

Supercritical carbon dioxide assisted electroless plating on polymer substrates - Effect of CO₂ and ethanol on plating reaction

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Abstract

An environmentally benign electroless plating process on thermoplastic polymers, which could significantly reduce harmful acids necessary for conventional process and provide high adhesiveness of metal film on plastics, was developed. The process consists of two steps, i.e., supercritical CO₂ impregnation and electroless plating reaction in the presence of ethanol and pressurized CO₂. In the scCO₂ impregnation step, a Pd precursor, which is used as a catalyst for electroless plating reaction, is infused into polymer by taking advantage of solvency and plasticization powers of scCO₂. Then, the polymer containing Pd is immersed in a Ni-P plating solution to conduct the electroless plating reaction. When ethanol and CO₂ are added into the solution, a composite layer of Ni-P alloy with substrate polymer is formed at the interface between metal and polymer substrate. This plays the role of metal anchors in enhancing adhesion strength of the metal film to the polymer. Thus, enhancing the diffusivity of plating solution in polymer and suppressing plating reaction could make the composite layer thicker. The effect of addition of ethanol and CO₂ into plating solution on plating reaction as well as diffusivity of plating solution in polymer was investigated. It was clarified that addition of ethanol and CO₂ plasticized the surface of polymer substrate and enhanced the diffusivity of plating solution in the substrate. At the same time, the addition suppressed the plating reaction and made the plating process diffusion controlled.

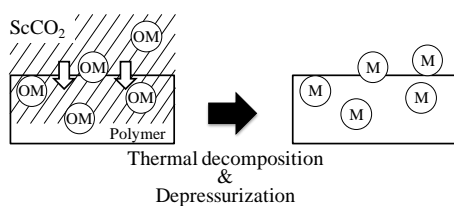
Introduction

Metallization of polymer substrate is an important technique for various applications. It has been used for decorating polymer surface, adding electrical conductivity to polymer, and providing electromagnetic shielding and weatherproofing abilities. Electroless plating is the most common methods of metallization of polymer substrate because of its convenience and its performance of uniformly coating to complicated-shape substrates [1]. Electroless plating conducts metal deposition with an autocatalytic redox reaction, in which the cation of metal is reduced at the surface of catalysts deposited on the polymer surface as well as the surface of metal features. A conventional process of the electroless plating on polymer substrates mainly consist of four steps, i.e.; degreasing, chemical etching, surface seeding with catalyst on polymer and electroless plating. The degreasing uses alkaline or acid solutions to remove organic chemicals from the polymer surface. The

chemical etching requires strong acids such as chromic acid to roughen the surface. The roughened surface enhances adhesion between metal film and polymer due to interlocking effect, which is called “anchoring effect.” Catalyst precursors such as SnCl₂ and PdCl₂ are seeded on the surface and activated by sulfuric acid in the step of catalyst seeding. These pretreatments, i.e. degreasing, etching and catalyst seeding, are inevitable before electroless plating. However, these pretreatments need a lot of chemicals and produce a large amount of wastewater. Therefore, it is desired to develop an environmentally friendly electroless plating technique that can realize strong adhesiveness of the metal film to the polymer.

In our previous work, we developed a novel process of electroless plating on polymer substrates by taking advantage of supercritical CO₂ (scCO₂) and ethanol. The developed process consists of two steps; supercritical CO₂ impregnation with catalyst and

1. Supercritical CO₂ impregnation with catalyst



2. Electroless plating

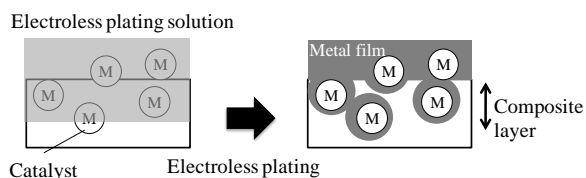


Fig. 1 Process of electroless plating on a polymer substrate.

electroless plating assisted by ethanol and CO₂ [2]. In the scCO₂ impregnation step, Pd(II)-hexafluoroacetylacetonate (Pd(hfa)₂) is used as a catalyst precursor and impregnated in polymer matrix through by utilizing solvency and plasticization powers of scCO₂ [3-5]. The precursor is thermally decomposed and transformed into Pd particle in polymer substrate by heating. In the electroless plating step, the Pd-impregnated polymer is immersed in electroless nickel-phosphorus (Ni-P) plating solution, whose major composition is water, and Ni-P alloy film is developed on the polymer substrate.

