits and composite surface layers with grain sizes smaller than 100 nm because such materials attract presently high technological and scientific interests due to their improved electrochemical, mechanical, and physical properties being useful for extensive applications. The attention is focused on nanocrystalline structures, surface roughness, hardness, and process parameters leading to major differences in final products.

Control of Nanocrystalline Copper by Current Waveforms

As we have already shown previously [13] copper electrocrystallization on high-end thin layers and on other product in cutting-edge technologies was at the very limit of what DC processes could achieve, and it turned out PPR technology could go beyond that. By varying the duty cycle, that is, on time/on time + off time, changes in electrocrystallized structure, mainly crystallite size, can be achieved, because of forced nucleation during each new cathodic pulse. In an acid solution, the cation Cu²⁺

associates with the anion SO_4^{2-} to form copper sulfate. At the cathode, the Cu^{2+} is reduced to metallic Cu by gaining two electrons. The result is the effective transfer of Cu from the anode source to a cathode plate. Current densities, cathodic (on time) and anodic (reverse on) times, as well as solution concentration and temperature can be varied independently, forming a fivefold parameter space [9].

The pulse current density, i_p , is divided into the capacitive current density, i_C , and the faradaic current density, i_F , as follows:

$$i_p(t) = i_C(t) + i_F(t) \quad (1)$$

The capacitive current density is related to the double layer potential by

$$i_C(t) = C_{dl} \frac{dv_1(t)}{dt} \quad (2)$$

where $v_1(t)$ is the potential drop within the double layer and C_{dl} is the capacitance of double layer. Since the applied current density is low, the relationship between faradaic current and overpotential can be assumed in the form

$$i_F(t) = \frac{v_1(t)}{R_{ct}} \quad (3)$$

where R_{ct} denotes the charge transfer resistance.

Combining Eqs. 1, 2, and 3 gives

$$C_{dl} \frac{dv_1(t)}{dt} + \frac{v_1(t)}{R_{ct}} = i_p(t) \quad (4)$$

The copper ions are firstly adsorbed on the electrode and reduced to copper adatoms in two steps. The first term on the left of Eq. 4 represents the reaction of copper ions disproportion, and the second describes the dissolution of metal. Similarly to $v_1(t)$, the response of the potential drop $v_2(t)$, corresponding to metal dissolution, is given by

$$C_{psd} \frac{dv_2(t)}{dt} + \frac{v_2(t)}{R_{sd}} = i_p(t) \quad (5)$$

where C_{psd} and R_{sd} denote the dissolution capacitance and resistance, respectively.

In this way the total surface overpotential $v(t)$ is determined by

$$v(t) = v_1(t) + v_2(t) \quad (6)$$

Early treatments correctly predicted that since the peak current densities in pulse electrocrystallization were higher than the time-average-equivalent DC current densities, the nonuniformity would be larger, according to

$$W_t = \frac{2.303RTk}{jZfL} = \frac{R_t}{R_e} \quad (7)$$

were R_t and R_e denote the charge transfer resistance and the ohmic resistance, respectively, with k as solution conductivity and L as length.

Under influence of PPR electric current, the following changes of ion concentrations take place:

During the current on interval, we have

$$c(t) = c_0 + c_j \left[1 - 8\pi^2 \sum_{m=1}^{\infty} A_m \right], \quad (8a)$$

with

$$A_m = \frac{1}{(2m-1)^2} \exp \left[\frac{\pi^2}{4} (2m-1)^2 a (t-PT) \right] K, \quad (8b)$$

$$K = \frac{1 - \exp \left[-\frac{\pi^2 a}{4} (2m-1)^2 \tau \right]}{1 - \exp \left[-\frac{\pi^2 a}{4} (2m-1)^2 T \right]}. \quad (8c)$$

where c_0 is the concentration of the electrolyte solution; c_j the parameter dependent on current amplitude I_p , diffusion layer thickness d , Faraday constant F , rate n of ion oxidation, and diffusion coefficient D ; P the number of current cycles; and T the absolute temperature.

During the current off interval, we obtain

$$c_p(t) = c_0 + c_j \left[8\pi^2 \sum_{m=1}^{\infty} A_{mp} \right] \quad (9a)$$

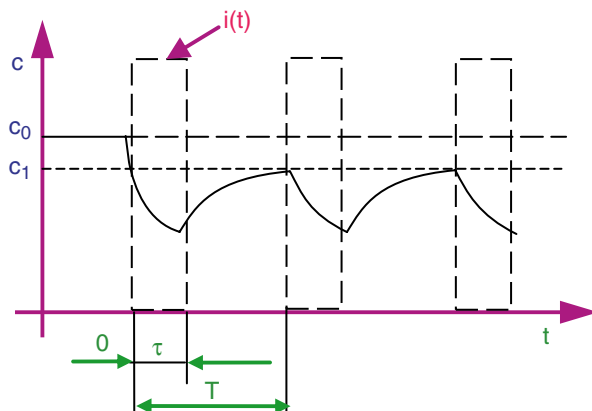
with

$$A_{mp} = \frac{1}{(2m-1)^2} \exp \left[\frac{\pi^2}{4} (2m-1)^2 a (t-PT) \right] K_p, \quad (9b)$$

$$K_p = \frac{1 - \exp \left[-\frac{\pi^2 a}{4} (2m-1)^2 (T-\tau) \right]}{1 - \exp \left[-\frac{\pi^2 a}{4} (2m-1)^2 T \right]} \quad (9c)$$

The above result indicates that the current amplitude I_p and the coefficient α of the current rate as well as frequency $f=1/T$ have significant influence on the quality of deposited copper layers. Applications of PPR current give relatively easy control of the microstructure, thickness, and useful properties of the nanocrystalline copper layers. The time-varying current and ion concentration in the diffusion layer during the copper electrocrystallization are demonstrated in Fig. 3.

Fig. 3 Variations of the current and ion concentration in the diffusion layer



It should be emphasized that the electrodeposition of Cu is strongly dependent on the structure of the substrate, supplying current and concentration of Cu^{2+} ions in the precursor electrolyte solution. Since the effect of increasing current density is to increase the electrode surface reaction, a faster surface reaction makes Cu^{2+} under-supplied from the electrolyte solution. Hence, the polarization is higher, and smoother film morphology is observed. Nevertheless, when the applied current density is greater than the limiting current density, it is impossible for the electrode to gain any Cu ions from the electrolyte solution, thereby leading to an increase in the Cu film surface roughness [8, 13].

Control of Nanocrystalline Copper Structures by Compositions of Electrolyte Solutions

Components of electrolyte solutions for Cu electrocrystallizations may vary widely depending on the substrate and the type of Cu deposit desired. The electrolytic solutions include acid solutions and alkaline solutions as well as some additives used to provide desired surface finishes for the Cu structure and to initiate bottom-up adhesion of surface layers. Successful PPR applications include the optimization of the electrolyte composition, additive package, solution agitation, and electrochemical reactor design. We have previously shown [13] that pure and other electrolyte solutions prepared at contents of appropriate additives are represented by Cu1, Cu2, ..., Cu8, respectively, and correspond to specifications given in Table 2. Organic additives are adsorbed on the surface of the substrates and slow down the diffusion of the chemicals in the electrolyte solution to the surface of the substrate. They are not incorporated into the deposit. Copper is unique in that at least one additive such as PEG (polyethylene glycol) is required to suppress the electrocrystallization rate in order to obtain smooth, dense nanocrystalline materials. The higher current densities used in PPR electrocrystallization force developing additives that can guarantee more stability at higher currents. Thus, the additive system must be designed to work at high current densities.

Table 2 Compositions of Co per electrocrystallization solution

Symbol	Additive substance	Content [g/dm ³]
<i>Cu1</i>	–	–
<i>Cu2</i>	HCl	0.01
<i>Cu3</i>	H ₂ N-CS-NH ₂	0.20
<i>Cu4</i>	HCl H ₂ N-CS-NH ₂	0.01 0.20
<i>Cu5</i>	C ₇ H ₅ NO ₃ S C ₁₂ H ₂₅ NaO ₄ S	0.20 0.44
<i>Cu6</i>	HCl C ₁₂ H ₂₅ NaO ₄ S C ₇ H ₅ NO ₃ S	0.01 0.44 0.20
<i>Cu7</i>	HCl Cu-189	0.01 6 ml
<i>Cu8</i>	HCl C ₁₂ H ₂₅ NaO ₄ S H ₂ N-CS-NH ₂	0.01 0.44 0.20

Important benefits in copper electrocrystallizations can be delivered by using appropriate acid copper electrolyte in combination with pulse period reversal current. Surface microstructures of Cu thin layer electrodeposits produced in different solutions are presented in Fig. 4. Their counterparts with nanosize grains are shown in Fig. 5. These images indicate that the electrocrystallization process appears as an easy way for surface modification of known materials, as well as newly received ones.

The produced micro- and nanocrystalline copper structures consist of agglomerates of copper grains being a function of the current density of the electrocrystallization process. Nanosized dimensions of copper grains are achieved by increasing the current density to the allowable higher level. The higher the current density, the finer the grains and the faster the electrocrystallization rate will be, although there is a practical limit enforced by poor adhesion and quality when the rate is too high.

