08. Author reference of scientific contributions in all works of Assoc. Prof. Dr. Maria Hristova Petrova - Nikolova presented for participation in a competition for professorship

The scientific works (70 in total, of which 48 are in Scopus) included in the author reference refer to one of the main thematic priorities of IPC, related to avant-garde materials and technologies based on electrochemically obtained metal, alloy and modified polymer coatings with protective, decorative and electro-catalytic properties. These articles are published mostly in foreign journals, 8 of them are in journals in Q1 group, 27 – in Q2, 5 – in Q3, 4 - in Q4, 2 - with SJR without IF, 2 – without SJR и IF, and the remaining 22 are published in non-refereed journals and in full text in proceedings of reports of symposia, congresses and conferences with Bulgarian and international participation. My Scopus Hirsch Index is 10. They have been discovered so far 693 citations of all my publications (without self-citation of co-authors), of which 489 in Scopus. 437 citations of them are citations issued after holding the academic position "associate professor".

Scientific works can be grouped into the following areas:

Area 1: Investigation of the process of electroextraction of zinc from sulfate electrolytes

On this subject 17 articles are published; 10 reports are presented at conferences and 407 numbers of citations are registered.

1.1. Influence of inorganic impurities and organic additives in the electrolytes for electroextraction of zinc.

1.2. Lead alloys in their role as anodes in the electroextraction of zinc.

Area 2: Chemical deposition of metal coatings on various types of substrates

On this subject 49 articles are published; 75 reports are presented at conferences and 81 numbers of citations are registered.

2.1. Chemical deposition of nickel/phosphorus and copper dispersed coatings on *solid (non-metallic and metallic) substrates*

2.1.1 Pretreatment of non-metallic substrates

2.1.2 Chemical deposition of dispersed coatings with various micro-and nanoparticles

2.1.3 Chemical deposition of coatings from formaldehyde-free environmentally friendly copper electrolytes and from electrolytes with low-pH

2.1.4 Chemical deposition of coatings on 3D - printed substrates

2.2. Chemical deposition of nickel/phosphorus and copper dispersed coatings on *flexible substrates*

2.2.1. Chemical deposition of nickel/phosphorus dispersed coatings

2.2.2. Chemical deposition of copper dispersed coatings

Area 3: Problems in the production of printed circuit boards

On this subject 4 articles are published; 2 reports are presented at conferences and 1 citation is registered.

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*The numbering of the publications cited in the text matches the numbering from the list of all publications (point 7) of Assoc. Prof. M. Petrova

The main contributions according to the above areas can be summarized by groups as follows:

Area 1: Investigation of the process of electroextraction of zinc from sulfate electrolytes

The investigations related to the hydrometallurgy (zinc electroextraction) are mainly carried out within the framework of the thesis for the acquisition of the scientific degree "Doctor" and they are included in the list of publications for holding the academic position "Associate Professor".

1.1. Influence of inorganic impurities and organic additives in electrolytes for electroextraction of zinc [1-7]

The intensive development of zinc extraction in our country using the hydrometallurgical method encountered problems, some of which have not been solved on a global scale. Two of them are related to the electroextraction of zinc, namely reducing the specific consumption of electrical energy and improving the structure of the zinc coating. Both problems arise primarily from the presence in the electrolyte of impurity ions of elements with a more electropositive potential than zinc. In this regard, in the Dissertation is investigated and clarified the mechanism of the processes in the initial stage of zinc electrodeposition from acidic sulfate electrolytes. The influence of nickel and cobalt ions, as well as of some organic additives on these processes is also evaluated.

The main results of the conducted systematic studies are published in 7 scientific works [1-7]. These results can be systematized as follows:

- For the first time, the mechanism of the initial electrodeposition of zinc from sulfate electrolytes (containing impurity of Ni^{2+}) on a spectrally pure aluminum cathode is clarified. In the initial stage of the electrochemical process, at more positive potentials, local electrodeposition of nickel begins on the aluminum cathode which catalyzes the discharge of hydrogen ions and thus, conditions are created for generation and development of a gas phase. It causes appearance of structural defects in the zinc coating. During the further co-deposition of nickel with zinc, conditions are created for the action of corrosion microgalvanic elements with hydrogen depolarization, which determine the observed self-dissolution of zinc.
- The electrochemical behavior of the aluminum cathode is extremely dependent on the impurities and, above all, on the presence of iron in it, which is uniformly distributed in the form of aggregates of different sizes. It is proven that in the initial stage of the electrochemical process, the iron phase locally catalyzes the discharge of hydrogen ions determining pitting defects in the zinc coating. The effect is further enhanced by the nickel deposited mainly on the iron aggregates.
- For the first time, a "synergism" effect is experimentally established at the joint action of metal ions as impurities in the sulfate electrolytes, determining the appearance of an "induction period" in the initial stage of zinc electrodeposition. It is expressed in strengthening of the negative action of Ni^{2+} in the presence of Co^{2+} in the electrolyte, leading to shortening of the time until the beginning of the self-dissolution of the deposited zinc. The observed effect is due to specific adsorption of cobalt complex ions on the cathode, which relieves the discharge of Ni^{2+} and leads to an increase of the nickel codeposited with zinc.
- It is found from the investigations with four organic additives to sulfate electrolytes in the presence of Ni^{2+} that the composition of EAA (hydroxyethylated butynediol), TEBA (triethylbenzylammonium chloride), AEC (alkyl ether sulfate) and Gelatin most strongly

increases the cathodic overvoltage, which is reflected positively on the structure of the zinc coating and on the current yield (up to 90% ÷ 98%). Another positive feature of this composition is also demonstrated in the elimination of the danger of the formation of sulfuric acid mist over the electrolytes in operating conditions.

