Producing Platinum Resistant Nanolayer by Electrodeposition Method and Investigation of its Behavior in Acidic and Chloride Media

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Abstract:

The purpose of this study is obtaining resistant platinum coating in acidic and chloride media. In this regard, gold coating as an interlayer coated on copper substrate was selected as the most beneficial substrate for platinum plating according to the study among different substrates. In this study, Chronoamprometry (constant potential) method was conducted as the electrodeposition process and scanning electron microscope (SEM) images were utilized to investigate the coating morphology. Cyclic voltammetry (CV) tests were performed in the hydrochloric acid bath to check the durability and stability of the resultant pt. coating. The results show that the resistant platinum coating has been obtained.

Keywords: Chronoamprometry method, Electrodeposition process, Coating morphology, Cyclic voltammetry test.

Introduction:

Nowadays, chemical and electrochemical deposition of precious metals, including platinum, has played an immense role in the development of technology. The prominent feature of the platinum group metals (platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), iridium (Ir) and osmium (Os)) is their catalytic property during various processes. Noteworthy is the fact that platinum metal has the minimum chemical reactivity among other metals. As well as this, its high durability and great corrosion resistance even in high-temperature corrosion environments, make it quite distinct from other metals. In this regard, a coating with controlled thickness can be obtained using the electrochemical deposition method. The thickness of coating resulting from electrical deposition depends on the current density, the current efficiency and the duration of operation. The physical properties of resultant coating are a function of the plating bath composition, temperature, current density, surface quality of the plating substrate and the additives to the plating bath [1].

Nowadays diverse baths are used for plating platinum deposition and their special chemical formulas have been released; among them, hexachloroplatinic acid (H_2PtCl_6) bath, P platinum salts and Q platinum salts are the most common and functional baths. The choice of plating bath type varies depending on the coating application, the physical requirements and desirable properties which should be fulfilled [2].

Metals' electrochemical deposition can be studied by various electrochemistry methods. Varied thermodynamic and kinetic variables have been measured by these studies and thus provide

different quantitative and qualitative criteria for the interpretation of deposition mechanisms. These methods include linear voltammetry studies, cyclic voltammetry and chronoamperometry [3].The layers with a few microns thickness obtained from the platinum electrochemical deposition using its electrolytes are usually porous, hence a suitable substrate with an electrochemical potential close to the potential of platinum metal is required to enhance the durability and coating resistance in corrosive and acidic environments [4]. As a consequence, in this study, electrochemical deposition of gold as a profitable interlayer coated on copper substrate was utilized for platinum plating.

Materials and experimental details:

In this study, copper metal in the shape of wire was used as the substrate in the process. The 1 mm diameter copper wire sample was first sanded and polished and then acidified in the nitric acid (HNO_3) solution. After the preparation process, the sample was placed in the three-electrode system in order to perform an electrochemical deposition process. This system consists of a copper wire as the working electrode, the silver/silver chloride (Ag/AgCl) electrode as the reference electrode with a potential of 196 mV versus SHE and the 1 cm^2 surface platinum auxiliary electrode. Autolab potentiostat/galvanostat which is equipped with Nova software was used for the sake of electrochemical deposition. Gold industrial cyanide bath and hexachloroplatinic acid (H_2PtCl_6) bath were used for electrochemical deposition of gold interlayer on copper wire substrate and platinum film on gold interlayer respectively. Chronoamprometry method was conducted to deposit materials. In order to perform cyclic voltammetry (CV) tests on the resultant pt. coating in the acidic and chloride media, hydrochloric acid (HCl) solution with 0.5 M concentration was utilized.

Results and discussion:

Platinum layers with a few microns thickness are usually porous; so, by exposing the coating to the corrosive environments such as acidic and chloride media, the pores cause direct contact between the base metal surface and the environment. Since platinum metal is electrochemically noble and shows low chemical reactivity to the environmental elements in comparison with other metals, the base metal and platinum deposit areas form the galvanic cell and due to the smaller anode surface relative to the cathode area, the base metal area is prone to the corrosion and the corrosion current increases, causing the coating failure.

In fact, direct deposition of platinum metal on the copper substrate reveals low corrosion resistance and increasing the thickness of platinum film has no effect on this matter. Moreover, the emergence of a probable crack in the platinum coating leads to the contact corrosion which occurs between the solution and the copper substrate, resulting in losing the coating durability and strength.