Our previous study showed that adhesibility of Ni-P film to the polymer was improved to an acceptable level for practical use by adding ethanol and CO₂ to the plating solution. The plasticization effect of ethanol and CO₂ promoted the sorption of the solution into polymer matrix and electroless plating was conducted on Pd in polymer. Thereby a composite layer of Ni-P and polymer was developed between the metal film and the polymer. The composite layer produced the excellent adhesibility of metal film to the polymer substrate.. The thickness of the composite likely has strong influence on the adhesibility of the metal.

In this work, the effect of ethanol and CO₂ on the adhesibility of Ni-P film was further investigated. Varying the plating conditions such as plating temperature, ethanol concentration in plating solution, and CO₂ pressure, the thickness of resulting composite layer was quantitatively measured from TEM image by a contrast analysis technique

Table 1 electroless Ni-P plating conditions

Sample num.	Temp.	Ethanol	CO ₂ -press.
	°C	vol.%	MPa
(1)	50	0	Non
(2)	50	20	Non
(3)	50	40	Non
(4)	60	0	Non
(5)	60	20	Non
(6)	60	40	Non
(7)	60	40	10
(8)	70	0	Non
(9)	70	20	Non
(10)	70	40	Non

Experimental

Materials

The thermoplastic polymer used in this work was polyamide 6 (PA6: Unitika, A1025; Mw = 14,000), A disk-shaped PA6 substrates 1.5 mm in thickness and 20 mm in diameter were prepared by an injection molding machine. The catalyst precursor Pd(hfa)₂ was purchased from Aldrich, USA. CO₂ 99.95% in purity was supplied by Kyoto Teisan. A set of electroless Ni-P plating solutions, DK-M (16% of phosphoric acid, 4% of adipic acid, 16% of complexing agent and 65% of water) and DK-1 (35% of nickel sulfate and 65% of water), was purchased from Okuno Chemical Industry Co., Ltd. A standard solution was also prepared by mixing 10% of DK-M and 5% of DK-1 with 85% of water. Ethanol of 99.5% purity was purchased from Wako Pure Chemical Industries Ltd. All chemicals were used as received.

Supercritical CO₂ impregnation with catalyst

A polymer substrate and 35 mg of Pd(hfa)₂ were placed together in a high-pressure vessel (70 cm³) and kept at 80°C using a temperature controller. The substrate was placed on a small metallic table and the Pd(hfa)₂ powder was put underneath the table so as not to direct contact with the substrate. The vessel was pressurized by CO₂ up to 10 MPa and kept the pressure level for 30 minutes to dissolve the Pd(hfa)₂ into scCO₂ and to impregnate the substrate with the Pd(hfa)₂. Then, the Pd(hfa)₂ was thermally decomposed by increasing temperature from 80 to 120 °C and keeping the temperature and CO₂ pressure for 30 minutes.

Electroless plating

The Pd-impregnated substrate was dried for more than 24 hours in a vacuum chamber to remove CO₂ remained in the polymer. Then, it was immersed in an electroless

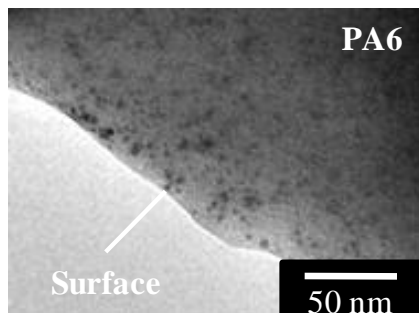


Fig. 2 A TEM micrograph of a cross-section of the Pd-infused PA6 substrate.

Ni-P plating solution in plastic cup made of poly (tetrafluoroethylene-perfluoroalkylvinylether copolymer; PFA). The electroless plating was conducted under different composition and temperature from 50~ 70°C. The experimental conditions are listed in **Table 1**. CO₂ was added to the solution by the pump in the high-pressure vessel.