It is worth noticing that in Cu nanomaterials, a non-negligible fraction of the atoms is on or close to the surface of the material. These surface atoms are surrounded partially by the material and partially by vacuum. The density distributions viewed from these atoms differ from those viewed from the deeply buried atoms.

Influences of electrolyte solution composition on the hardness of copper thin layer produced by DC process are presented in Fig. 6. The diagram shows that the highest hardness of copper electrocrystalline bulk material can be obtained at bathes Cu4 and Cu5 at current density 5 A/dm².

The performed studies lead to the statement that the hardness and tensile strength are inversely proportional to the grain size – so a pulse supplying current produces harder copper electrocrystallites than switch mode current or DC in the absence of additives [11].

Exceptional technological features consist in the relatively low processing temperature and the high selectivity. The low processing temperatures minimize interdiffusion, whereas the high selectivity of electrocrystallization processes allows uniform modification of surfaces and structures with complicated profiles.

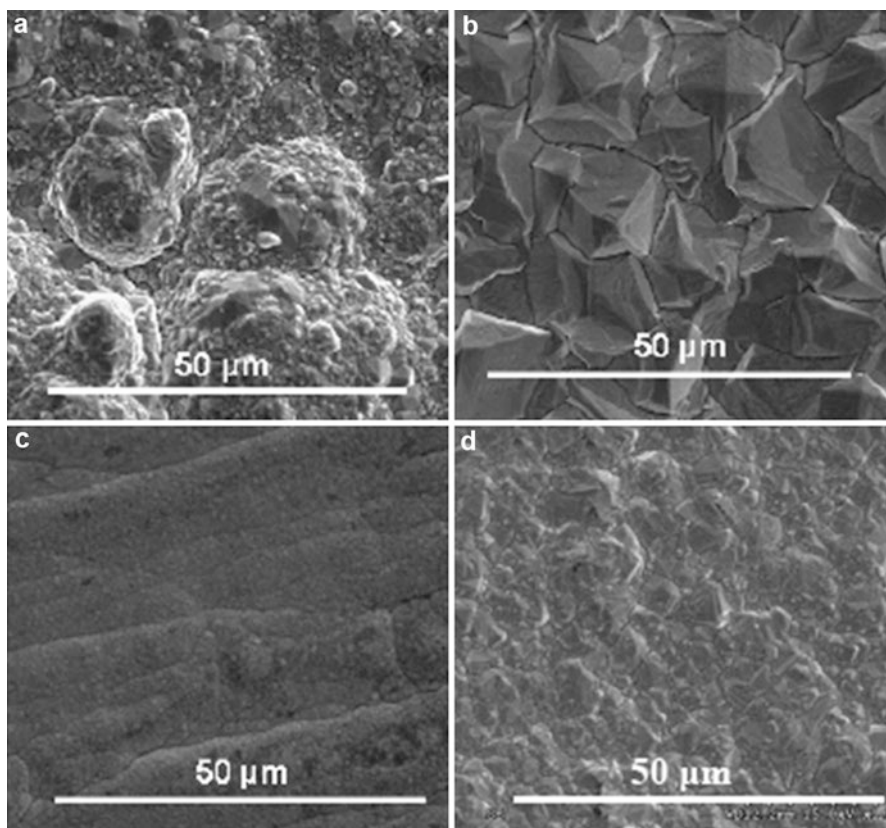


Fig. 4 Surface microstructures of Cu thin layer electrodeposits produced with $J = 5 \text{ Adm}^{-2}$ in different solutions: (a) microcryst., CuSO_4 and H_2SO_4 ; (b) microcryst., CuSO_4 , H_2SO_4 , and HCl ; (c) nanocryst., CuSO_4 and additive D1; (d) nanocryst., CuSO_4 , H_2SO_4 , and HCl ; and organic additive D1

Simultaneous influences of the current density and kinds of the electrolyte solution on the surface morphology of microcrystalline copper are illustrated in Fig. 7.

Applications of PPR current give relatively easy control of the microstructure, thickness, and useful properties of the deposited copper layers. Differences in the surface morphologies of microstructure electrocrystallized copper are shown in Fig. 8a–c for various current waves in absolute values of positive and negative current pulses during the symmetric semi-periods, respectively.

We have observed significant growth of selected grains in a polycrystalline interconnect, which subsequently become more susceptible to surface offset formation with further cycling (Fig. 9).

These materials can be used together with the substrate or separated from it. Apart from the known uses for protecting the substrate material in corrosive conditions or to improve the mechanical properties surface, they can extend the life of the tool and ensure its longer life. This is particularly important if, in these operating

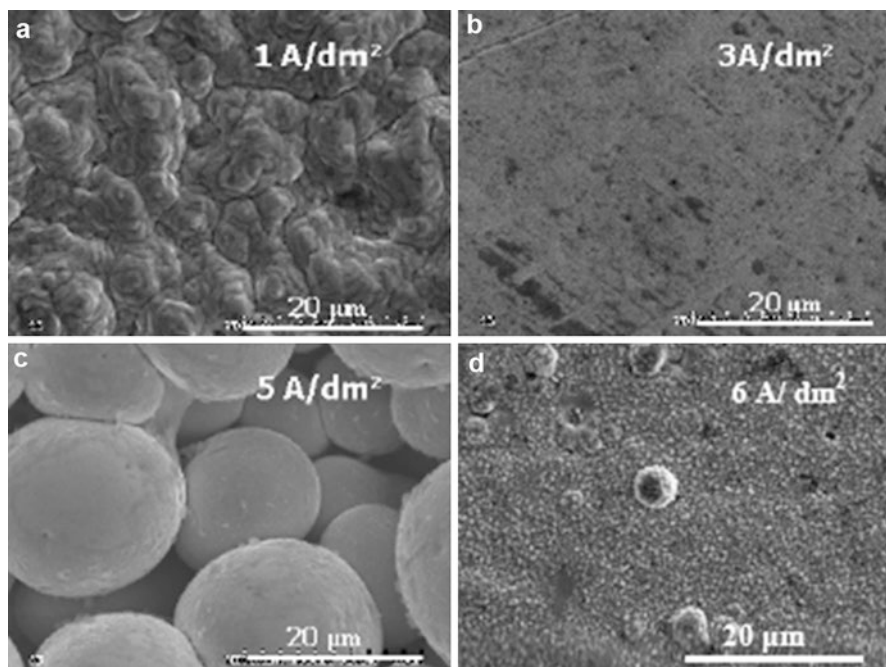


Fig. 5 Surface of Cu nanocrystalline thin layer electrodeposits produced with different current densities in CuSO₄, H₂SO₄, HCl, and organic additive D1 solution

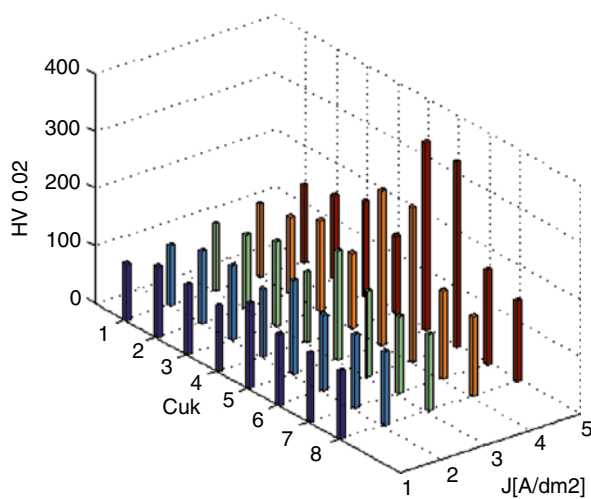


Fig. 6 Hardness of the copper deposits versus DC current density and bath composition

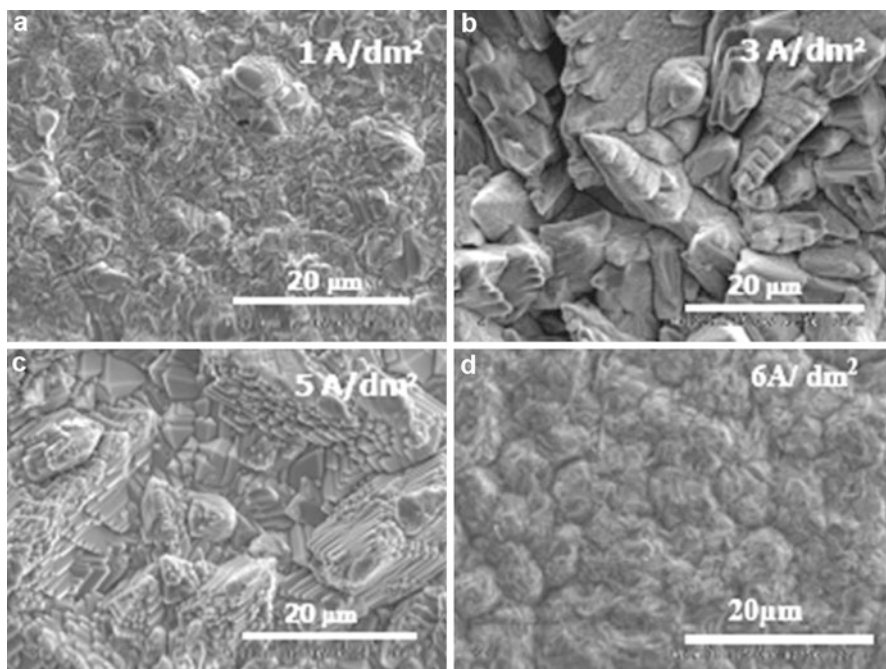


Fig. 7 Microcrystalline structure of Cu thin layer electrodeposits produced with different current densities in CuSO_4 , H_2SO_4 , and H_2NCSNH_2 solution: (a) 1 A/dm^2 and HCl, (b) 3 A/dm^2 , (c) 5 A/dm^2 and an organic substance, (d) 6 A/dm^2