1.2. Lead alloys in their role as anodes in the electroextraction of zinc [8 ÷ 17]

One of the most significant problems in electroextraction of zinc from sulfate electrolytes is the insoluble anodes. The needs and requirements for the purity and quality of the cathodic product are closely related to the creation of new anodic materials possessing increased resistance in combination with other technological and electrochemical properties.

The influence of the method of preparation and plastic processing of binary (Pb-Ag and Pb-Ca) and ternary (Pb-Ag-Ca) alloys, used as anodes in the electroextraction of zinc, on their electrochemical behavior and corrosion resistance is evaluatedd [8]. It is established that the rolled Pb-Ag alloys have higher corrosion resistance and lower anodic polarization compared to the cast Pb-Ag ones, due to the finer structure and homogeneity of the plastically deformed anodes. The plastic deformation of the ternary alloys (with calcium content of 0.06%) causes precipitation of Pb_3Ca in the solid solution. The hot-rolled alloys form α-solid solution of Pb_3Ca with a fine-grained structure, which is deformed along the direction of rolling. Cold-rolled alloys have clearly defined structures also oriented in the direction of rolling.

Cast and plastically deformed Pb-Ca anodes have better electrochemical and corrosion characteristics than pure lead, but significantly higher anodic polarization and lower corrosion resistance than Pb-Ag-alloys. Both Pb-Ca systems with Ca content of 0.8% or 0.11% are very suitable for preparation of ternary Pb-Ag-Ca alloys. The latter (Pb-0.5%Ag-0.11%Ca) have better electrochemical and corrosion characteristics than the double Pb-Ca ones. Only the triple rolled alloys have the same corrosion and electrochemical properties as those of the Pb-Ag (1%) alloy used in the practice.

The electrochemical behavior of Pb and its three types of alloys - double (Pb-Ag and Pb-Ca) and triple (Pb-Ag-Ca) is investigated by cyclic voltammetry [9]. X-ray and SEM methods are used to analyze the phase composition and the surface structure. It is found that only the ternary ductile alloys (Pb-0.5%Ag-0.11%Ca) are similar to the industrially used Pb-Ag anodes. It can be assumed that in the case of the ternary alloys, the catalytic layer is composed of a dense non-conductive MnO_2 layer of crystals, serving as the main centers for oxygen evolution.

A new anode material of Pb-Co (0.5% – 6%) is obtained which can be used for electroextraction of zinc from sulfuric acid electrolytes [11, 17]. The properties of these anodes, based on a fundamentally different method of preparation, are investigated by electrochemical methods. The data are compared with those of Pb-1%Ag anodes that are used in industry. They reveal that anodes with more than 0.5% Co have better corrosion resistance, and also that at 3% Co, the anode overvoltage is about 0.08V-1V lower than that of Pb-1%Ag alloy. The anodic layer of Pb-Co anodes, which is dense and tightly adhered to the surface, consists of β-PbO_2, MnO_2 and $PbSO_4$. The Mn^{2+} ions, present in the electrolyte, are anodically oxidized to Mn^{4+} and they are incorporated into the forming anode layer.

Area 2: Chemical deposition of metal coatings on various types of substrates

Chemical metallization of dielectrics is a very effective, economically advantageous and promising method for obtaining new functional materials that would find application in modern technologies in the production of: new materials for electronics, energy, fine mechanics, optics, wear and corrosion resistant materials, printed circuit boards with metallized holes, etc. It is not related to the distribution of electric current, which allows deposition of a coating with uniform thickness on parts of complex configuration, provided that the solution has access to the coated surface.

In mechanical engineering and electrical engineering, and especially in micro-engineering, in order to reduce weight, many metal parts are replaced by polymer ones.

As a rule, metallized dielectrics are more resistant to corrosion compared to the parts made of the corresponding metal under the same operating conditions.

In recent years, massive penetration of nanotechnologies in science and technology, as well as in the field of electroplating is observed. For this purpose, metal dispersed coatings are of interest, which are obtained by embedding a solid dispersoid in the coating on a metal or polymer surface. Through its incorporation, a number of physico-mechanical, anti-corrosion and other properties of the base metal are improved, avoiding as much as possible the deterioration of some of its desirable properties.

Investigations in this area are related to the chemical deposition of nickel/phosphorus and copper dispersed coatings on two types of substrates: solid (non-metallic and metallic) and flexible.

2.1. Chemical deposition of nickel/phosphorus and copper dispersed coatings on solid (non-metallic and metallic) substrates

2.1.1. Pretreatment of non-metallic substrates [60, 70]

Dielectrics are substances that conduct electricity poorly (or not at all) and they can generally be metallized by chemical methods. The dielectrics do not have their own catalytic action and it is imperative that they are subjected to pre-treatment, which is expressed in several successive operations: degreasing, etching (micro-roughening of the surface), pre-activation, activation (adsorption of catalytically active metal centers from a solution of palladium-tin colloidal activator), acceleration (removal of the tin hydrolysis products and of the stabilizing shell of the most adsorbed Pd–Sn cores) and chemical metallization. The properties of the metallized dielectrics are largely determined by pretreatment operations.

One of the most used polymers in practice is acrylonitrile butadiene styrene (ABS), which is easily metallized and provides good adhesion to the metal coating. ABS is a thermoplastic copolymer based on acrylonitrile, butadiene and styrene. It is a three-component two-phase plastic in an amorphous state. One phase is a copolymer of styrene with acrylonitrile and it forms the solid (SAN)-matrix, i.e. the skeleton of the plastic. The second phase of grafted huge number of poly-butadiene (PB) globules is distributed in it. Acrylonitrile ensures the chemical resistance and increases the heat resistance, butadiene improves the strength of impact and styrene adjusts the hardness and good processing of ABS. It is used in mass production as a substitute of the solid metal substrates.