Morphology evaluation of surface and cross-section

The cross-section of the plated polymer substrates was observed by using a transmission electron microscope (TEM, JEM-1010, JEOL). The substrate was coated by a 5 nm carbon layer using a carbon-coater and embedded in epoxy resin for TEM observation. Ultra-thin cross section was prepared using an ultra microtome (ULTRACUT-J, Leica) and examined via TEM.

Measurement of Sorption of the solvent

To evaluate the solubility and diffusivity of the plating solutions into the polymer substrates, the substrates were immersed either in water or mixtures of water, ethanol and CO₂. Then, the solvent uptakes were measured by weighing the immersed substrates after wiping out their surface.

Measurement of reaction rate

To measure the reaction rate of the electroless plating under several conditions listed in **Table 1**, a Ni sheet was immersed in the plating solution and conducted plating experiments with different ethanol concentration and CO₂ pressure. The reaction rate was estimated by weighing the deposited Ni-P uptakes on the Ni sheet.

Results and discussion

Fig. 2 shows a TEM image of a cross sectional area of the Pd-impregnated PA6 substrate. Numerous Pd nanoparticles could be observed in the substrate. **Fig. 3** is a top view of the substrate plated under the condition (7) in **Table 1** (60°C, 40%-EtOH, 10 MPa-CO₂). The

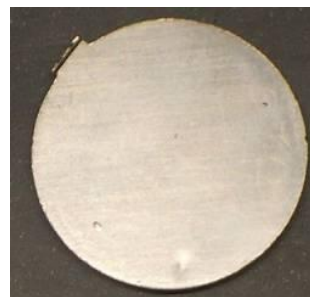


Fig. 3 Top view of an electroless Ni-P plated PA6 substrate prepared by 40% ethanol bath at 60°C and 10 MPa CO₂.

PA6 substrate was conformally coated by Ni-P alloy film. Some TEM images of cross sectional area of the sample plated under different conditions are shown in **Fig. 4**. As shown in **Fig. 4(a)**, **(b)**, and **(c)**, the interface between metal film and PA6 was clear and flat when ethanol and CO₂ were not used. Even for the case **Fig. 4(c)**, the metal film dropped out from the substrate when cutting the sample for TEM observation. Either adding 40%-ethanol or using both 40%-ethanol and 10 MPa-CO₂ made the interface between metal and polymer fuzzy. Metallic nanoparticles were observed in polymer as illustrated in **Fig. 4(d)-(j)**. The number density of nanoparticles in the cross sectional area increases as it closes to surface of the material. From the observation of STEM-EDS, we could confirm that the black color regions in TEM image as well as particles in **Fig. 4** were made from Ni-P alloy. It can be considered that the polymer and Ni-P alloy composite layer provides an anchoring effect to Ni-P film and thus, the thickness of the composite layer determines the adhesiveness of Ni-P metal film to the polymer substrate.

By a contrast analysis of image processing technique, the thickness of the composite layer was estimated from TEM images: The image contrast between polymer phase and Ni-P film was normalized into 0 to 1 as illustrated in **Fig. 5**. The region where the contrast was in the range from 0.1 to 0.8 was regarded as a metal-polymer composite layer. The thickness of the composite layer for all samples was measured and illustrated in **Fig. 6**. As can be observed, the thickness increases as the plating temperature decreases. It is also observed that addition of ethanol to the plating liquid and CO₂ pressurization made the composite layer thicker. This was caused by the plasticization effect of ethanol and CO₂ on PA6 substrate.