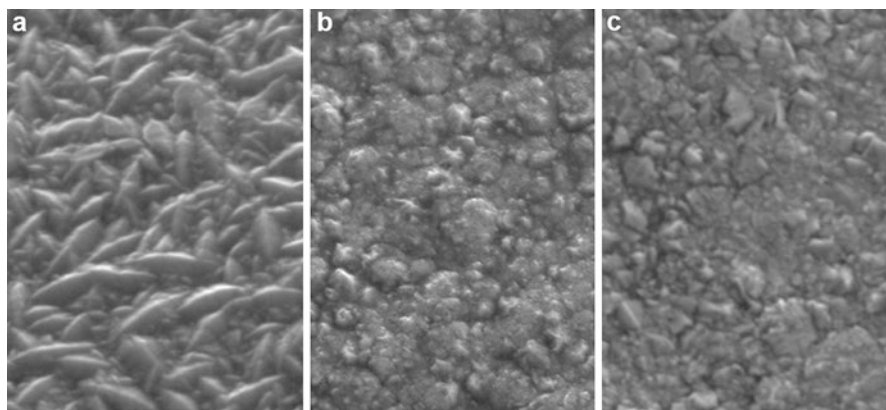


Fig. 8 Surface morphology of copper electrodeposits produced with $J = 1.1 \text{ A/dm}^2$: (a) DC, (b) PC at $f = 0.5 \text{ kHz}$, (c) PC at $f = 10 \text{ kHz}$

Fig. 9 Influence of the PPC frequency on crystallite dimensions

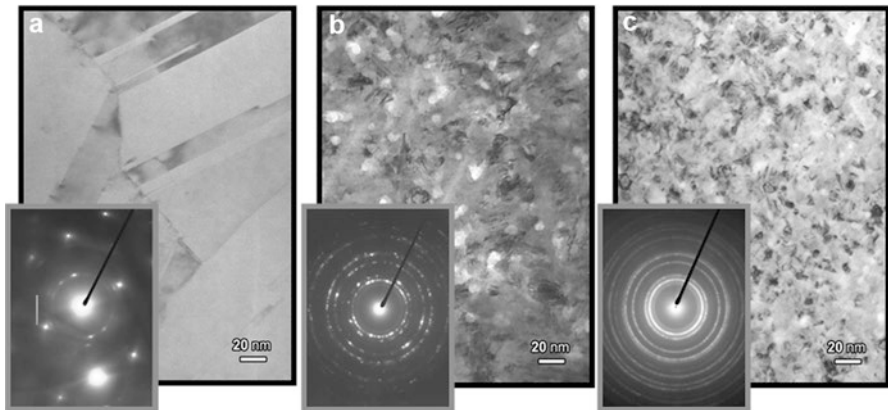
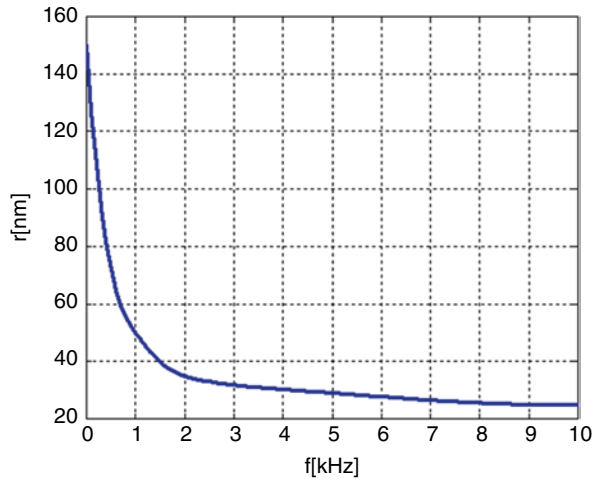


Fig. 10 The images of internal nanostructure of produced copper: (a) without additives, (b) additive D1, (c) additive D2

conditions, it is not possible to select a material resistant to providing differentiated factors (corrosion resistance, good mechanical properties, or the specific physical characteristics). In this case, the substrate may provide one kind of properties, the coating surface layer excites others.

The benefits of reverse pulse current plating are evident because it allows a precise control of the deposited material, including its composition, crystallographic structure, and texture and grain size. The higher the current density, the finer the grain. Hardness and tensile strength are inversely proportional to the grain size – so a pulse supply will produce harder deposits than switch mode or DC in the absence of additives (Fig. 10).

Effects of the electrocrystallization process of producing nanocrystalline copperware depend in a clear manner on chemical composition of the used electrolyte solution. Some organic additives denoted by D1 and D2 being supplements to the basic solution (CuSO_4 , H_2SO_4) play important roles in shaping internal structure of the produced nanocrystalline material. Figure 10 demonstrates diversity of the internal structure of nanocrystalline copper caused by appropriate additives in the electrolyte solution [22].

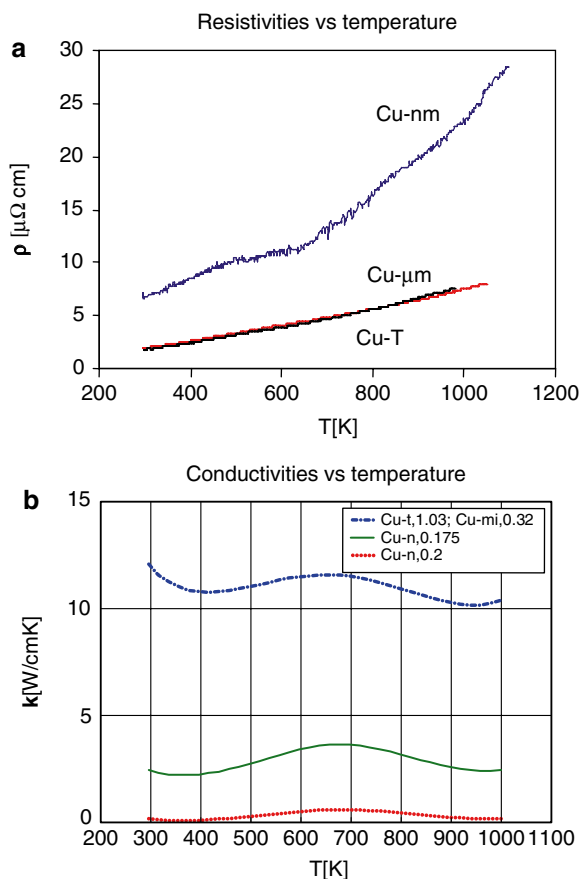
Although electrodeposition has been one of the methods for nanocrystalline material manufacturing, properties of nanocrystalline copper electrodeposits are less evaluated, especially for tribological applications or potential applications in very large scale of integration devices such as micro- and nano-electro-mechanical systems.

The SEM micrographs illustrating the morphology of copper deposits formed under current constant density and various electrocrystallization times clearly suggest the case of instantaneous nucleation of crystallites. Instantaneous nucleation corresponds to a slow growth of nuclei on a small number of active sites, all activated at the same time. It can be noted that in most of the samples, the nuclei may be formed almost simultaneously, as confirmed by their similar size. In other words, i.e., at high nucleation rates (instantaneous nucleation), all nuclei are formed immediately after imposition of the current and grow at the same rate. As a result, they are all of the same age, and their number remains constant. As nucleation progresses, the nuclei begin to overlap. Each nucleus is defined by its own diffusion zone through which copper diffuses, thus representing the mass supply mechanism for continuation of growth. Progressive nucleation corresponds to fast growth of nuclei on many active sites all activated during the course of electroreduction.

Electrical and thermal properties of nanocrystalline copper are very sensitive to the inner structure of a material, so theoretical prediction of these properties is a difficult task [6]. Defects of crystalline structure influence useful properties of the electrocrystallized copper. Moreover, in layers of thickness comparable or smaller than the characteristic lengths of carriers, new physical phenomena occur, and in this case theoretical models describing a copper layer as a continuum medium cannot be used for the description of its thermal properties. Figure 11 shows selected diagrams of electrical resistivity and thermal conductivity for various kinds of the copper.