Due to the specificity of production, dielectrics are usually lubricated with mineral oils and plastic lubricants, which are used to preserve the injection molds. For this reason, the process of degreasing or preliminary cleaning of the surface from organic and inorganic contaminants is an important part of the pretreatment. The next step in the pretreatment is the etching operation, which is surface treatment of the dielectrics with different solutions, leading to changes in the morphology of the surface layers due to their dissolution. As a result of etching, the rubber globules are oxidized and dissolved, and caverns and channels of different sizes and complex shapes are formed on their place. The deposited chemical coating fills the resulting cavities, and by this way it is mechanically anchored to the polymer surface. The kinetics of chemical deposition is controlled by gravimetric determination of the thickness of the deposited dispersed coating, for which certain peculiarities must be taken into account: by the gravimetric method, an average thickness of the metal coating is actually determined, which is different on the polymer surface and in the depth of the caverns. Even using the information from the quantitative X-ray microprobe analysis on the dispersoid embedding in the metal matrix, exact results regarding the true thickness of the metal coating can not be obtained. This method also gives approximate information about the thickness of the metal coating on the highly roughened polymer surface.

For the purpose of chemical metallization of ABS, systematic investigations of different compositions and modes of operation of solutions for degreasing and etching of ABS are carried out with a view to their impact on obtaining a chemical nickel-phosphorus coating [60].

The criteria for the pretreatment effectiveness are the properties of the subsequent nickel-phosphorus coatings deposited by chemical nickel plating process, included as a finishing step in the pretreatment of the dielectric. The changes in the roughness and of the surface morphology of the dielectric material as a result of the two pre-operations are evaluated using profilometer-profilograph and scanning electron microscopy (SEM). It was established that degreasing in a solution of the surfactant (sodium lauryl sulfate - NaLS) provides more uniform subsequent etching of the dielectric surface. On the other hand, the addition of NaLS and Pd(II) in the etching solution leads to an increase of the degree of roughness of ABS compared to samples treated in a solution without these additives, to better adhesion between the deposited metal coating and the substrate, as well as to increase of the thickness of the Ni-P coating.

Due to the fact that the surface of the polymer samples is too smooth, an additional operation “swelling” is performed before the etching operation. It aims to increase the roughness of the surface and to facilitate the subsequent operations [70].

The investigations are carried out by using three types of organic solvents (toluene, xylene or acetone) at different temperature and treatment time. It is found that the swelling time has no significant effect on the degree of swelling, but it influences on the thickness and on the adhesion of the deposited chemical copper or nickel coatings. Temperature has a different effect when using different solvents. In the case of toluene, an increase in the degree of swelling is observed with increasing solution temperature, while in the case of xylene, the inverse dependence is observed. In the case of acetone, no effect of the temperature is registered. High values of the degree of swelling of the polymer surface decrease the thickness and deteriorate the adhesion of the deposited metal coating. This effect is probably due to the over-etching of the surface because of its overdevelopment. Adhesion tests, as well as the AFM and SEM analyzes of the untreated and swollen samples show that during the swelling process a partial dissolution and roughening of the samples takes place. Relaxation of the internal stresses is also probable.

In conclusion it can be summarized that by using acetone, the deposited chemical copper or nickel-phosphorus coatings are uniform over the entire surface of the polymer samples without cracks and with best adhesion.

2.1.2. Chemical deposition of dispersed coatings with various micro- and nano-particles

The replacement of the classic metalic coatings with micro- and nano-dispersed coatings enable further improvement of a number of valuable physico-mechanical properties. Therefore, from a scientific and technological point of view, the type of the electrolytes and the conditions under which dispersed coatings can be deposited on non-metallic and metallic substrates is of great interest.

Systematic investigations are carried out regarding the influence of the main components of the electrolytes for chemical nickel or copper plating and of a number of additives such as stabilizers, surfactants, etc. The influence of the nature and concentration of the dispersoid on the structure, properties and deposition rate of dispersed coatings is also examinated.

A. Chemical deposition of ***nickel/phosphorus dispersed coatings*** on non-metallic (ABS) and metallic substrates [18, 19, 21, 22, 23, 31 - 37, 41, 42, 57]

ABS substrate

The chemical deposition of dispersed nickel/phosphorus coatings is carried out according to the following standard technological scheme: degreasing, etching, activation with colloidal palladium, acceleration in an alkaline solution and chemical metallization. The last operation is conducted in the presence of two types of dispersoids:

- micro-particles with a size of about 1µm - SiC [18, 31] and Diamond [57].
- nano-particles with a size between 30nm and 60nm: - SiO_2 [22,31] and TiO_2 [19, 31, 32, 33].

The morphology (SEM), the content of dispersed particles included in the coating (EDS) and the specific electrical resistance of the investigated dispersed coatings are examined with the help of equipment designed and manufactured at TU-Sofia.

For first time, NiP-dispersed coatings on ABS-polymer with SiC dispersoid are electroless deposited from alkaline electrolytes [18]. Of interest are the experimental data that the thickness of these coatings are smaller than those of NiP-coatings obtained from the base electrolyte without addition of a dispersed phase. The difference is larger at long delay times. The probable reason for this behavior is the embedded SiC micro-particles in the NiP-matrix, which partially block the active growth centers of the metal coating. However, the increase of the thickness of the dispersed coating leads to a continuous increase of the specific electrical resistance.

More and more often in practice and especially for the needs of micro-technology, it is necessary to obtain thin NiP-dispersed coatings. This requirement cannot be met by dispersed layers with embedded micro-particles with a size about and above 1 μm. Thus, the influence of nano-dispersoids of TiO_2 and SiO_2 with a size between 30 nm and 60 nm on the changes in the thickness of NiP-dispersed coatings, on the content of titanium, resp. silicon in these coatings and on their specific electrical resistance is investigated [19, 22, 32, 33]. The different course of the curves, reflecting the changes in the thickness of the coatings, can be explained by the difference in the relative density of the two types of dispersoids.