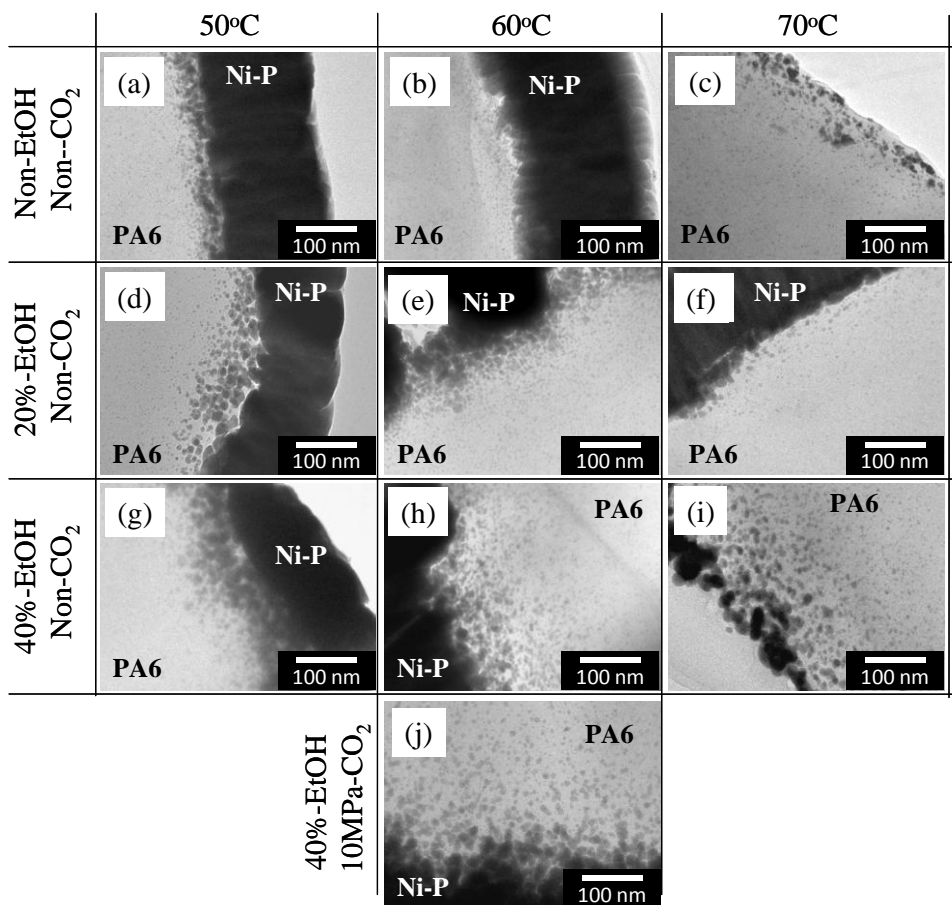


Fig. 4 STEM images of the cross-sectional area close to plating surface. (a) EtOH 0%, non-CO₂, plating temp 50 °C, (b) EtOH 0%, non-CO₂, plating temp. 60°C, (c) EtOH 0%, non-CO₂, plating temp. 70°C, (d) EtOH 20%, non-CO₂, plating temp 50 °C, (e) EtOH 20%, non-CO₂, plating temp 60 °C, (f) EtOH 20%, non-CO₂, plating temp 70 °C, (g) EtOH 40%, non-CO₂, plating temp 50 °C, (h) EtOH 40%, non-CO₂, plating temp 70 °C, (j) EtOH 40%, CO₂-10MPa, plating temp 50 °C.

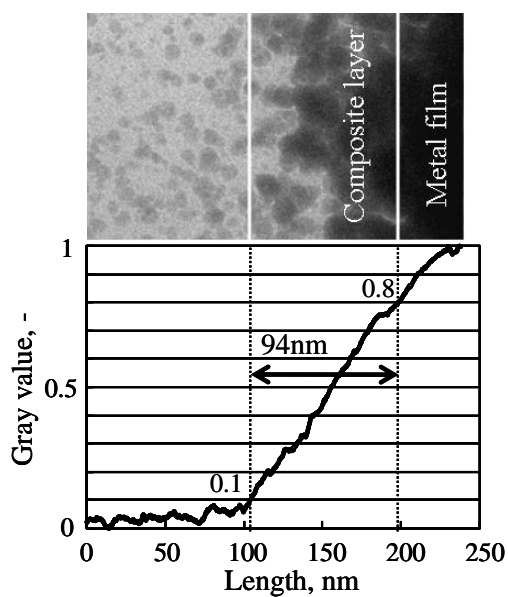


Fig. 5 Contrast analysis of TEM image.