The given plots exhibit an important decrease of the electric and thermal conductivities of nanocrystalline copper thin layers when comparing them with that of bulk copper being widely up to date used in the practice (Cu-T). In polycrystalline copper layers, the scattering on grain boundaries dominates over scatterings on layer boundaries and causes an additional reduction of the electrical and thermal conductivity. The observations obtained in this investigation reveal that the thermal conductivity of nanocrystalline copper thin layers takes maximal values in the temperature range of 600–700 K. However, the layer thickness has an additional influence on the thermal conductivity of copper surface electrodeposits.

Fig. 11 Electrical and thermal properties of crystalline copper: (a) electrical resistivity, (b) thermal conductivity



Electrocrystallization of Nanostructured Nickel

In the completed studies, nickel layers were produced by the electrochemical reduction method in multiple electrolyte solution of a Watts type. An equal width of cathodic surface periodic pulse current of 3 A/dm^2 and carry out ratio $\alpha = 10 \%$ was used in the processes for producing nanocrystalline nickel layers. The current frequency was varied in the range of 0–10 kHz.

The structure of the produced nickel was studied by X-ray diffraction (X) and by scanning electron microscopy (SEM) approaches. The influence of the current type and the frequency of pulsed current on the topography and morphology of the surface of the produced nickel are illustrated in Fig. 12.

The structure of electrocrystallized nickel produced in the basic electrolytic solution (Watts bath) without organic additives is characterized by a large grain size and develops a rough and dull surface (Fig. 13a). In contrast, the surface of nanoelectrolytic nickel formed in a solution of nickel modified with organic additives D1 and

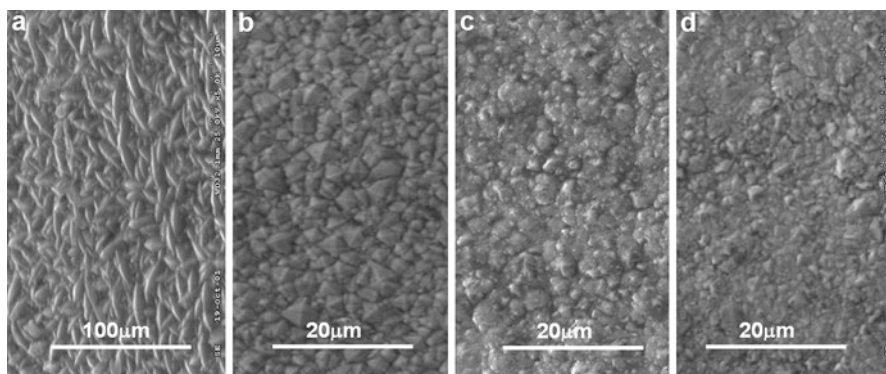


Fig. 12 The topology and morphology of the surface of the deposited nickel layers: (a) microcrystalline, by DC; (b–d) nanocrystalline, by PPR with the frequency 0.5, 5, and 10 kHz, respectively

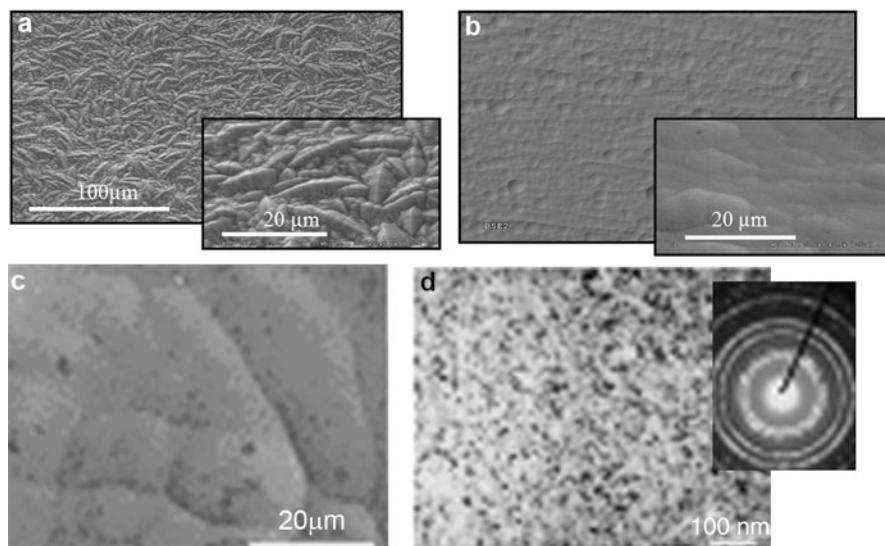


Fig. 13 Morphology of produced nickel deposits examined by using SEM and TEM: (a) microcrystalline, (b, c, d) nanocrystalline

D2 (Fig. 13b–d) is smooth, glossy, and less developed than that of layers of microcrystalline material [20].

Differences in the topographies and structures of such materials appear as an effect of different atomic arrangements within the material volume and on the layer surface. The presented, selected area, diffraction pattern (Fig. 13d) of the nanocrystalline Ni exhibits a variation in the grain size that is visible both on the material surface and within the material volume. Moreover, the diffraction patterns of such

materials with spots situated on the ring circumferences indicate nanocrystalline textured structures.

The internal structure of the material has a decisive influence on its properties. Comparison of abrasive wear of nickel materials produced electrochemically by applying the DC and periodic pulse current is illustrated by the graphs shown in Fig. 14. The materials formed by periodic pulse currents, which are composed of nanocrystallites, exhibit a lower degree of wear [28].

All produced nanonickel materials are characterized by a compact structure. Both the type of supplying current and the frequency, in the case of pulsed current, affect the topography of the material surface and the size, diversity, and shape of crystallites. Selected results of research carried out on the surface of nanocrystalline nickel are shown in Fig. 15. The fine grain material deposited here exhibits layered structure. Each layer, being parallel to the substrate surface, is made of spherical nanocrystalline agglomerates. Increased refinement of grain structure increases the hardness and stress resistance of the material and thereby reduces its plasticity. Grain boundaries may strengthen the structure and prevent deformations or may facilitate grain sliding along the boundaries and lead to formation of intergrain cracks.

Dimensions of the nickel crystallites depend on the chemical composition of the electrolytic solution used for process realization, as well as on process parameters such as density and the type of supplying current and temperature of the solution. The addition of organic matter D1 and D2 inhibits crystal growth processes and promotes the formation of new crystal nuclei, leading to crystal structures of nanometer grain size. The produced nanocrystalline nickel exhibited grain size of the order of 25 nm.

Diversity of the intensity of diffraction peaks at various diffraction patterns provides a significantly textured material. Diffraction line profiles indicate that the nickel layers formed in the basic electrolytic solution are characterized by a greater primary grain size and the special crystallographic direction $\langle 200 \rangle$.

In the case of nanocrystalline nickel which has been formed in the solution modified with organic additives, preferred crystal growth orientation takes the direction of

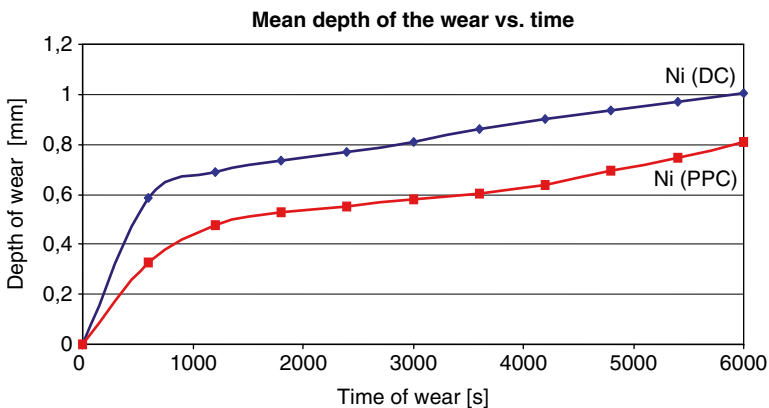


Fig. 14 Abrasive wear of the nickel surface produced by applying: DC-Ni (DC), PPC-Ni (PPC)

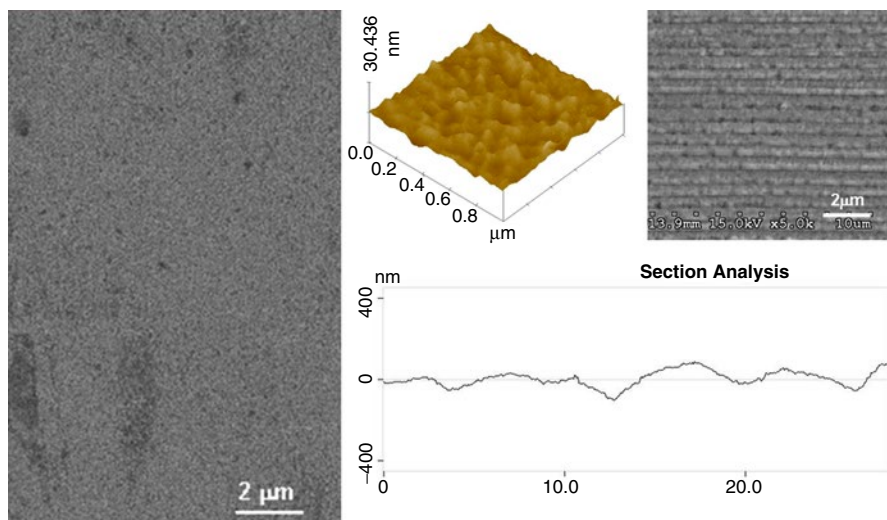


Fig. 15 Topography and surface geometric profile and layer cross section of nanocrystalline nickel

$\langle 111 \rangle$, and the increased width of the reflections indicates the nanosized dimension of the produced crystallites. From the set of diffraction patterns based on the broadening of X-ray reflections and using the Scherrer relationship in the following form:

$$\beta_k = K \lambda / D_{hkl} \cos(\theta_{hkl}) \quad (10)$$

where

β_k – reflex width depending on the size of the crystallites [rad]

K – Scherrer constant close to unity

λ – wavelength of X-rays [Å]

D_{hkl} – average crystallite size in a direction perpendicular to the planes (hkl)

θ_{hkl} – angle reflections, the size was determined of crystallites occurring in the nickel material formed as the nanocrystalline structure [18].