The conclusion made for the NiP-SiC coating that their thickness is significantly smaller compared to the thickness of the Ni-P coating is also valid for the nano-disperse coatings. It is found that the duration of deposition of the dispersed coating has no effect on both the silicon content in it and the specific electrical resistance.

The obtained results confirm one of our assumptions that the kinetics of the chemical deposition of NiP-dispersed coatings on ABS is not influenced by the nature of the solid nano-particles embedded in the coating, provided that they are of similar size, surface micro-geometry and electrical charge.

The corrosion resistance and microhardness of chemical Ni-P and Ni-P/D coatings (with diamond particles of 14-20μm) are investigated at two values of pH (3.8 or 4.8) of the electrolyte [57]. It is found that with increase of pH of the electrolyte, the thickness and the microhardness of the Ni-P coatings also increases, while the P content in them decreases. Corrosion tests show that as the residence time in the neutral salt spray chamber increases, the coating loses weight, with larger loss being registered in the case of the coatings with particles. At recording the anodic polarization curves in a sulfate medium up to the potential of oxygen evolution, the coatings are not completely dissolved. Ni-P/D coatings dissolve more uniformly than Ni-P coatings, retaining their amorphous structure and moreover, they show a lower corrosion rate.

Metal substrate

Taking into account the scientific interest to the preparation of nano-dispersed coatings on microstructures used in microelectronics, investigations are carried out on preparation of NiP- and dispersed NiP-coating with nano-dispersoids of Al_2O_3, SiO_2, TiO_2 on various metal substrates (Al, Fe, Ti, Ni or Cu), as well as on microstructures [37, 41] (provided by colleagues from TU-Ilmenau, Germany, with whom we had a common project).

A comparison is made between the results obtained from electroless [32, 34, 35, 36 and 42] and galvanic [21] deposited dispersed nano-coatings. It is found that a quality dispersed coating can be obtained without special pre-activation with a palladium salt, which is only necessary for copper substrates. In this case, the base metal in its pure state acts as a catalyst for the deposition. The optimal conditions of preliminary preparation of the various metal substrates (Al, Fe, Ti or Ni) are determined, and original methods are used for their chemical metallization.

The investigations are carried out with two types of nickel electrolytes (acidic and alkaline). The addition of nano-particles to the electrolyte has a very strong influence on the kinetics of the process, but the type of the substrate has little influence. Al_2O_3- and SiO_2-nano-particles, due to their inhibitory effect, greatly reduce the speed of the Redox process, while the opposite dependence is observed in the case of TiO_2-particles [33, 35]. With Ti-substrate, the deposition of a metal layer is observed only when TiO_2-particles are added, while with the other substrates, the obtained metal layers are completely uniform for all types of dispersoids. Alkaline electrolytes are less sensitive to added nano-particles. Incorporation of the dispersoid into the coating is qualitatively determined by microprobe analysis. Quantitative data are not obtained due to their minor embedding, but the embedded particles of the dispersoid are optically determined by cross section.

With increase of the concentration of nano-particles in the electrolyte during galvanic deposition, an increase of their inclusion in the coating is observed, as well as of its hardness [21]. At 50g/l nano-particles in the electrolyte, their incorporation increases by 2-3%, while in the case of chemical electrolytes at the maximum used concentration of 5g/l, the incorporation cannot be qualitatively determined. There is a problem regarding the non-uniform embedding of the nano-particles in the electro-deposited metal layers.

Since only copper substrates [32, 34] require a special pre-activation with a palladium salt, investigations are carried out aimed at creating a suitable activating solution and an effective and economically appropriate technology for electroless deposition of NiP- and NiP-dispersed coatings in view of its implementation in the production of printed circuit boards and in obtaining of microstructures for the needs of micro-technics [37]. A new generation of activating solution based on palladium sulfate and a complexing agent is proposed. It is found that the concentration of palladium in these solutions can be varied widely (20mg/l ÷ 50mg/l Pd) in order to obtain uniform and sufficiently thick NiP-dispersed coatings. After activation, without additional operations, chemical nickel plating in weakly acidic electrolytes is carried out immediately. The resulting coatings have a good morphology, and their micro-hardness is more than 30% greater than that of ordinary NiP-coatings.

The developed technology is applied in the production of printed circuit boards and in particular, in the deposition of the final double layer Ni/Au coating on the exposed copper surfaces. At the same time, this technology is characterized by selective activation, resp. chemical nickel plating of the copper part in the copper/polymer system, which is of relevance to the micro-technics.

NiP dispersion coatings on a steel substrate are obtained from an acidic electrolyte with diamond particles. It is found that the highest percentage of inclusion of particles is achieved at the small sizes (4÷8μm or 10÷20μm), and these coatings show better wear resistance compared to dispersed coatings with larger particle sizes.

During my specialization in IMM Mainz, Germany, galvanically obtained nickel dispersion coatings are also investigated, as well as their properties such as the crystal structure, hardness and embedding of the nano-particles in the nickel matrix [21]. Powdered SiC, diamond, ZrO_2 and TiO_2 (between 20nm and 50nm) are used as dispersoids. Their incorporation into the coating is indirectly determined, and for this purpose the coatings are dissolved in 35% HNO_3 and by means of the turbidity of the solution compared to water, the concentration of the nano-particles is determined (UV/VIS-Spektrophotometer Hitachi U 3000). It is found that their embedding in the nickel matrix increases in the order diamond – SiC - ZrO_2, while the micro-hardness increases in the order TiO_2 – SiC – diamond. At 10g/l diamond, the micro-hardness of the as-deposited nickel coating shows a maximum value that is approximately twice as large compared to the nickel matrix without dispersoid.