Furthermore, the preparation of substrate surface has a significant effect on the coating properties and also its appearance; regarding this point, the substrate surface being properly prepared ends in the production of highly reflective deposit.

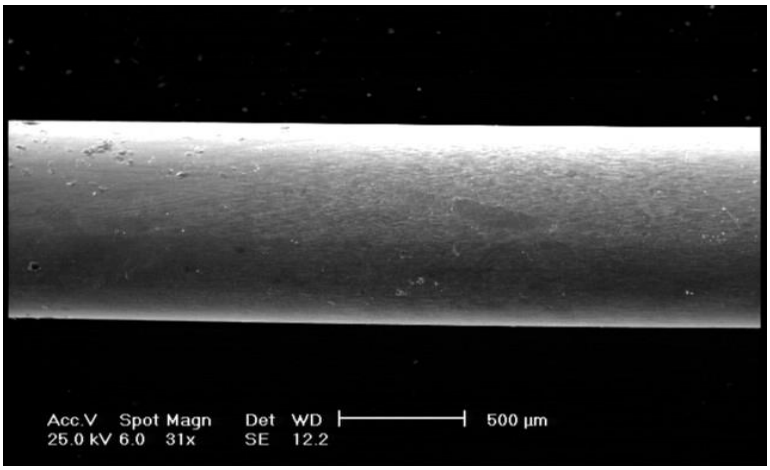

Figure 1. Scanning electron microscope (SEM) image of the copper wire substrate after surface preparation.

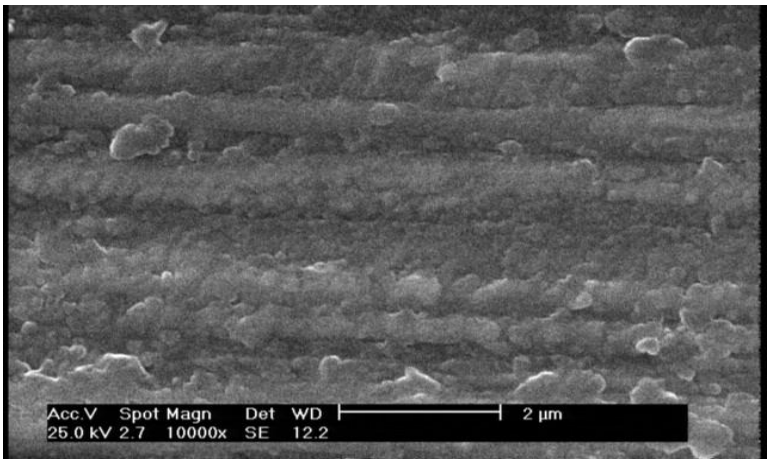

Figure 2. Scanning electron microscope (SEM) image of the prepared copper substrate.

As well as these mentioned points, due to the fact that the electrochemical potentials of platinum group metals (PGM) are more positive compared to the other metals, when metals such as copper with lower potential are placed in the PGM plating bath, prior to applying the electrical current, weak and non-adherent deposits are formed on the base metal. This matter causes the pollution of plating bath as well as a decrease in the amount of PGM bath potential.

It is worth noting that the use of a middle thin film has a profound effect on improving the corrosion behavior of platinum coatings. The bath used for the electrochemical deposition of platinum is hexachloroplatinic acid (H_2PtCl_6), which may corrode the copper substrate because of its acidity feature. Since gold is known as a noble metal and its electrochemical potential is close to that of

platinum, it can be useful in order to prevent galvanic cell formation and substrate corrosion. In this regard, electrical deposition of gold on copper substrate has been carried out through chronoamprometry method.