The electrocrystallization process is suitable for producing surface nanostructured nickel layers. In addition to the compact construction and a good adhesion to the material of the substrate, the surface nanocrystalline nickel layers significantly increase the performance of the products in which they are embedded. It was observed a significant increase in the corrosion resistance as well as impact properties, such as hardness, or resistance to tribological wear.

Electrocrystallization of Nanostructured Composites

Advanced composites are already extremely important to the defense industry and will be more critical in the near future because they offer the greatest strength and stiffness-to-weight ratio among engineering materials. Composites are expected to

be a key enabler in the development of light and more mobile not only military force but also cars, planes, buildings, and so on. They also offer the simplest route for embedded sensors, actuators, and other elements, thus providing much sought-after multifunctionality. Revolutionary advances in composites result from the use of nanotechnology, wireless technology, and self-healing mechanisms. Provided that the cost of composite manufacturing continues to decline, composites could displace steel and aluminum as the primary materials in manufacturing, transportation, and construction. In electronics, carbon-based nanocomposites could potentially replace silicon as the basic building blocks for chips and circuit boards.

It is interesting to note that due to the charge transfer effect, the electrical conductivity of the composite can be higher than the conductivity of both of the components considered separately. Moreover, preparation of a nanocrystalline composite can be achieved with commercially available low-cost reagents, which enable large-scale production. Hence, there are significant challenges in developing nanostructured composite materials for a large displacement of classic materials and a rapid response to the needs of highly advanced technology as well as in developing compatible fabrication methods. The extraordinary mechanical, optical, and electrical properties of nanostructured composites are implementable into working devices [12, 23].

Nanocrystalline Composites with Nickel Matrix

Nanocrystalline composites with nickel matrix create a good potential for designing and producing materials proving favorable properties. One of the possibilities in this domain appears to be nanocrystalline nickel layer composed of pure metal Ni and modified by disperse phase in the form of ceramic silicon carbide SiC, silicon nitride Si₃N₄, or molybdenum disulfide MoS₂. Introduction of the disperse phase to the metal matrix appears as an efficient way to increase the hardness and resistance to frictional wear of the resulting material while maintaining the corrosion resistance of the matrix material. Selected disperse phase in the nickel modifies significantly the surface properties of the composite material. Silicon carbide SiC is a ceramic material, characterized by a favorable physicochemical properties, such as high hardness and thermal as well as chemical resistances and good thermal and electrical conductivities. In contrast molybdenum sulfide MoS₂, as a material with strong ionic bonds and the layered crystal structure, has low hardness and good mechanical and chemical resistances and lubricating properties.

The combination of nickel nanocrystalline material as the matrix and the disperse phases in the form of SiC or MoS₂ creates the possibility of forming high potential output properties of the produced composite material. Combinations of two such different materials allow completion of their measurable characteristics, while the interactions between these different phases of such a modification induce these properties. For the disperse phase, by selection of particle size and their content in the matrix material, it is possible to design the respective properties of the composite material produced by electrocrystallization processes. This type of

nanocomposite surface layers can perform optimally a variety of functions in the art, and above all where the products and devices are placed particularly as high technical requirements.

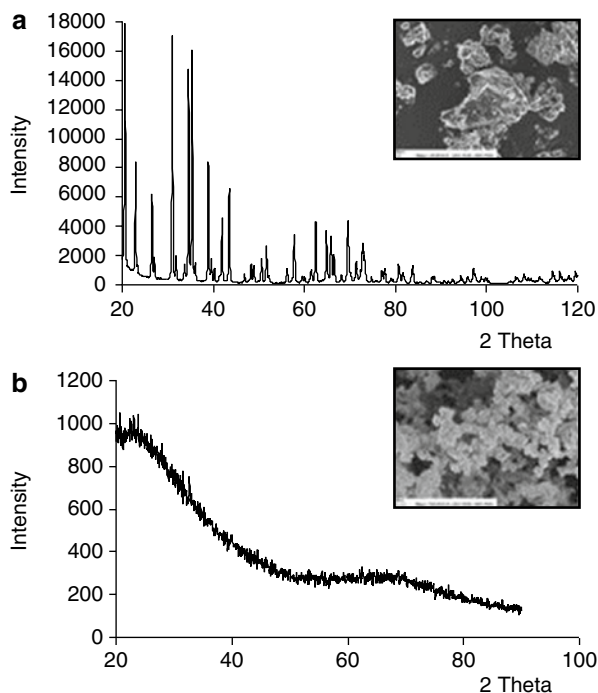
Disperse ceramic phase was used for the production of composite layers Ni/Si₃N₄, constituted by the microcrystalline structure of polydisperse Si₃N₄ powder containing both crystalline forms α and β of the hexagonal structure and a large variety of grain size (Fig. 16a), while for the production of composite layers of Ni/Si₃N₄ having nanometric structure, an amorphous silicon nitride powder (Fig. 16b), with an average grain size of 15 nm, was applied.

The topography of the nickel and composite layers (Fig. 17), the diversity of their morphology and their internal structures and thickness, and the distribution of particles of the ceramic phase in a volume of the composite material were determined by using a scanning electron microscope Hitachi S-3500 N equipped with an EDS spectrometer (Norman Vantage). The content of the disperse ceramic phase Si₃N₄ in the composite material of the layers was determined by quantitative metallography methods and computer image analysis.

Measurements of microhardness within the cross sections of the material layers were performed by the Vickers method at a load of 20G (HV 0.02) using a microscope NEOPHOT-1 with the Hanemann attachment.

The volume fraction of the disperse phase in layers containing micrometer Si₃N₄ powder was reduced from 18 % vol. in layers produced by DC to 14 % in layers produced by periodic pulsed current, and in the case of nanometric layers with Si₃N₄

Fig. 16 Diffractograms and SEM images of Si₃N₄ powders: (a) crystalline, (b) amorphous



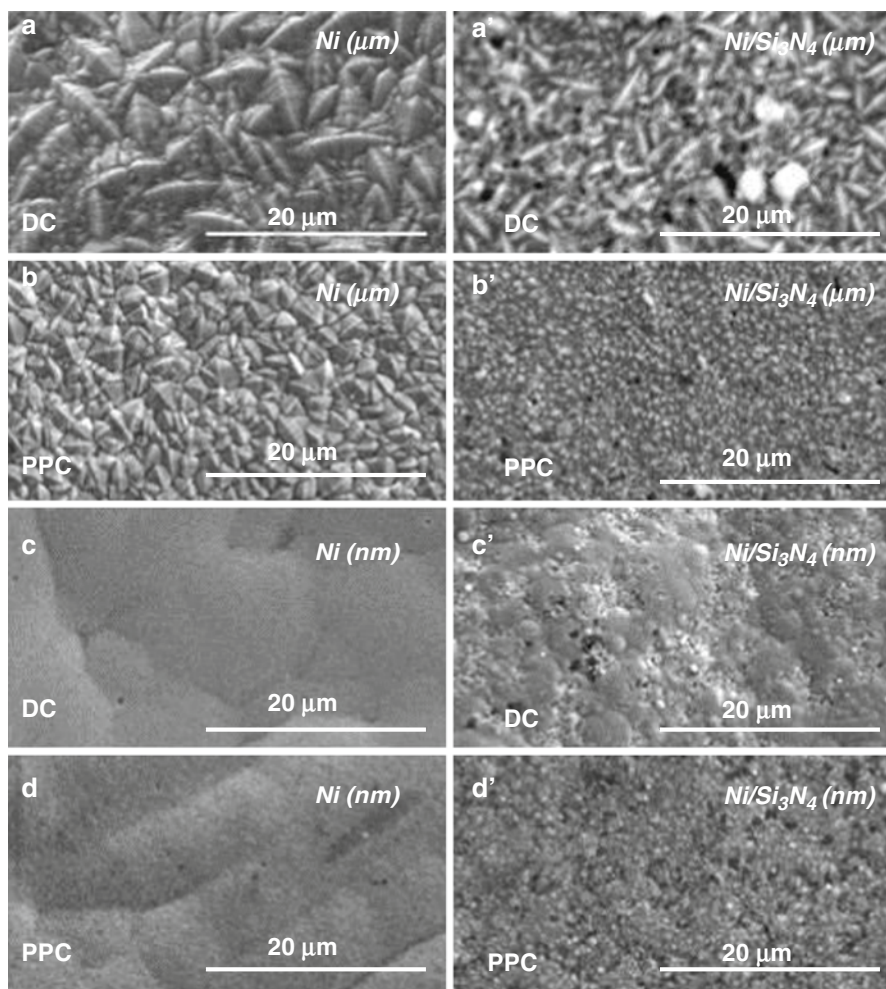


Fig. 17 Morphologies of produced nickel and composite layers: (a, a', c, c'), direct current (DC); (b, b', d, d'), periodic pulse current (PPC)

powder, the decrease corresponds from 8 % vol. up to 5 % vol. (Fig. 18), respectively.