B. Chemical deposition of *copper dispersed coatings* on ABS substrate [25, 26, 27, 30, 31, 40, 54, Patent 1]

In order to find the optimal composition of the copper electrolyte, the influence of the concentration of NaOH and Trilon B, as well as of two stabilizers (stabilizer 1 - from the group of organic nitrogen-containing compounds and stabilizer 2 - from the group of sulfur-containing compounds) is successively investigated.

An advantage of the copper electrolyte composition proposed by us [Patent 1, 40] is that it shows a constant deposition rate with time and allows a significantly faster increase of the deposition rate with increasing CH_2O and $CuSO_4.5H_2O$ concentration compared to analogous electrolytes proposed by other authors.

For first time, copper micro-dispersed (with SiC and polyamide) and nano-dispersed coatings (with SiO_2) are chemically obtained from alkaline electrolytes on ABS substrates [25, 26, 27, 30]. It is established that with increase of the thickness of the dispersed coatings, it becomes difficult to embed micro-particles (SiC and PA) in the copper matrix [26]. This causes a slight decrease of the specific electrical resistance, which is a function of the dielectric properties of SiC and PA. The resulting dispersed coatings are characterized by a four to five times higher wear factor and based on this, technologies are developed for their application in micro-technics.

When replacing SiC with SiO_2 [27] with nano-sizes (30nm - 60nm), the same dependence "coating thickness/SiO_2 concentration" is observed, i.e., as the concentration of SiO_2 in the electrolyte increases, the thickness of the Cu-SiO_2-dispersed coating decreases.

Basically, this negative influence of embedded nano-particles on the kinetics of the process is explained by partial blocking of the active centers on which the autocatalytic reduction of copper (II) ions takes place. Therefore, this thickness is smaller compared to the thickness of copper coatings without dispersoids. The deposited Cu-SiO_2-dispersed coatings have a significantly greater thickness compared to the Cu-SiC-coatings under the same conditions of their preparation. The reason for this behavior is probably the smaller degree of embedding of SiO_2 nano-particles in the copper matrix, which is determined by the lower content of silicon in it.

The performed systematic investigations gave us reason to draw the important conclusion that the nature and the size of the dispersoid particles have no significant influence on the kinetics of the autocatalytic reduction of copper (II) ions on the ABS surface.

2.1.3. Chemical deposition of coatings from environmentally friendly copper electrolyte - formaldehyde-free and with low-pH [58, 61, 62, 65, 66, 67, Patent 3]

The chemical deposition of metals on dielectrics is based on the autocatalytic reduction of metal ions to metal on a catalytically active surface under the influence of a reducing agent added to the working solution. The most commonly used reducing agents are hydrogen-containing compounds (CH_2O, N_2H_4, etc.), which are highly toxic to the environment and in accordance with European Union directives, their use is not recommended.

For this reason, investigations are carried out with new, named by us “environmentally friendly” solutions for chemical deposition of copper layers that do not contain the traditional toxic reducing agent (CH_2O). In this case, the role of the reducer is performed by Sn^{2+} ions, which are previously adsorbed on the surface of the dielectric in the activation process. Their presence allows technological simplification of the pre-treatment operation (elimination of the intermediate acceleration stage), protection of the solutions from decomposition processes and long-term exploitation of the electrolyte for chemical metallization. In the method proposed by us, directly after activation, the details are immersed in a solution containing the relevant metal ions (Cu^{2+}), complexing agents, pH-correctors, buffering substances, etc.

The development of these new innovative environmentally friendly electrolytes is an important step towards finding combined approach of chemical and subsequent electrochemical deposition, aiming high-speed growth of metal layers on dielectrics but only after their preliminary chemical metallization with thin films.

When using these new approaches, it is necessary to investigate new solutions (compositions and modes of operation) for pre-treatment of the samples, since it has a significant impact on the metallization process and on the quality of the deposited metal coating. As a result of the performed investigations [61], the optimal concentrations of the solutions for degreasing, etching, reduction, pre-activation and activation in a colloidal solution are determined.

The samples treated by this way are chemically metallized in an environmentally friendly electrolyte that does not contain a reducing agent (formaldehyde) (pH 12-13), the composition of which is published in Patent 3 (2021).

In [65], comparison is made between copper layers obtained by two different deposition schemes: in the first one, an environmentally friendly electrolyte for chemical copper plating which does not contain a reducing agent is used, while in the second one, copper trilonate electrolyte with a formaldehyde reducing agent is used. The results show that the obtained layers by the environmentally friendly electrolyte are formed by copper (I) oxide and they are uniformly distributed on the surface of the dielectric. Their thickness is too small (~ 0.3µm), but sufficient to wire a dielectric base aiming subsequent thickening by an electrochemical method.

To date, commercial electrolytes for chemical deposition of copper contain formaldehyde or its derivatives as a reducing agent and operate at pH values above 11. This makes these electrolytes potentially unstable, due to the spontaneous nucleation as a result of the local changes in pH or to the reactions taking place between the products and the metal ions and by this way, insoluble salts are formed in their volume. On the other hand, the high pH is not compatible with some dielectric or photo-resist materials, and also formaldehyde is highly toxic. This required development of another composition of weakly alkaline copper electrolyte (pH 9) which does not contain formaldehyde [62, 66].

In this type of electrolyte, sodium hypophosphite is used as a reducing agent and the deposition process is autocatalytic, allowing the formation of layers of several µm.

The influence of the concentration of Cu^{2+} ions and of the reducing agent ($NaH_2PO_2.H_2O$), as well as the influence of pH, temperature and deposition time on the thickness of the copper coatings is investigated. The chemical composition of the coatings is determined by EDS analysis, the thickness of the copper coatings by XRF analysis and the morphology of the coatings by scanning electron (SEM) or by optical microscopy. The obtained copper coatings are thin, but the investigations show that this thickness is sufficient for further electrochemical thickening of the coatings.

