

Research on the process of plating Ni and Cu by chemical method on non-conductive substrates

Truong Thi Thu Huong¹, Ly Viet Anh²

^{1,2} Thai Nguyen University of Technology, No.666, 3/2 Street, Tich Luong Ward, Thai Nguyen province, Vietnam
This research is funded by Thai Nguyen University of Technology, Vietnam.

Date of Submission: 28-03-2023

Date of Acceptance: 07-04-2023

ABSTRACT

In the manufacturing industry of non-conductive products, in order to improve mechanical properties and aesthetics, plating methods are often used at the product finishing stage. However, nowadays plating on non-conductive substrates is usually done using chromic acid containing 6+ valence chromium to activate the surface thereby increasing the negative impact on the environment and increasing the cost (increasing amounts of rare, expensive metals - Palladium). This article will discuss the design of a chemical coating process for Ni and Cu coating on non-conductive substrates to ensure environmental friendliness, minimizing the risk of toxicity to human health and rare and expensive metal in the coating stage.

Keywords: Plating, coating, non-conductive substrate, machine manufacturing technology.

I. INTRODUCTION

Products made from non-conductive materials such as plastic, glass, etc. are widely used in industry by some basic characteristics such as light load system, high corrosion resistance. To improve the mechanical properties and aesthetics of plastic products, at the product finishing stage, people often use plating, coating or painting methods. Among them, the coating method is considered to be popular because it can create conductivity, optical properties, anti-interference, and create functional coatings in favorable micro-mechanical technology [2].

However, currently the plating process on non-conductive substrates is usually done using chromic acid containing 6⁺ valence chromium to activate the surface. This method increases the negative impact on the environment and increases the amount of rare, expensive metal (usually Palladium). Therefore, the "Research on the process of plating Ni and Cu by chemical method

on non-conductive substrates" ensures environmental friendliness, minimizing the risk of toxicity to human health and rare and expensive metal in the coating stage is a necessary and meaningful issue.

II. CONTENT

2.1 Overview of plating on insulating materials

To clarify the nature of plating on insulating materials (non-electrical plating), we first analyze the plating process on conductive materials (electroplating).

Electroplating is an electrolytic process to coat metal on a conductive material by attaching the object to be plated to the cathode, and the plated metal to the anode of the power source in the dielectric solution. The anode of the power supply will attract e⁻ electrons during oxidation and release positive metal ions. Under electrostatic force, these positive ions will move to the cathode. Here they receive back e⁻ in the redox process forming a metal layer on the surface of the plated object.

Different from electroplating method, the electroless plating method product of desired coatings from aqueous solutions without an application of the electrical external current and/or potential. This method controlled autocatalytic deposition of a continuous layer on a catalytic surface by the reaction of a complex compound and a chemical reducing agent.

Two commonly used methods of metal plating on the surface of insulating materials include physical plating and chemical plating.

- Physical plating method

Physical plating methods are divided into two types including physical vapor deposition (PVD) and chemical vapor deposition (CVD).

The principle of this method is to create a coating on the substrate through the precipitation of

metal from the gas phase under low pressure conditions.

The vacuum chamber contains the evaporator, plated holder and shielding elements, along with sensors for process control. During evaporation, the metal changes from a solid to a vapor under low pressure conditions through thermistor, electron beam bombardment or arc. The metal-containing vapors then condense on the plastic surface creating the required coating. Physical evaporation is usually carried out in a vacuum or in an inert gas environment. The vacuum is created by the series of suction pumping systems located outside the vacuum chamber [1,3].

The PVD method has the advantage that it is very suitable for coating a large number of products, suitable for industrial production. In addition, this method allows for easier control of the coating quality than conventional electrochemical plating. However, it has the disadvantage that it requires expensive equipment, complicated technology, and high cost. Therefore, this method is only suitable when the technological process is complete [1, 3, 4].

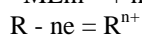
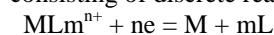
- Chemical plating (galvanizing without electrodes)

The principle of chemical plating is to create a leading layer on an insulating material by chemical methods (not using an external power source but through chemical reactions). Therefore, the chemical plating is also called electroless plating. This paper studies the plating of insulating materials based on the principle of electroless plating.

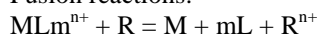
2.2 Status of the chemical plating process on insulating materials

Currently, chemical plating on insulating materials is usually carried out according to the following process: (1) Pre-washing; (2) Solvent treatment; (3) Cavitation; (4) Neutralization; (5) Preactivation; (6) Activation; (7) Acceleration; (8) Chemical plating; and (9) Enhanced electroplating: Copper (Cu); Nickel (Ni); Chromium (Cr) [1].

