Pd is prevalently utilized in the application of catalytic converters due to its high catalytic activity for a breadth of chemical reactions, such as hydrogen evolution reaction and methane oxidation. In addition, Pd is capable of activating the non-active surface prior to the membranes. Electroless deposition of Pd has proven to be a versatile technique, and various methods have been implemented to synthesize Pd films or membranes. Electroless deposition of Pd has proven to be a versatile process in the preparation of Pd films, in which numerous electroless baths with different compositions have been reported in literature.

There are two primary classifications of electroless Pd plating solutions: (1) a galvanic displacement bath that is characterized by the redox reaction between Pd ions and a reductant, and (2) an immersion bath that is characterized by the displacement reaction between Pd ions and a sacrificial metal such as Cu, Zn. Electroless deposition of Pd has been proven to be a versatile process in the preparation of Pd films, in which numerous electroless baths with different compositions have been reported in literature.

To perform micro-indentation measurements, the Ni-P coated Cu sheets (10 mm × 20 mm × 0.2 mm) were used as the substrates in this investigation. The procedure of Ni-P coated Cu sheets is briefly presented as follows: first, the copper sheets were degreased (1 wt% HCl, 5 wt% LOP-10 2 min), micro-etched (3 wt% H2SO4, 2 min) and then activated (1 wt% H2SO4, 20 ppm PdSO4) at room temperature for 2 min. Then, the sheets were immersed into the electroless Ni-P bath (0.1 M NiSO4·6H2O, 0.2 M NaH2PO2·H2O, 0.2 M DL-Lactic acid, 0.05 M Propionic acid, 0.15 M CH3COONa, 10 ppm Propargyl alcohol propoxylate, pH 5.4, 80°C, 30 min.) to deposit a layer of 3 - 4 µm thickness of Ni-P. To perform electroless Pd deposition, the Ni-P coated Cu (Ni-P/Cu) sheets were dipped in the Pd bath (0.01 M PdSO4, 0.15 M Ethylenediamine, 0.1 M FA, 0.025 M EDTA-2Na, 0.2 M Na2HPO4, pH of 6.5, 60°C). All reagents used in this study were of analytical-reagent grade. The experimental apparatus and tests of electroless Pd deposition from different baths are shown in Scheme 1. The reaction is controlled by varying the composition of the bath. All electrochemical measurements were performed via a three-electrode electrochemical cell by a CHI760D electrochemical workstation. A Hg/Hg2SO4 (SMSE) and Pt plate were used as reference and counter electrodes, respectively. Open circuit potential with time (OCPT) curves was employed to evaluate the electrochemical properties during the electroless Pd deposition process on Ni-P surfaces. The Ni-P coated Cu sheets were used as working electrode. The cyclic voltammetry (CV) curves were employed to evaluate the oxidation of FA at Ni and Pd electrodes (electrode area: 0.5 cm2). The CV curves were investigated from ~0.7 to 0.7 V vs. Hg/Hg2SO4 at a scan rate of 0.01 V·s⁻¹.

Results and Discussion

The OCPT curves of Ni-P/Cu and Pd/Ni-P/Cu electrodes in the electroless Pd bath (or base electrolyte without FA) are shown in Fig. 1. The line 1 curve represents the variation of the open circuit potential (Eoc) of Ni-P/Cu as a function of time in the base electrolyte without FA. Eoc slowly increased in the initial stage from 0 to 180s until a plateau is reached at ~0.62 V. The increase of Eoc in line 1 is attributed to the deposition of Pd as a result of the following reaction:

\[
\text{Ni + Pd}^{2+} \rightarrow \text{Ni}^{2+} + \text{Pd}
\]

Experimental

Ni-P (9.4 wt% P) coated Cu sheets (10 mm × 20 mm × 0.2 mm) were used as the substrates in this investigation. The procedure of Ni-P coated Cu sheets is briefly presented as follows: first, the copper sheets were degreased (1 wt% HCl, 5 wt% LOP-10 2 min), micro-etched (3 wt% H2SO4, 2 min) and then activated (1 wt% H2SO4, 20 ppm PdSO4) at room temperature for 2 min. Then, the sheets were immersed into the electroless Ni-P bath (0.1 M NiSO4·6H2O, 0.2 M NaH2PO2·H2O, 0.2 M DL-Lactic acid, 0.05 M Propionic acid, 0.15 M CH3COONa, 10 ppm Propargyl alcohol propoxylate, pH 5.4, 80°C, 30 min.) to deposit a layer of 3 - 4 µm thickness of Ni-P. To perform electroless Pd deposition, the Ni-P coated Cu (Ni-P/Cu) sheets were
In the presence of FA, the open circuit potential of Pd/Ni-P/Cu electrode $E_{OCP}$ shows an initial rapid decrease and then reaches a steady value of $-0.93$ V: it is an autocatalytic reaction. The electroless Pd plating reactions are given below:

$$\text{Pd}^{2+} + \text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{Pd} + \text{HCO}_3^- + 2\text{H}^+$$ \hspace{1cm} [2]