A specific feature of the electrochemical deposition is that the current supply, i.e. of the electrons required for the copper deposition reaction takes place at certain contact points. Because of this, low sheet resistance of the chemical copper is required for uniform electrochemical deposition [66].

Two electrolytes are used for conducting these investigations – the first one containing no reducing agent and the second one containing sodium hypophosphite as a reducing agent. The experimental data for the coating thickness and for the sheet resistance are compared with those of a conventional chemical copper electrolyte with a formaldehyde reducer. It is found that the chemically deposited layers have a greater thickness at the bottom of the samples, while after the subsequent electrochemical thickening, a decrease of the thickness is observed with the distance from the connection point, and the sheet resistance increases.

From the same composition of the copper electrolyte (pH 9) and at two temperature regimes (75ºC or 80ºC), copper is deposited on ZrW_2O_8 particles [67]. The interest in this topic is driven by the possibility of using such a material in the preliminary stage of obtaining metal-ceramic composites of Cu/ZrW_2O_8 type with low or zero CTE (coefficient of thermal expansion). Some properties of the composite material are compared to those of samples obtained from a solution containing formaldehyde with high alkalinity (pH 13) at 45°C. The influence of three different methods for homogenization of the solution (by air bubbling, by ultrasound or by both ("combined method") on the properties of the copper coatings is investigated.

Using two copper electrolytes of low pH (pH 9 [58]) and pH 5-8) with reducing agent phosphoric acid [63]), the deposition processes of chemical copper on a matrix of nano-porous anodic alumina (AAO) on an aluminum substrate are investigated. This substrate is widely used as a dielectric layer in which various elements for microelectronics, printed circuit board production, optics, etc. can be embedded. The contact-deposited copper layer at the Al/AAO interface is used to catalyze the chemical deposition of a copper coating. The optimal compositions and the regimes of operation of the copper electrolyte are established [63]. It is also found that the deposition takes place along the entire nano-porous matrix and at pH greater than 5, the chemical copper is mainly in the form of Cu_2O. The characterization of the obtained copper layers is performed by optical and scanning electron microscopy, as well as by EDX and XRD analyses.

In connection with a joint project with colleagues from UCTM under the Scientific Research Fund, systematic investigations are performed on the properties and indicators of combined Al-O-Ag coatings obtained on technically pure AA1050 aluminum [59]. By analyzing the data obtained from various analytical instrumental methods (SEM, AFM, EDX, XPS and Nanoindentation), a comprehensive model is proposed, that describes the kinetics of formation of complex Al-O-Ag coatings and the interrelationship between the applied growth conditions and the obtained characteristics, properties and morphology of the coatings.

2.1.4. Chemical deposition of coatings on 3D-printed substrates [64, 68]

In recent years, new industrial revolution is observed and 3D printing finds application both in the production of prototypes and in regular production in the following sectors: architecture, construction, automotive, aircraft, biotechnology, fashion, etc. Different technologies for 3D-printing are proposed. Among them, the technology FDM (Fused Deposition Modelling) has the greatest application in the industry due to the low cost and simplified operations. This technology is suitable for 3D-printing of various polymers (polyethylene terephthalate (PET), acrylic nitrile butadiene styrene (ABS), polylactate (PLA), glycol-modified polyethylene terephthalate (PETG), etc.). They can be metallized by electroless deposition in order to obtain an even metal coating with good adhesion to the base polymer.

The properties of chemically metallized 3D printed ABS samples obtained by FDM technology with different filling densities of the internal layers (5, 10 or 100%) are investigated and compared with those of ABS obtained by injection molding [64]. The morphology and structure of the deposited metal coating are determined by scanning electron microscopy (SEM), the elemental composition by EDS, the surface roughness by AFM and the adhesion of the coatings is measured by a standard adhesion tape test (Tast-Method ASTM 3359-83). The samples are etched in chromic sulfuric acid etching solution and activated in a colloidal Pd/Sn activator at different temperatures ($20\ ^{o}C \div 50\ ^{o}C$). It is found that as the activation temperature increases, the roughening of the sample and the amount of sorbed palladium also increases, as well as the rate of metallization. The coatings are obtained from four different electrolytes: copper and nickel electrolytes containing reducer and those containing no reducer (CH_2O and NaH_2PO_2, respectively). The resulting metal coatings on the parts with a lower density of the inner layers are thicker, which is due to the larger amount of polymer with a lower density and more porosity. The experimental results show that the standard technology for metallization of injection-molded ABS-polymer parts can also be applied to 3D-printed ABS parts.

Chemical metallization of another type of 3D printed samples of PLA and PLA flex is also performed [68]. PLA is a polymer derived from renewable sources such as corn, potatoes, etc. with a high starch content, which is converted into polylactide acid. It cannot be recycled, but decomposes in manure for about 12 days, while for the others it takes 100 to 400 years. PLA is a strong and hard material that withstands up to $60^{o}C$ and its properties deteriorate if it is left for a long time in the sun. In this case, it is suitable to carry out the operations of degreasing and etching in an alkaline environment (NaOH) at the same time. Investigations show that the high temperature and concentration of the etching solution do not improve the properties of the coating. Etching accelerates metal deposition and slightly reduces the phosphorus content of the Ni-P coating. Regarding the wetting and adhesion properties of the Ni-P coating, the best results are obtained at etching solution concentrations of 100 to 200g/l NaOH and at a temperature of 20°C ÷ 40°C.

The experimental results allowed us to conclude that 3D PET samples can be etched both with chromium-sulfuric acid etching solution and with NaOH solution. Since Cr^{6+} compounds are harmful for the environment, it is preferable to use alkaline base as an etching solution.