When plating, the metal complex ion MLm^{n+} will reduce to a metal atom M, and the reducing agent R is oxidized to form Rn^{+} . These reactions are similar in nature to electrochemical reactions, consisting of discrete reactions [2].



Fusion reactions:



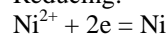
The Ni or Cu chemical coating before electroplating is usually activated in 5% sulfuric acid solution, then the electroplating solution

includes: $NiCl_2 \cdot 6H_2O$ (24g/l), HCl (1.18g/l), current density 2A/dm² in 5-7 minutes plating.

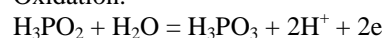
It can be seen that, the chemical plating has a number of important advantages such as: No need for an external power source, the reaction occurs under the redox processes of metal salts present in the plating solution; The plating layer has a more uniform thickness, low porosity, so it has good corrosion resistance in many different environments, has high wear resistance and higher mechanical properties than electrolytic plating. Besides, the resulting plating has better distribution than electroplating. It can be applied to non-conductive objects such as glass, plastic, ceramics,... Polymers, when chemically plated, will have a thin metal layer on the surface, which will become a new material widely used in electronics and industry [3]. Using this method, we can create new materials by changing the plating structure such as composite chemical plating such as Ni - P - Diamond, Ni - P - Graphite... especially Ni - PTFE (polytetrafluoroethylene - Teflon) help for increasing self-lubrication, high corrosion resistance, and low friction.

However, the chemical plating has some disadvantages such as: Plating speed is slower than electroplating; the thickness of the chemical coating is small, the ductility and expansion are low; The composition of the plating solution is not stable; the quality of the material to be plated is reduced due to impurities; must be performed at relatively high temperatures. For plating with non-conductive materials, we can use electrodeless chemical plating method. When plating, do not use external power supply [5].

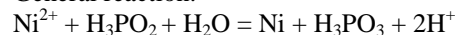
Reducing:



Oxidation:



General reaction:



2.4 Design of metal plating system on insulating materials

The process of plating metal on insulating materials can be proposed to include the following steps.

a. Prepare the substrate

The selected substrates are ABS resins and plastic glasses are cut into pieces with dimensions of 40x40 (mm²), then they are cleaned in an ultrasonic machine, the cleaning solution is distilled water. Next, the substrate plate was washed twice in 700 distilled water and alcohol solution, and finally the plate was dried by dryer for about 1-3 minutes.

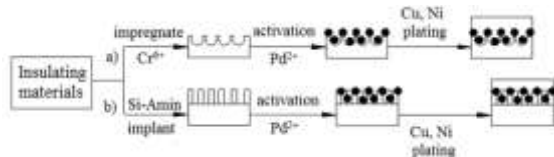


Figure 1. Copper plating process on the surface of ABS material

- a) Plating by the traditional method;
b) Plating by new method

b. Mixing solution for plating process

- Surface pretreatment with Hydro-Peroxide Acid solution: Solutions used to pre-treat ABS surfaces include: 37% HCl solution; Hydrogen peroxide H_2O_2 50%; and distilled water at a ratio of 1:1:5, with a temperature of about $80^{\circ}C$, kept for 8-12 minutes.

- Silane-Amin-Palladium complex group implant

The inoculation solution consisted of 88% $PdCl_2$, mixed with 100ml of HCl solution. Continue heating the solution to $65^{\circ}C$ so that $PdCl_2$ converts itself into H_2PdCl_4 . Mix 1.12ml of 3-propyl ethylene-diamine and 49ml of distilled water to make 50ml of solution. Slowly pour 50ml of this solution into 100ml of H_2PdCl_4 solution. Continue adding 25ml of NH_4OH solution to form a complete implant solution. The reactions in solution will form the Silane-Amin-Palladium complex group. The process of implanting the complex group on the ABS plate will take place in about 25-30 minutes, then the plate is washed with distilled water and dried.



Figure 2. Experimental system

c. Copper (Cu) plating on insulating substrates implanted with complex groups

Cu plating solution including $CuSO_4 \cdot 5H_2O$ 10g/l; NaOH 10g/l; HCHO (37-41%) 10ml/l; K-Na 50g/l. The copper plating is done at normal temperature, about $25-30^{\circ}C$, from 7-15 minutes. After being plated with Cu, the ABS sheet is washed in an ultrasonic bath with distilled water and dried with a dryer.

d. Nickel (Ni) plating on insulating substrates implanted with complex groups

The chemical nickel plating solution used experimentally has the following plating

composition and parameters: Nickel chloride ($NiCl_2 \cdot 6H_2O$) 20g/l; Sodium hypophosphate ($NaH_2PO_2 \cdot H_2O$) 10-36 g/l; Sodium acetate (CH_3COONa) 10g/l; Succinic acid ($C_4H_6O_4$) 10g/l; pH 4-5; Temperature $80 - 90^{\circ}C$; The pH of the solution was adjusted with 5% NaOH solution.