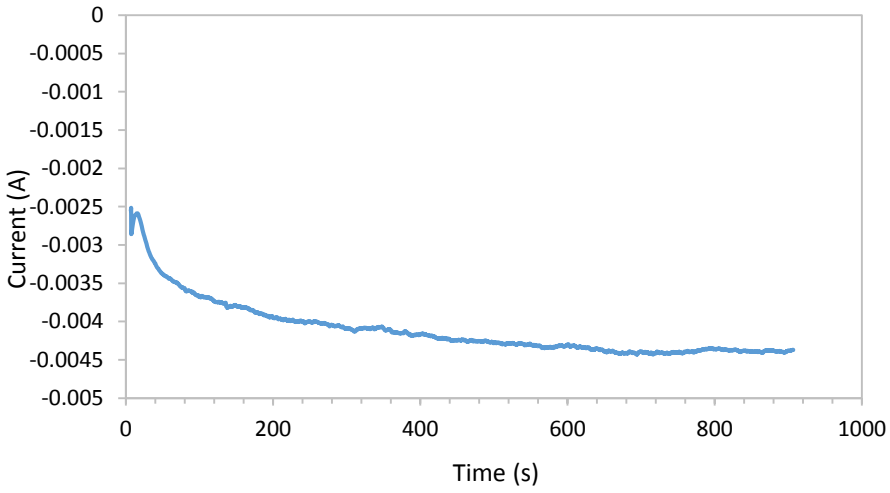

Figure 3. The graph of gold Electrodeposition from its cyanide bath on copper substrate via chronoamperometry (constant potential) method.

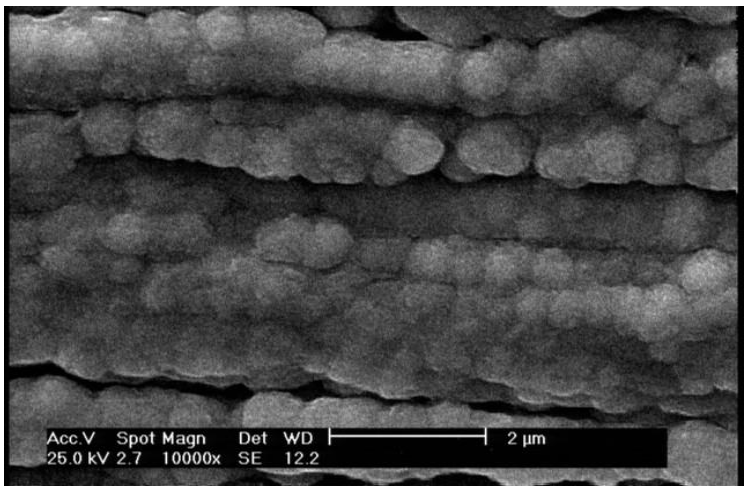

Figure 4. Scanning electron microscope (SEM) image of gold coating on copper substrate which is deposited by chronoamperometry method from gold cyanide bath.

According to the previous studies, higher rates of deposition can be obtained by using the chronoamperometry (constant potential) method compared to the other electrochemical approaches and the obtained deposit yields less amount of stress in comparison with resultant coatings from the chronopotentiometry (constant current) method [5,6]. As a consequence, in this study the chronoamprometry method was selected and utilized to electrochemically deposit platinum from the hexachloroplatinic acid bath on the gold interlayer.

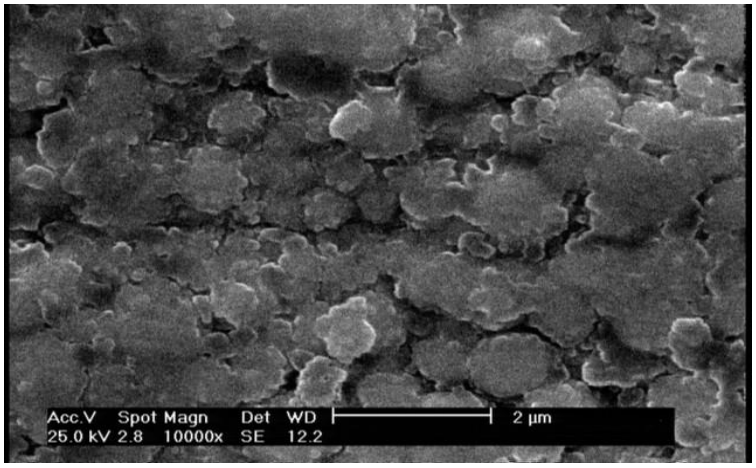

Figure 5. Scanning electron microscope (SEM) image of platinum coating on gold coating using chronoamperometry method from hexachloroplatinic acid bath.

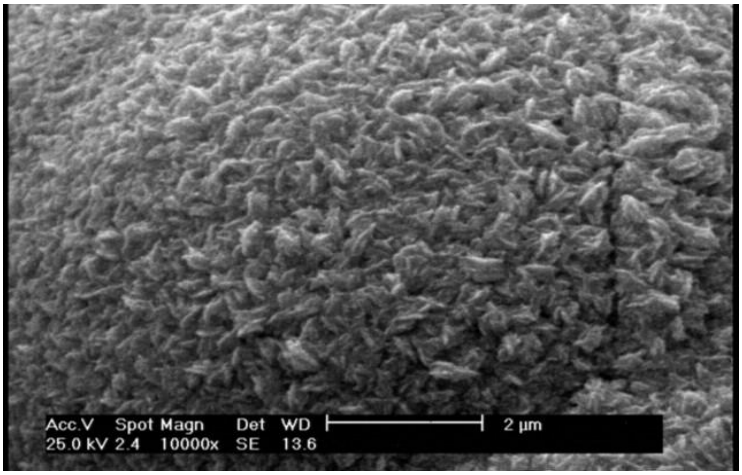

Figure 6. Scanning electron microscope image of platinum coating using chronopotentiometry method.