2.2. Chemical deposition of nickel/phosphorus and copper dispersion coatings on *flexible substrates*

The preparation of dispersed materials that combine the properties of metals (specific structural features, strength, plasticity, elasticity, electrical conductivity, thermal conductivity, etc.) and non-metals (high hardness, chemical resistance, heat resistance, etc.) is a subject of extensive and intensive research through the last years. The inclusion of dispersed particles in the metal matrix on flexible substrates, achieved through the process of chemical co-deposition, led to the production of a new generation of dispersed materials characterized by certain chemical and physical properties. Dispersed materials with highly solid dispersed particles are increasingly being developed and used.

The best results are obtained when the coatings are deposited on a polyethylene terephthalate substrate (flexible pressed textile – PET), which is a linear homo-polymer with a dominant composition of polyester fibers. It can be heated and processed into various forms such as fibers, sheets, etc.

A technology is developed for the pretreatment of the substrate before the deposition of the metal coatings, and also the compositions and conditions for the chemical deposition of copper or nickel metal coatings are established. On the basis of these metal matrices, composite coatings with different types and sizes of dispersoids are obtained and investigated: diamond, ZrO_2, SiO_2, Al_2O_3, TiO_2, hBN and cBN. The obtained coatings have greater wear resistance and micro-hardness.

2.2.1. Chemical deposition of nickel/phosphorus dispersed coatings [50, 52, 53, 55, 56, 69]

NiP dispersed coatings are deposited on a flexible PET substrate with optimized in composition and mode of operation electrolytes containing different types of dispersoids: diamond [55], SiC [53], ZrO_2 [50], BN (alpha and cubic) [56]. It is shown that increasing the temperature can be used as an effective "tool" to increase the deposition rate of the nickel matrix. The stability of the solution for chemical nickel plating with the use of various stabilizers, as well as the influence of certain surface-active substances are investigated and established.

Laboratory technology is developed and experimented for both chemical and electrochemical deposition of dispersed coatings based on a nickel matrix with dispersoid diamond particles (with sizes from 3/7μm to 225/300μm) [55]. The influence of temperature, nickel plating time, pH and hydrodynamics of the solution, as well as the amount of diamond particles included in the deposited coating on the thickness and properties of the coating is investigated. The upper limit of the size of the diamond particles is established, allowing the preparation of nickel-diamond composites with a desired number of particles in them. Under the determined optimal working conditions, samples of abrasive tools are made with dimensions close to those used in the industry.

Analogous investigations are carried out with two other types of dispersed particles: SiC [53] and ZrO_2 [55], which show good mechanical characteristics depending on the amount of included dispersoid.

When choosing dispersed materials, alpha and cubic boron nitrite (BN) are chosen, because they have a practical application for the production of ultra-hard materials for increasing the wear resistance of machine elements, as well as for restoring worn working surfaces of friction parts [52, 56]. The mass and the related thickness of the obtained dispersed coating are determined depending on the size of the dispersoid, on its concentration in the working solution and on the content of the reducer in the electrolyte. Based on the obtained data, it is concluded that the incorporation of hBN and cBN into the nickel matrix is very good and as a result, quality thick coatings are obtained. Investigations are also conducted with pre-metallized cBN. The titanium layer pre-deposited on cBN grains does not affect the rate and structure of the subsequent nickel or cobalt plating. The growth processes of these two types of layers differ significantly from each other. While no helical growth of the layer is observed at the cobalt plating, the growth is helical at the nickel plating. The metallized ultra-hard cBN material is used for embedding in dispersed coatings, applied in the production of abrasive materials.

It is concluded from the conducted investigations that the developed nickel and cobalt dispersed coatings can be used as an alternative to hard chromium plating and thus, the use of highly toxic hexavalent chromium to be avoid. Abrasive, cutting and polishing tools can be made from these dispersed coatings.

Tribological tests of the obtained Ni-P coatings with three types of dispersed particles (diamond, BN and SiC) deposited on PET are carried out with specially developed equipment at IPC-BAS [69]. They show that the dispersion coatings are promising with regard to the possibility of their use as abrasive tools for surface treatment of rock materials. The next step would be to optimize the tribological conditions - load on the abrasive disc and duration of the treatment.

2.2.2. Chemical deposition of copper dispersed coatings [43 - 49, 51, 53, Patent 2]

One of the most common metal coatings obtained by chemical way is copper. Since the copper is on a second place after the silver in terms of electrical conductivity, it is used to produce a number of products. Dispersed copper coatings, despite being little used, find practical application due to their high thermal conductivity, high resistance to electro-migration and low specific resistance.

In view of their application in various fields, dispersed coatings (with different types of dispersoids) are deposited on flexible substrates, and they are investigated:

- Dispersoids with nano-sizes - SiO_2, Al_2O_3 and TiO_2 [47]
- Dispersoids with micro dimensions - graphite [47], SiC [48, 53], diamond [45, 46] and hBN, cBN. [49, 51]

Initially, solutions with different composition for chemical copper plating are investigated with the aim of maximum deposition rate. The X-ray structural and electron-microscopic analyses show that, both morphologically and structurally, chemically deposited copper coatings are significantly different from electrochemically obtained ones (matte or bright) [43, 44, Patent 2].

For the first time, chemical composite coatings (Cu/D, Cu/BN and Cu/SiC) with a wide range of dispersoid sizes (3/7µm ÷ 100/125µm) are obtained from trilonate electrolyte on a flexible substrate of polyethylene terephthalate [45, 46, 48, 49, 51, 53]. The most suitable hydrodynamic rejime and treatment of the dispersed particles with a suitable surfactant (NaLS) are determined with a view to incorporate dispersed particles with sizes up to 20/28µm into a copper matrix. It is shown that for larger particles (over 60/70µm) it is more appropriate to pre-metallize them before their adding to the chemical metallization solutions, while for the largest particles (up to 195 µm) electrochemical co-deposition is suitable. These dispersed coatings are investigated in detail, due to the fact that they can be used for the final processing of hard materials (corundum, hard alloys, etc.), since during the operation of the tool, the small particles of the processed material are included into the soft copper matrix and thus, they do not damage its surface.