Method of making plating solution: Mix chemicals including Nickel Chloride (Aldrich 99.8%), Sodium Acetate (Aldrich 98%) and Succinic Acid (Aldrich 98%). This solution will be heated to about $40^{\circ}C$, added with sodium hypophosphite and further heated to plating temperature.



Figure 3. Experimental chemicals

2.5. Experimental process

Step 1. Surface pretreatment with hydroperoxide acid solution

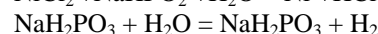
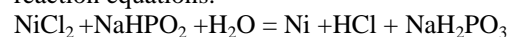
The chemical plating process on the surface of the insulating material is shown in Figure 4.



Figure 4. The chemical plating process on the surface of the insulating material

The works performed include:

- (1) Pre-washing: Remove impurities from the substrate by distilled water.
- (2) Cavitation: Using CrO_3 solution 850-900 g/l add a small amount of H_2SO_4 . The temperature of cavitation is more than $70^{\circ}C$, for 6-8 minutes;
- (3) Neutralization: The polymer after cavitation will be neutralized with sodium bisulfate $NaHSO_4$ solution;
- (4) Preactivator: Increases the ability to create a strong foothold for the activator;
- (5) Activation: Create a layer of Palladium glue on the plastic surface to catalyze the chemical plating process with 0.5% solution of $PdCl_2$ and HCl;
- (6) Acceleration: Increase the activity of Palladium catalyst by washing off the Hydroxide layer on the plastic surface at about $35-40^{\circ}C$ and for 3-5 minutes;
- (7) Chemical plating: The process of plating Ni on the polymer surface is shown by the following reaction equations:



(8) Ni-enhanced electroplating: Increase the mechanical properties of the coating by using a solution consisting of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (24 g/l), HCl (110ml/l); Current density $2\text{A}/\text{dm}^2$, for 4-5 minutes.

2.5 Experimental results

a. Evaluation of the microstructure of the plating layer

By SEM technology, micro image of ABS plastic surface before and after plating is obtained. Before plating, the surface of the ABS substrate is rough. After plating, the surface of the ABS substrate is more smooth, uniformly organized, shiny, beautiful.

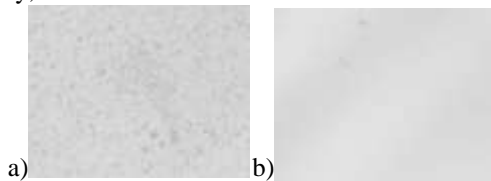


Figure 5. ABS plastic surface before and after Cu plating

b. Evaluation of the chemical composition of the coating

The chemical composition of the coating can be assessed by EDX (Energy-dispersive X-ray spectroscopy) technology through energy-dispersive X-ray spectroscopy or Energy Dispersive Spectroscopy.

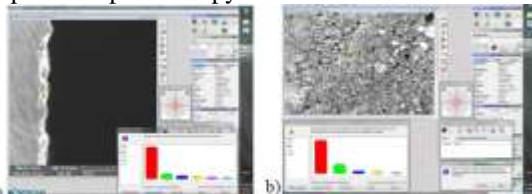


Figure 6. Evaluation of the chemical composition of the coating

a) Cu plating on plastic, b) Ni plating on plastic

The analysis results of Cu coating on plastic by EDX technology show that the coating adheres well to ABS plastic. After plating 7 minutes, the coating thickness is about $12\mu\text{m}$, evenly distributed on the substrate surface even at the corner of the plastic sheet.

The results of analysis of Ni coating on plastic by EDX technology show that there are 72% Ni, 18% C; 5.1% O; 3.5% Al and 0.6% Fe and other impurities. Thus, the total substances including Ni, O and C account for 95.1% of the coating content.

c. Evaluation of coating adhesion

The adhesion of the coating is checked with an adhesive tape according to ASTM D test standards.

The adhesion of the coating is considered guaranteed when it has 0% of the coating area lifted by the adhesive tape.



Figure 7. Evaluation of coating adhesion

A grid (4 lines x 4 lines, each line is spaced 1mm apart) is cut and placed on the Ni-plated KMPR sheet. Stick this test tape on the scratched KMPR sheet. The results show that after peeling off the adhesive tape, there are no peeling squares. Therefore, it can be said that the Ni coating has satisfied the required adhesion.