As can be seen, a uniform coating containing spherical pt. nano-particles can be obtained using the chronoamprometry method compared to the chronopotentiometry process. The effect of electrochemical potential is that by applying more negative and reductive potential for the sake of pt. electrochemical deposition, the hydrogen reduction reaction is intensified and reduces the current efficiency of platinum plating and also raises the possibility of stress existence in the coating structure. In fact, the morphology of resultant deposit varies related to the amount of applied potential. With applying more negative potential, the morphology of platinum coating shifts from spherical to angular shapes. Additionally, the appearance of deposit changes from gray to black as the applied potential in the deposition process becomes more negative.

Therefore, with regard to these provided images, the type of deposition method and the amount of applied potential are directly influenced the created deposit morphology and its structural properties. As well as this, how temperature affects is that the electrochemical deposition of metals during higher deposition temperatures ends in finer grain size compared to the low temperature

processes. In order to evaluate the coating performance in acidic and chloride media, the 0.5 M hydrochloric acid (HCl) bath was used. The pt. coating showed proper strength and durability during the cyclic voltammetry tests and without signs of failure after tests in the corrosive condition of hydrochloric acid solution with applying 50 consecutive anodic cycles.

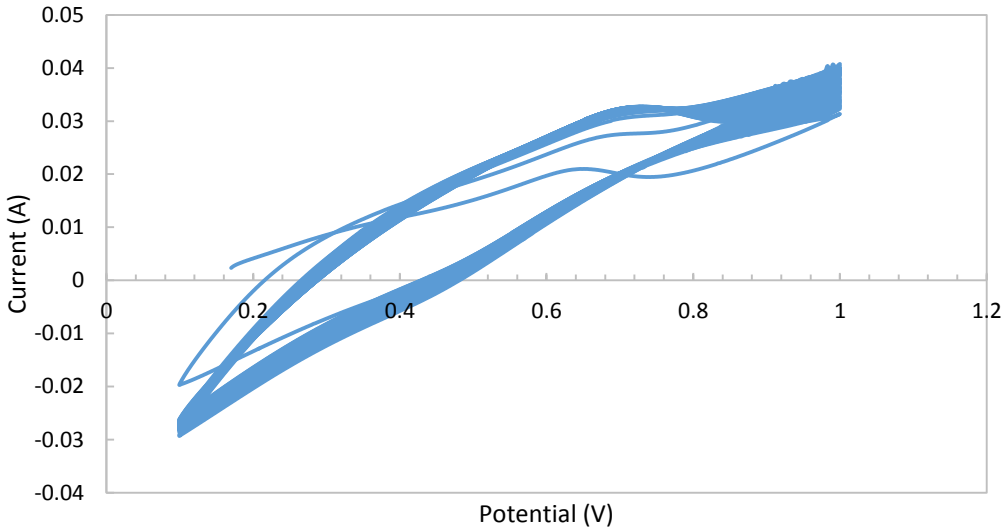

Figure 7. Cyclic voltammetry (CV) diagrams with the scan rate of 80 mV/s were taken from the 50 consecutive anodic cycles, given potentials are measured versus the Ag/AgCl reference electrode.

Conclusion:

In order to reach a platinum resistant coating in acidic and chloride media, the use of gold coating as an interlayer improves the corrosion resistance property and enhances the durability and stability of the resultant coating. Further, the use of chronoamperometry method for the sake of obtaining uniform deposit was found to be effective. Applying more negative potential results in reaching darker pt. deposits and decreasing the current efficiency of electrical plating. In order to evaluate the coating characteristics in the corrosive environments, cyclic voltammetry (CV) tests were performed with 50 consecutive anodic cycles in 0.5 M hydrochloric acid (HCl) which is a corrosive medium and it was seen that at the end of the CV tests the pt. coating did not lose its resistance and strength and also indicated suitable durability.

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