Investigations are carried out confirming the possibility to incorporate un-metallized and pre-metallized cBN grains into a copper matrix deposited on PET [49, 51]. The obtained results give reason to plan experiments aiming the metallized cBN to be successfully incorporated into other metal, ceramic or plastic matrices in view of their application in manufacturing abrasive tools by high-temperature sintering. The results show that it is expedient to work with smaller fractions of BN grains in order to avoid the economically disadvantageous long time of copper plating.

In order to produce an abrasive material for grinding and fine polishing, dispersed coatings with dispersoid SiC (from 10/7µm to 75/63µm) are obtained [48, 53]. The addition of surfactant to the metallization solution greatly increases the incorporation of SiC particles into the copper matrix, and the best results are obtained with the finer-grained fractions of the dispersoids.

Copper coatings on woven and non-woven flexible materials are obtained with incorporated nano-particles (SiO_2, Al_2O_3 and TiO_2) [47], which are uniform in thickness, semi-bright and giving the fabrics beautiful appearance. They can be used as radio-protective screens against electromagnetic interference, as well as they can find application in industry, agriculture and for domestic use.

The tests for the polishing effect of the obtained under laboratory conditions dispersed layers (by chemical deposition - PET/Cu-D, PET/Cu-cBN, PET/Cu-SiC, and by electrochemical deposition - PET/Cu-D) on samples of limestone and two types of marble showed Rz and Ra values fully corresponding to the data obtained with the commercial products for finishing surface treatment of similar rock materials (Rz and Ra are coefficients characterizing the change of the surface roughness and they are measured by a profilograph – profilometer unit). The tests were carried out with equipment constructed at IPC.

Area 3: Printed circuit board manufacturing problems

Early publications [20, 28, 29, 38] are devoted to various aspects of printed circuit board manufacturing problems.

Final stage of pre-treatment in metallization of printed circuit boards [20]

One of the methods for cleaning epoxy-based printed circuit boards from resin impurities is treatment with a $KMnO_4$ solution.

The process consists of three stages: treatment with an alkaline aqueous solution of an organic solvent (stage I), treatment of the boards in an aqueous solution of $KMnO_4$ (stage II) and removal of the residues from the treatment with KMnO4 (stage III). The described investigations relates to the third stage. To perform them, a solution with two components that have different functions is used:

a) Neutralizing component - converts the residues of $KMnO_4$ and the resulting MnO_2 by reduction into a soluble compound of Mn^{2+}

b) Etching component - leads to removal of each free glass fiber in the openings and prepares the glass surface for adsorption of the activating metal.

The following three systems are used to remove the residues of $KMnO_4$ and MnO_2: H_2O_2/H_2SO_4, $H_2C_2O_4/H_2SO_4$ and $H_2C_2O_4/HBF_4$. Concluson is drown on the basis of the experimental data that the greatest reduction of the mass of samples is achieved when using a solution of sulfur and oxalic acids, and the thickest copper coating is obtained with the use of H_2O_2 and H_2SO_4solution. This solution is also economically more appropriate, because of which it is implemented by colleagues from TU - Sofia in the production of printed boards.

Passivating solution for Copper in the production of printed circuit boards [38]

In order to prevent the corrosion of copper under the influence of atmospheric conditions, as well as to store the soldering of the copper surface of the printboards in the technological process, passivating solutions are used, which lead to significant material and financial savings. Such inhibitor investigated by us is the organic protective coating OSP (Organic Solder Preservative), which is applied to copper foil samples of about 0.1mm thickness and to bilateral printed circuit boards based on epoxy fiberglass (FR-4) with metallized openings.

By spectrophotometrical method is determined the thickness of the coatings in dependence on the processing time, the temperature and pH of the solution. By SEM photos is shown the type of the deposited inhibitory coating. Its corrosion resistance is determined under the action of 50% HNO_3, and it is established that at 30s processing time it is good enough. Experimental data from the corrosion tester measurements show that the test can be used for qualitatively determination of the thickness of the inhibitor layer. The soldering of the copper surface is stored for a long time and the treatment with an inhibitor improves the wetting of the copper surface by the solder.

Chemical deposition of Tin from acid electrolytes [28, 29]

Interest to chemical tinning is extremely increased in the recent years due to its application in electronics and in particular, in the producing the printed circuit boards. This stimulates investigations on optimization of the composition of the acid electrolyte for chemical tinning of copper surfaces, on determination of the effect of the components and on clarification of the mechanism of the process.

Experiments are performed with copper foil samples (99.7% Cu) about 0.1 mm thick. Direct gravimetric determination of the thickness of chemically deposited tin coating is not correct due to the partial dissolution of the copper surface as a result of an immersion reaction:

$Cu + Sn^{2+} \rightarrow Sn + Cu^{2+}$.

The experimental data obtained for the influence of the deposition duration on the thickness of the tin coating, as well as on the dissolution of the copper surface in the base electrolyte without and with $NaH_2PO_2.H_2O$ indicate that the deposition of the coating is a result of two parallel reactions:

1. Reduction of Tin (II) ions by copper, especially at the short times, as a result of the immersion reaction.

2. Redox process running under the action of imported into the electrolyte reducer- $Sn^{2+} + Red \rightarrow Sn + Ox$. While at the short times the influence of the reducer is very weak, at longer times (over 30min) it begins to participate in the process more actively. Especially at 120min, the thickness of the coating is increased by 2.3 times in the presence of the reducer, until the dissolution of copper is increased by 1.15 times. Therefore, the deposition rate is twice higher as a result of the reduction action of $NaH_2PO_2.H_2O$.