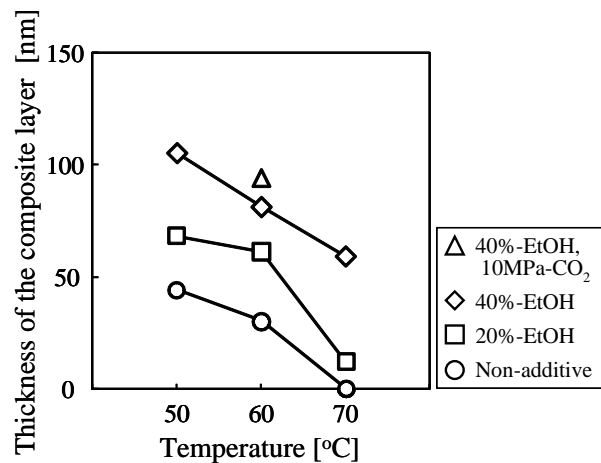


Fig. 6 Thickness of Ni-P-PA6 composite layer.

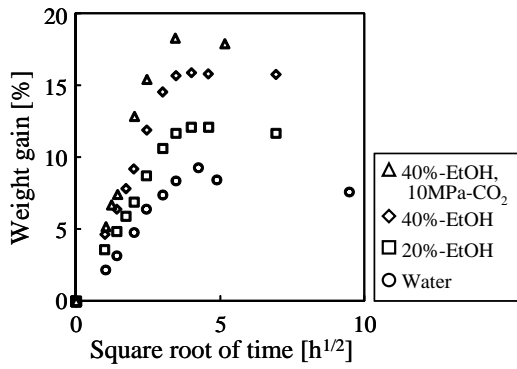


Fig. 7 Sorption of water and EtOH in the PA6 substrate.

Fig. 7 shows the measured weight gain of PA6 substrate in sorption experiments. Assuming that the sorption behavior follows the Fickian's law, the weight gain, M_t , in time t is given by

$$\frac{M_t}{M_\infty} = 2 \left(\frac{Dt}{l^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nl}{\sqrt{Dt}} \right\}, \quad (1)$$

where D is the diffusion coefficient and M_∞ is maximum weight change of the substrate $2l$ in thickness [6].

From the initial sorption behavior, the diffusion coefficient as well as the saturation concentration was estimated by fitting Eq. (2) to the experimental data in **Fig. 7**.

$$\frac{M_t}{M_\infty} = 4 \sqrt{\frac{D}{\pi}} \frac{\sqrt{t}}{2l}. \quad (2)$$

Diffusion coefficient, D , and saturated concentration of solute, M_∞ , were calculated and the results are given in

Table 2 Diffusion coefficients and equilibrium sorption amounts.

Temp. °C	Ethanol vol.%	CO ₂ -press. MPa	M_∞ wt.%	$D \times 10^{12}$ m ² /s
50	0	Non	9.08	5.92
50	20	Non	11.90	5.80
50	40	Non	13.48	8.89
60	0	Non	9.23	8.44
60	20	Non	12.03	9.82
60	40	Non	15.89	10.0
60	40	10	18.23	11.9
70	0	Non	8.39	17.2
70	20	Non	12.46	17.8
70	40	Non	15.76	20.3

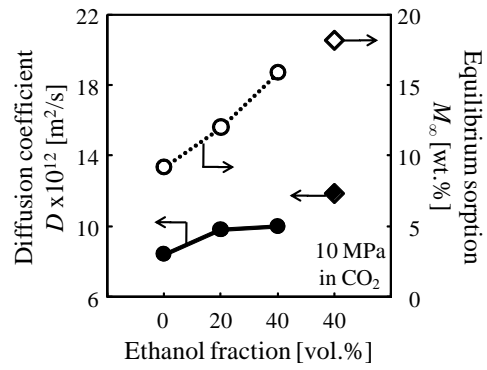


Fig. 8 Effect of ethanol on diffusivity of the solution (water and ethanol mixture) and equilibrium sorption amount at 60°C.