Reaction 1 can be separated into the below anodic (Reaction 3) and cathodic (Reaction 4) reactions:

$$\text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + 2\text{H}^+ + 2\text{e}$$ \hspace{1cm} [3]

$$\text{Pd}^{2+} + 2\text{e} \rightarrow \text{Pd}$$ \hspace{1cm} [4]

However, in the case of a Ni/P/Cu electrode, the $E_{OCP}$ slowly decreases during the period from 0 to 130 s and then the $E_{OCP}$ sharply declines until a steady potential of $-0.94$ V. When immersion times is longer than 130 s, $E_{OCP}$ variation is similar to $E_{OCP}$. It is likely that Reaction 2 occurs at the latter stage of the electroless Pd deposition on Ni-P surfaces using FA as a reducing agent.

CV measurements provide information for describing the oxidation properties of FA on Ni and Pd electrodes, as displayed in Fig. 2. Comparison of the CV curves of Ni in various solutions, as shown in Fig. 2a, the oxidation current portrays negligible change with the addition of FA to the system. However, the Pd electrode accelerates FA oxidation resulting in a higher oxidation current relative to the Ni electrode (Fig. 2b). This result suggests that Reaction 3 (oxidation of FA) can be successfully carried out on the Pd surface, but not on Ni surface; therefore, the initial stages of electroless Pd deposition on Ni-P surfaces consists of only a galvanic displacement reaction between Ni and Pd\(^{2+}\) (Reaction 1). When the Ni-P electrode surface is gradually coated with deposited Pd, the autocatalytic reaction takes place on the Pd surface. Based on the above results, it is reasonable to assume that electroless Pd deposited on Ni-P surface is composed of a two stage reaction process.

In order to confirm the two-stage reaction process, the displacement reaction was controlled by varying the concentration of ethylenediamine. According to Nernst equation, $E(\text{Pd}^{2+}/\text{Pd}) = E^0(\text{Pd}^{2+}/\text{Pd}) + (RT/2F)\ln[\text{Pd}^{2+}]$, and the stability constants, log $\beta(\text{Pd(EN)}^{2+}) = 26.9$. The addition of Ethylenediamine (EN) will reduce the value of $[\text{Pd}^{2+}]$, and the $E(\text{Pd}^{2+}/\text{Pd})$ decrease. The displacement reaction becomes less likely to occur. Fig. 3a illustrates the OCP curves of Ni-P/Cu electrodes in solution with different amounts of ethylenediamine. Comparing the OCP curves obtained in baths containing different ethylenediamine concentrations, it is clearly observed that a higher concentration of ethylenediamine can significantly impede the deposition process. When the ethylenediamine concentration reaches 0.15 M, the electrode potential remains unchanged after 200 s. This result indicates that the displacement reaction cannot take place in a bath with ethylenediamine concentration higher than 0.15 M. As shown in Fig. 3b, while the Ni-P/Cu sheet is directly immersed in the electroless Pd bath containing 0.2 M ethylenediamine, the reaction of Pd deposition cannot be performed. However, while the activated Ni-P/Cu electrode is immersed in the electroless Pd bath, the OCP displays an initial rapid decrease, consistent with the autocatalytic reaction process shown in Fig. 1 (line 3). When the activation time is 1 min, the electrode possesses the highest activity. Experimental results suggest that the displacement reaction is a necessary prerequisite for the autocatalytic reaction in electroless deposition of Pd on Ni-P surfaces using formic acid as a reducing agent.

Summary

The pure Pd film is synthesized via electroless Pd deposition on Ni-P surfaces using FA as a reducing agent. A comprehensive analysis of the deposition processes in terms of the electrochemical reactions
Figure 3. Open circuit potential - time curves of (a) Ni-P/Cu electrode in baths (0.2 M Na₂HPO₄, 0.01 M PdSO₄ and without FA) with different amounts of Ethylenediamine; (b) Effect of Ni-P/Cu electrode activation time on OCPT in electroless Pd bath containing 0.2 M ethylenediamine.

and characteristics of the Pd deposition process were investigated. The OCPT curve verifies a two-stage reaction process of electroless Pd deposited on the Ni-P surface, this conclusion is supported by CV tests. The CV results assume that the autocatalytic reaction solely occurs on the Pd surface rather than the Ni surface. During the electroless Pd deposition process, a galvanic displacement reaction between Ni and Pd²⁺ takes place during the initial stage then Pd is deposited via an autocatalytic reaction on the coated Pd surface. In subsequent experiments, it is confirmed that the displacement reaction is a necessary prerequisite for occurrence of the autocatalytic reaction. When the displacement reaction is prevented, the autocatalytic deposition of palladium could not occur.

Acknowledgments

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