The decrease in the volume fraction of the ceramic phase in the layer of Si_3N_4 formed a nickel by pulsed current with respect to their counterparts produced by DC reduces the microhardness of the layers of composite as shown in Fig. 19.

The use of the periodic pulse current instead of direct current leads to the production of layers with a lower surface development and smaller grain size of nickel and also affects the amount of ceramic phase embedded in the matrix material. In this way, it is possible to improve the hardness and corrosion resistance of the $\text{Ni}/\text{Si}_3\text{N}_4$ surface layers.

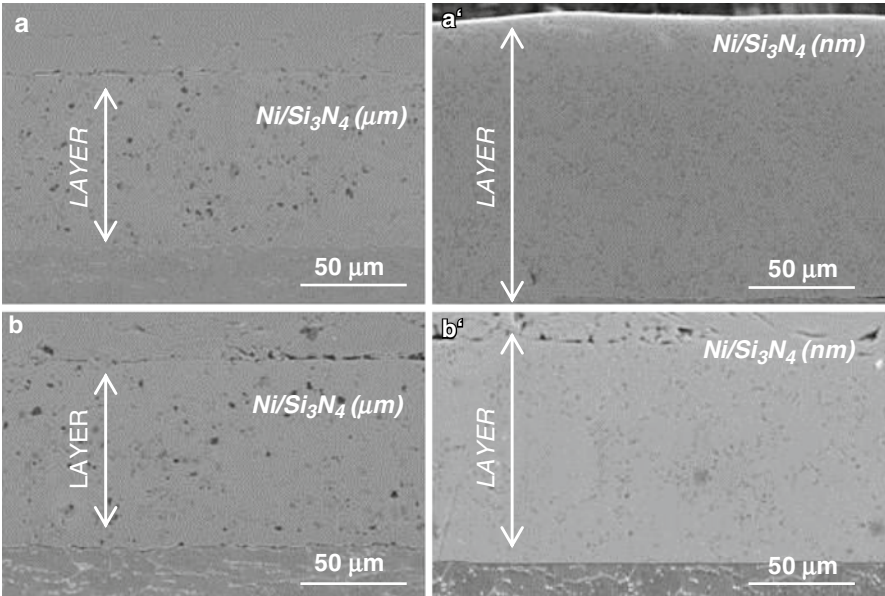
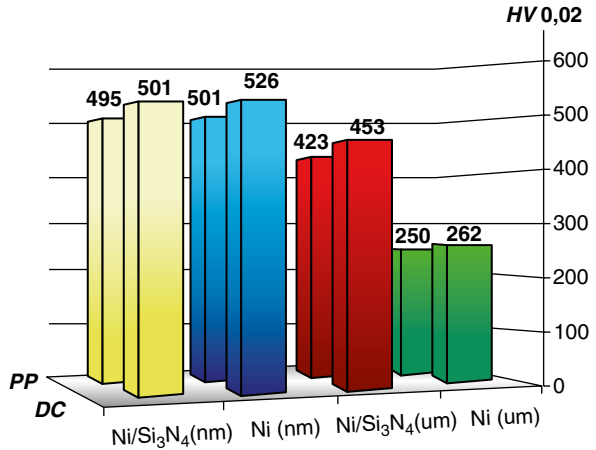


Fig. 18 The distribution of the ceramic phase Si_3N_4 within the volume of composite layers: (a, a'), direct current (DC); (b, b'), periodic pulse current (PPC)

Fig. 19 Hardness of the Ni and $\text{Ni/Si}_3\text{N}_4$ layers produced by direct and pulse periodic currents



Recently, there has been an explosion of interest directed toward depositions of nickel-nanostructured composite thin layers containing ceramic Al_2O_3 disperse phase. By decreasing the particle size of composite constituents, one can obtain nanocomposite layers with considerably better properties compared to those of its previous classic equivalent. Such type of nanocomposite materials also exhibits differences in the structure of the matrix and in the sizes and shapes of the disperse phase [30, 31].

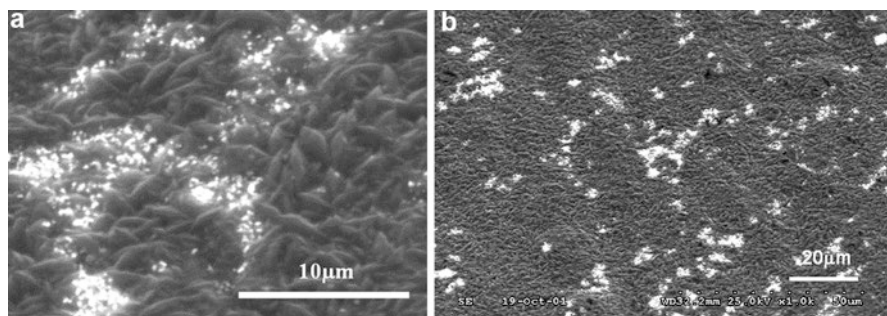


Fig. 20 Ni/Al₂O₃ composite layers: (a) coarse grain powder, (b) fine grain powder

The SEM pictures of the surface of the composite Ni/Al₂O₃ layers produced by the electrochemical method with a matrix formed by microcrystalline nickel and ceramic phase characterized by different grain sizes are presented in Fig. 20. They reveal that on the surface of the composite layers, agglomerates of nanometric (Fig. 20a) and reasonably homogeneously distributed (Fig. 20b) Al₂O₃ powder particles are seen. Increased refinement of grain structure amplifies the stress resistance and hardness of the material and thereby reduces its ductility.

Nanocrystalline Composites with Nickel Matrix and Disperse Phases Built from Carbon

Carbon, as one of the widely known and used chemical elements for many decades, was considered as the elementary component of both diamond and graphite. Since then, more allotropes of carbon have been reported, and a large scientific community has been passionate about deciphering the properties of this element that can adopt many structures ranging from diamond and graphite (3D), graphene (2D), nanotubes (1D), or fullerenes (0D) as illustrated in Fig. 21. With the exception of diamond, it is possible to think of fullerenes, nanotubes, and graphite as different structures built from the same hexagonal array of sp² carbon atoms, namely, graphene. Indeed, fullerenes and nanotubes can be mentally visualized as a graphene sheet rolled into a spherical and cylindrical shape, respectively, and graphite can be described as a stack of alternately shifted graphene sheets. The rapid adoption of graphene as a material of interest lies in its actual availability by the range of techniques and methods well known and also because monolayer and few layer graphene and graphene oxide exhibit a diverse set of exceptional properties. Graphene is, according to many experts, the electronics material of the future [24, 26].

Graphene, graphite, diamond, and nanotubes attest each set built of their own data in terms of mechanical robustness, be it hardness or strength modulus. However, the mechanical behavior of graphene has been much less investigated than its electronic and optical properties. It has to be emphasized that graphene possesses a

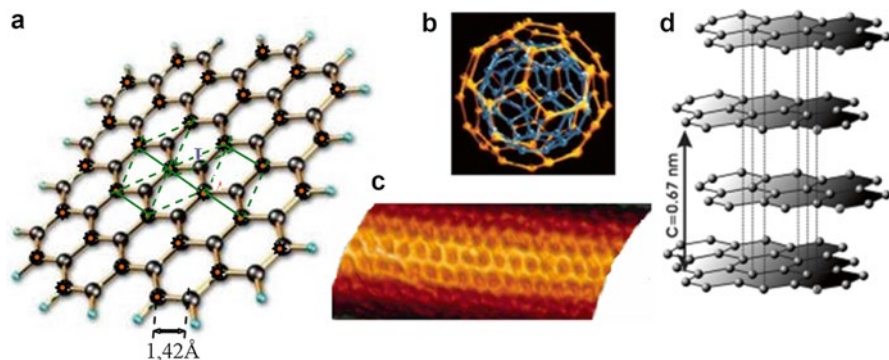


Fig. 21 The crystalline structure of carbon: (a) 2D (graphene) (b) 0D (fullerene), (c) 1D (nanotube), (d) graphite

combination of special properties which come out against answers for several limitations of currently known materials and systems.

Graphene, a single sp^2 -bonded carbon atomic sheet, has great potential for microelectronics applications, including conventional components such as high-frequency analog devices, and devices in emerging fields such as spintronics, terahertz oscillators, and single-molecule gas sensors. More recently, graphene has been the focus of considerable attention, due to its unusual density of states.