The XPS analysis of the original KMPR surface and the treated KMPR surface is illustrated as follows:

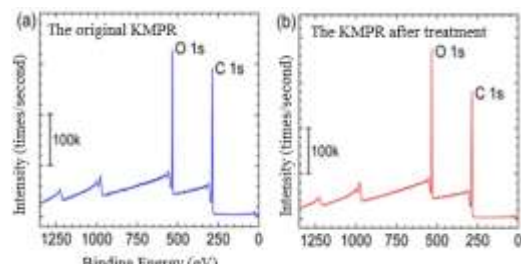


Figure 8. Analysis of KMPR surface by XPS

a) The original KMPR surface;
b) The KMPR surface after treatment

Waves 1000 - 1275 (cm^{-1}) have the appearance of Phenyls; Phenyl nuclei appear at wave number 1500 (cm^{-1}); $-\text{CH}_3$ and $-\text{CH}_2$ groups appear at wave numbers between 2850 - 3000 (cm^{-1}). The most notably, in the wave number 3000 - 3500 (cm^{-1}), characteristic appearance of Hydroxide ($-\text{OH}$) groups.

The carbon spectral resolution of the original KMPR surface (a) and the treated KMPR surface (b) is shown in the following figure:

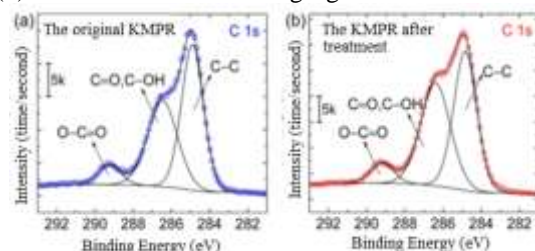


Figure 9. The carbon spectral resolution of the KMPR surface

The O/C atom ratio of KMPR increased from 0.31% to 0.34%. This explains the formation

of Oxygen groups on the surface of KMPR and is very important for discovering the chemical properties of Oxygen groups on the KMPR plate through XPS survey of the spectral level of Carbon nuclei.

X-ray fluorescence spectroscopy (XPS) shows the position when binding energy at 284.8 eV appear C=C bond; at 286.4 eV appear C=O and C-OH bond and at 289.2 eV appear O=C=O bond.

Với bề mặt KMPR nguyên bản tỉ lệ nguyên tử C-C; C=O/C-OH và O=C-O lần lượt là 51,4%; 41,4% và 7,2%. Sau khi tấm KMPR được làm sạch bằng SC₂ tỉ lệ này được thay đổi lần lượt là 47,7%; 43,3% và 7,0%. Rõ ràng là trong khi tỉ lệ của nhóm Cacboxyl hầu như không có sự thay đổi ($\approx 7\%$) thì việc làm sạch dẫn đến sự thay đổi tương đối đáng kể của các nhóm C-C và C-OH.

With the original KMPR surface, the ratio of C-C atoms; C=O/C-OH and O=C-O are 51.4%, 41.4% and 7.2%. After the KMPR sheet was cleaned with SC₂, this ratio was changed to 47.7%, 43.3% and 7.0%. It is clear that while the proportions of the Carboxyl groups were almost unchanged ($\sim 7\%$), the cleaning resulted in a relatively significant change of the C-C and C-OH groups.

III. CONCLUSIONS

The results of research and testing have provided a basic survey on the method of treating insulating materials before plating, plating and evaluating the quality of the surface of the coating when plating on an insulating substrate. Since then, the article has proposed a plating process on insulating materials that does not need to use chromium but is performed by implanting organic groups of amines associated with Silane and Palladium during surface treatment. This new method performs Surface Treatment at 60⁰C, about 20⁰C lower than traditional methods and without the strong oxidation of CrO₃. At the same time, SEM technology was used to evaluate the microscopic image of the plating layer.

Through SEM images, it has been demonstrated that the plating distribution is uniform and the plating layer covers well the surface of the insulating substrate; using EDX and XPS technology to indicate the chemical composition of the plating, the ratio of elements on the plating. Since then, the existence of the plating layer on the product has been evaluated, the surface pretreatment process can be adjusted to obtain OH-groups to create a better bond between the substrate material and the Palladium catalyst and ensure good adhesion between the base material and the Ni and Cu plating.

REFERENCES

- [1]. Mai Thanh Tung (2003), Plating technique on plastic background, Publishing House of Hanoi University of Science and Technology.
- [2]. Do Ngoc Hieu (2017), Non-electrode plating of nanostructured Nickel films at selected sites for micro-mechatronics applications, Master's Thesis, Hanoi National University.
- [3]. Ha Manh Chien (2015), Research on chemical plating technology to create coatings of Composite Ni/dispersed particles (AL₂O₃, PTFE), PhD thesis, Hanoi University of Science and Technology.
- [4]. Dang Thu Ha (2007), Research on fabrication technology and properties of oriented carbon nanotube materials, Master's Thesis in Physical Science, Vietnam Institute of Science and Technology.
- [5]. Le, X.T., Poirier, J.-S., Michel, S.: Completely aqueous route for metallization of structural polymeric materials in micro-electro-mechanical systems, Journal of the Electrochemical Society, under review.