During the past decade, several outstanding advancements in graphene growth technology have been achieved. Novoselov et al. demonstrated mechanical exfoliation of graphene from graphite, permitting the first observations of some of the highly. The growth of graphene by thermal desorption of Si from SiC (sublimated epitaxial graphene: S-EG) was developed by Berger et al. [25]. Attractive and novel physical properties of graphene follow the early experiments of Van Bommel et al. Further improvements in the quality of S-EG were realized by sublimating Si at elevated temperatures in argon (Ar) atmosphere rather than in vacuum. However, vacuum sublimation is still successfully applied with a Si vapor pressure control system.

The most important physical properties of graphene are (i) a two-dimensional lattice $a=0.142$ nm, (ii) the greatest surface-to-volume ratio, (iii) very good heat conductivity (4800–5300 W/mK), (iv) low electrical resistance, (v) very high electron mobility $\mu=20,000$ cm^2/Vs , (vi) very high electron velocity $v=10^8$ $\text{m}\cdot\text{s}^{-1}$, (vii) almost complete optical transparency, (viii) molecular opacity for transmission, (ix) extremely high mechanical strength $\gamma\approx 1$ Tpa, and (x) quantum Hall effect.

One of the effective technologies is producing graphene film epitaxy by growth on a substrate with a 6H-Si(C). Image of the surface of graphene produced using such a method is presented in Fig. 22.

Theoretical analysis of doped graphene layers and research experiments suggest that they exhibit potential applications, among others, in transparent electrodes, photodetectors, touch screens, lighting elements, photovoltaic elements, optical filters, optical power limiters, and elements of terahertz systems.

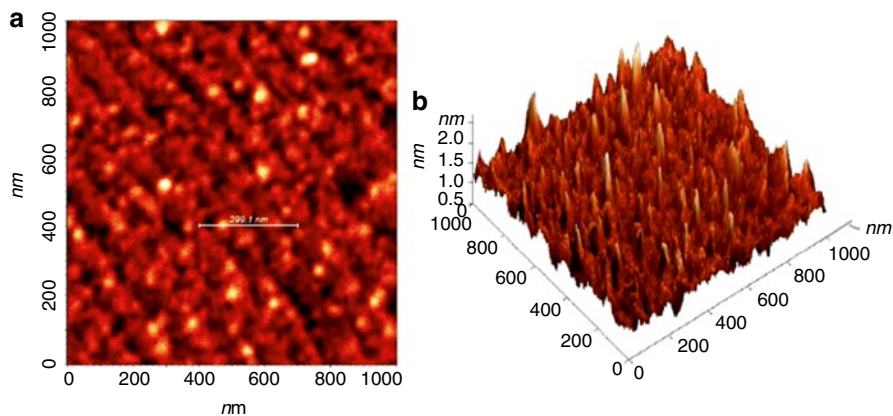


Fig. 22 AFM surface images of 2D graphene produced on 6H-Si(C) substrate: (a) topography, (b) morphology

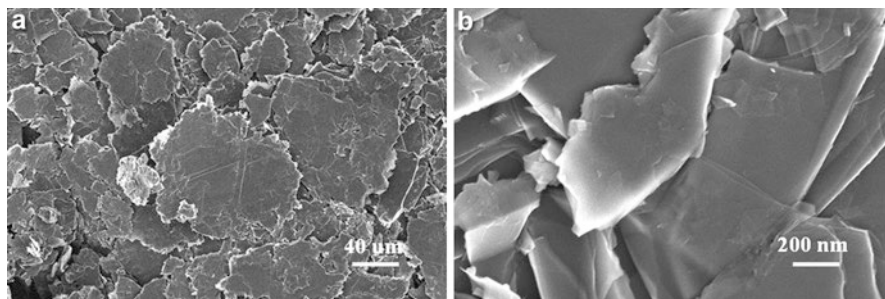


Fig. 23 Images with different magnifications of graphene structure applied in the study

Layered composite Ni/graphene was prepared by the electrocrystallization process on the substrate of carbon steel S235JR in the bath composed of sulfate (VI) nickel (II) chloride, nickel (II), boric acid, organic compound additives, wetting, and graphene as a dispersed phase in the 0.5 g/dm³ bath. Electrodeposition process was carried out in the bath at a temperature of 45 °C at a current density equal to 3 Adm⁻²; the process time was chosen to give a layer thickness of about 30 μm. A mixing agitator 50 rpm./min was used.

Graphene in the form of flakes with dimensions for thickness of 5–8 nm, diameter of 5 μm, and the area of 120–150 m²/g was used as a disperse phase (Fig. 23). SEM images of the produced nanostructured Ni/C_{graph} are presented in Fig. 24.

For the production of composite layers of Ni/CNTs, we used carbon nanotubes (CNTs) having a tendency to agglomerate in an aqueous medium as a dry suspension. Images of carbon nanotubes of polyhedral structure (MWCNTs) made up of several layers of graphene spaced at the same distance which were used as disperse phase in the manufacturing of nickel-based composite are shown in Fig. 25.

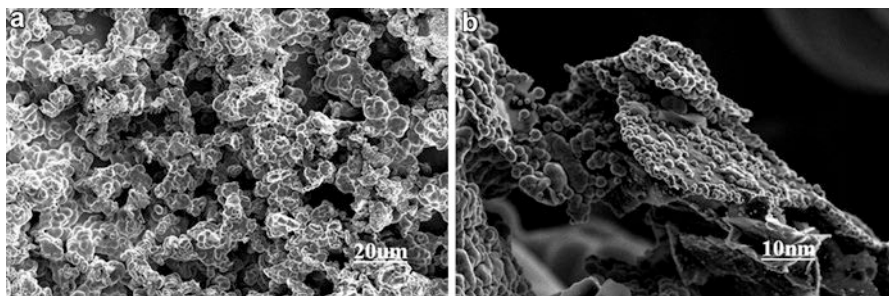


Fig. 24 SEM images of produced Ni/Cgraph nanocomposite: (a) topography, (b) morphology

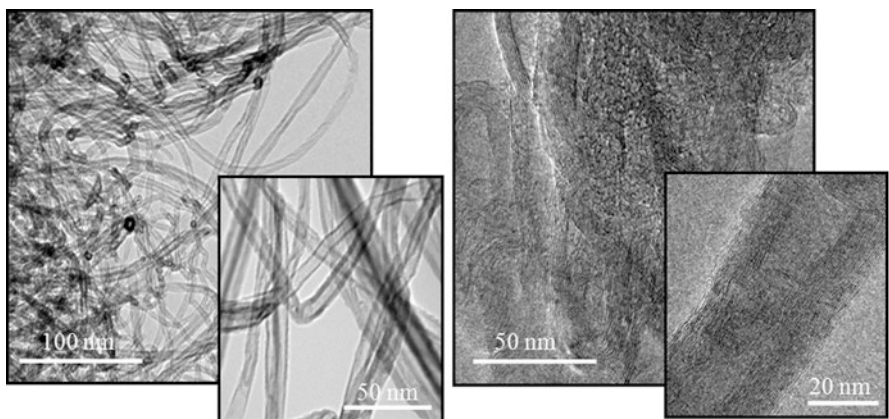


Fig. 25 TEM images of MWCNTs at different reinforcements

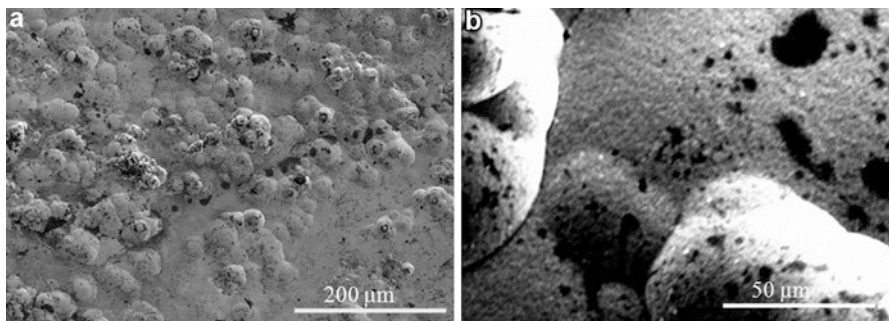


Fig. 26 Morphology of Ni/CNTs composites at different reinforcements

The resulting nanocomposite layer Ni/CNTs (Fig. 26) have a more developed surface as compared with the layers of nanocrystalline nickel (Fig. 10). On the surface of the composite layers are visible agglomerates CNTs that are not completely enclosed by the deposited nickel [16].

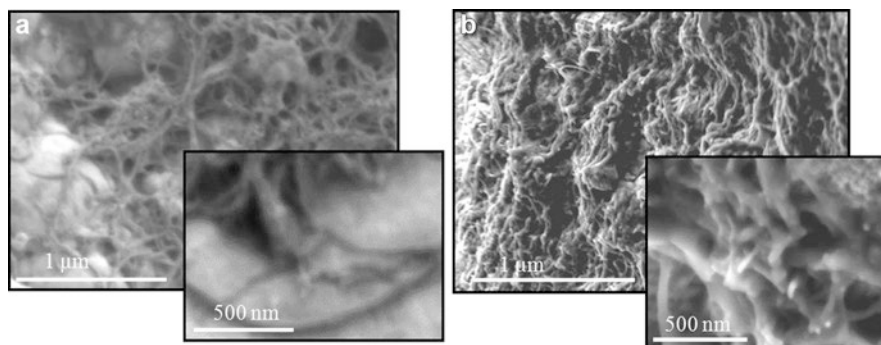


Fig. 27 Nanocrystalline Ni-P/CNTs composite: (a) surface, (b) cross section

The distribution of CNTs built-in nickel matrix within the whole composite material is illustrated in Fig. 27. Dispersed carbon nanotubes due to their nanometric dimensions pose some difficulties in their identification in a matrix of nanocrystalline nickel. One of the most effective methods for identification and characterization of CNTs is the Raman spectroscopy. Characteristic elements of the Raman spectra of carbon nanotubes are D and G mods. Mod G allows to determine the purity of CNTs, while mod D indicates the presence of functional groups or defects on the surface of carbon nanotubes.

Plots of the Raman spectra of a nanocrystalline materials related to Ni/CNTs composite are shown in Fig. 28. Comparing these spectra, it is easy to show that the D and G characteristic modes of CNTs (Fig. 28a) are also present in the produced Ni/CNT nanocomposites (Fig. 28c).

Nanocrystalline Composites with Copper Matrix

To modify the properties of copper products and in particular their surface layers produced by the electrocrystallization method, disperse phases were applied in the forms of graphite powder and carbon nanotubes. Graphite, built as the disperse phase, is characterized by good lubricating properties, low hardness in one direction, and electrical and thermal conductivities similar to those of most metals. Soft graphite particles embedded in the metal layer create a wide possibility for improving the lubricity and increase the electrical and thermal conductivities of the surface layer.

Carbon nanotubes as the disperse phase, because of its unique mechanical properties; chemical, electronic, optical, and magnetic recording; and unique structure (high ratio of length to diameter), allow to improve the mechanical, tribological, corrosion, and thermal and electrical conductivity of the surface layers of the material.

Composite layers with copper matrix were prepared by electrochemical reduction in the Watts bath of the following composition: CuSO_4 , H_2SO_4 (conc). This bath was modified with both organic substance and a disperse phase in the form of

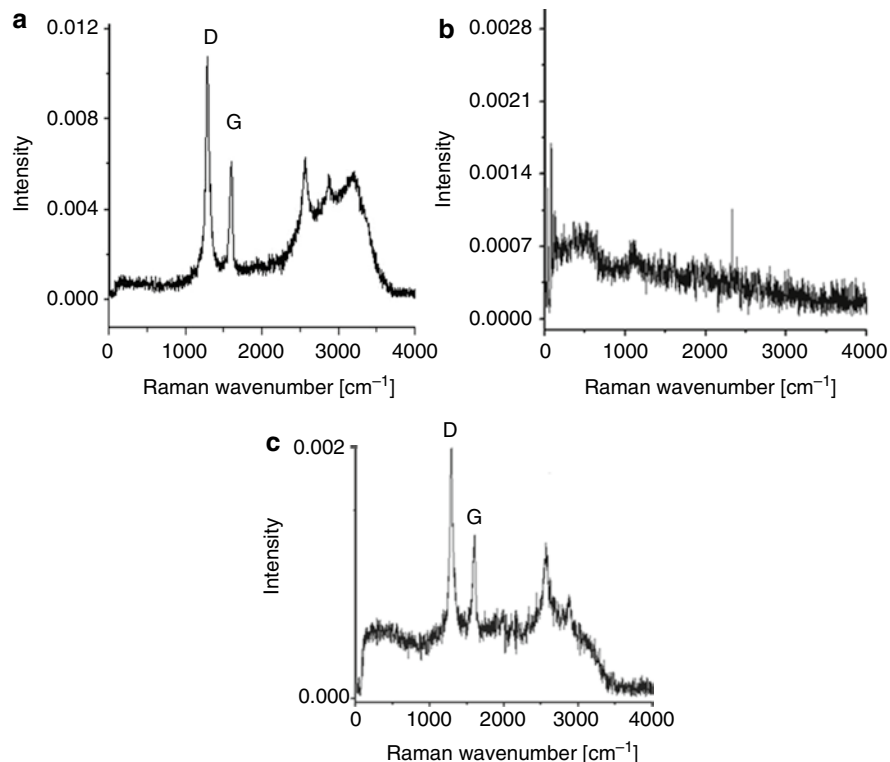


Fig. 28 Plots of Raman spectra for nanocrystalline materials: (a) CNTs, (b) Ni, (c) Ni/CNTs composite

graphite powder or carbon nanotubes. In addition, to make possible the fragmentation of the structure, some organic additives were used. The suspension of both graphite and CNTs in the solution was mixed in advance by ultrasounds, and during the process realization, a mechanical stirrer was used in order to prevent reagglomeration of CNTs and graphite powder.

Introduction of graphite particles or carbon nanotubes into Cu layer results in changes in the structure of the material layer. The composite layers are more developed, and on their surfaces, there are particles of graphite or CNTs completely encased by copper. CNTs are incorporated in the composite layers as individual particles or in the forms of different clusters. Images illustrating the composite layers with a copper matrix are presented in Fig. 29.

CNTs due to their nanometric dimensions make it difficult to identify them in the copper layers produced by electrocrystallization method. Their existence in the copper composite layers was confirmed by Raman spectroscopy exhibiting in the spectra of peaks with characteristic values for CNTs.

The results of performed studies revealed that the incorporation of graphite in the Cu layer reduces its microhardness and thus improves the lubricating properties and

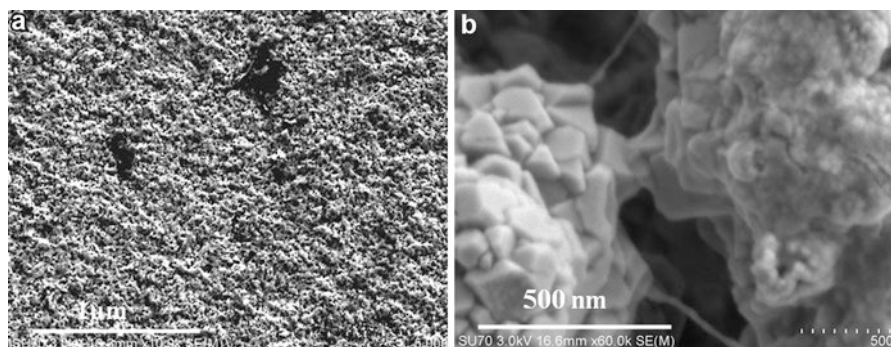


Fig. 29 Nanocrystalline layers produced by electrochemical reduction: (a) Cu/C_{grafite}, (b) Cu/CNTs

tribological properties of the material. In contrast, introducing CNTs into the copper composite layers produced by electrochemical reduction method greatly increases the microhardness of these layers. Moreover, the growth of microcomposite layers affects not only the CNTs presence but also the additions of organic substances into the electrolyte solution.

Summary and Conclusions

In this chapter, an attempt has been put on the description of a new method for electrocrystallization process realizations which take into account the activation energy and mass transfer effects. It is based on non-sinusoidal periodic excitations of the electrolytic reactor and controls of the measured response waveforms. This is done through the use of time-pulse periodic currents of suitable amplitudes and frequencies, and it is not recommended to introduce a DC for supplying the reactor, because it may induce disadvantageous electrochemical activities. Emphasis has been placed on nanocrystalline copper electrodepositions and manufacture of surface thin layers because these are the most important of the electrochemical cutting-edge industries in terms of quality improvements and possible energy savings.

This chapter presented results of studies focused on electrocrystallization on nanostructured materials that enable the production of nanocrystalline Ni and nanocomposite Ni/CNTs. Both nanocrystalline materials exhibited uniform structures and good adhesion to the substrate. Incorporation of carbon nanotubes in the nickel matrix has a significant impact on the structure, morphology, and topography of the resultant material and improves its mechanical properties.

It has been experimentally observed that most of the enhancement in the performance of materials thus far achieved has been due to lowering of the thermal conductivity.

Here, we showed that using two types of ceramic powder grains introduces another strategy to enhance the performance of the bulk material through enhancing the power factor in addition to reducing the thermal conductivity.

Therefore the electrocrystallization can be 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 varying from structural and functional to advanced biomedical in vivo and in vitro applications. Moreover, the advantages of the electrocrystallization method can be pointed out including the possibility of synthesizing materials in an automatic regime under mild conditions at temperature below 100 °C on substrates of complex shape by using simple apparatus.

Electrodeposition allows a precise control of the material, including its composition and its crystallographic structure, texture, and grain size. Temperature- and corrosion-resistant materials will be in demand for the automotive and aerospace sectors of the industrial market, while silicon and various thin films will be the leaders in photovoltaic and microelectronics industry.

In summary, we have demonstrated that using the modulation-doping approach, one can enhance significantly the power factor of electrocrystallized materials.

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