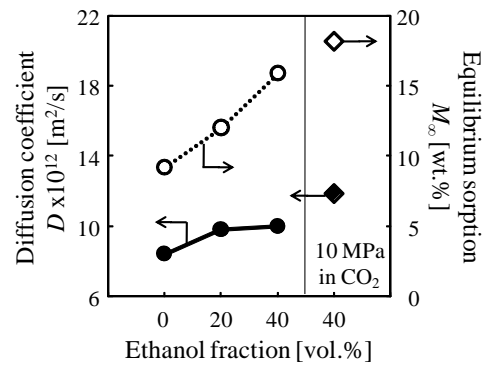


Fig. 9 Effect of temperature on diffusivity of solution and equilibrium sorption in 40 % ethanol contained solution.

Table 2 and **Figs. 8-9**. When ethanol and CO₂ were added, D and M_∞ were increased as illustrated in **Fig. 8**. D also increased with the increase of the temperature as illustrated in **Fig. 9**.

The effect of plating temperature, ethanol and CO₂ on the plating reaction rate was also investigated by immersing a Ni sheet in the plating solution and conducted plating experiments with different ethanol concentration and CO₂ pressurization. **Fig. 10** shows the amount of reacted Ni at time t during the plating process conducted under various plating condition. The amount of reacted Ni was calculated from the weight gain during plating. The amount of reacted Ni was reduced either by decreasing the temperature, addition of ethanol in the plating solution or CO₂ pressurization. It is apparent that the presence of ethanol and CO₂ in plating solution increases the diffusivity, decreases the plating reactivity and makes the composite layer thicker. On the other hand, lowering temperature makes both diffusivity and plating reactivity lower. The reduction of plating reactivity dominantly affects the thickness of composite

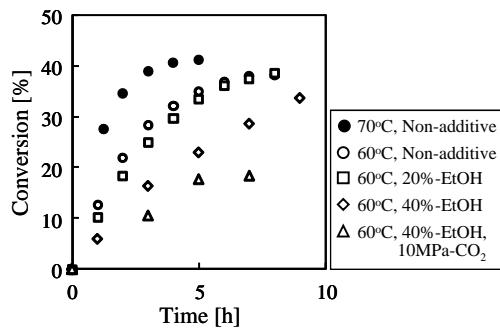


Fig. 10 Weight gain of Ni-P plated on Ni metal sheet in different plating solutions

layer than the reduction of diffusivity.

To make the composite layer thicker, the reactant ions such as nickel ion should be impregnated into polymer substrate as deeply as possible. Therefore, the ion mobility in polymer is an important factor and it depends on diffusivity of the plating solution in polymer and the degree of polymer swelling. As the plating reaction proceeding, metal particles grow and they prevent the reactant ions from diffusing into the polymer. Once the metal film covers the surface of the polymer, the ion can not be penetrated into the substrate and the growth of the composite layer is stopped. Therefore, the composite layer can be made thicker by keeping the diffusivity higher, the plating reactivity lower and increasing the ions penetration into the polymer substrate.

Conclusion

When ethanol and CO₂ are added into the plating solution, metal-polymer composite layer is formed at the interface between metal and polymer substrate, which plays the role of metal anchors in enhancing adhesion strength of the metal film to the polymer. The thickness of the composite layer was determined by the diffusivity of plating solution in polymer and plating reactivity. It was made clear in this study that ethanol addition and presence of CO₂ in electroless plating process can increase the diffusivity of plating solution and decrease the reactivity.

Reference

- [1] M. Charbonnier, M. Romand, *Int. J. Adhes. Adhes.* 23 (2003) 277-285.
- [2] H. Adachi, K. Taki, S. Nagamine, A. Yusa, M. Ohshima, *J. Supercrit. Fluids* in press.
- [3] I. Kikic, F. Vecchione, *Curr. Opin. Solid State Mater. Sci.* 12 (2003) 399-405.

[4] X. Zhao, K. Hirogaki, I. Tabata, S. Okubayashi, T. Hori, *Surf. Coat. Technol.* 201 (2006) 628-636.

[5] Y. Zhang, C. Erkey, *J. Supercrit. Fluids* 38 (2006) 252-267.

[6] J. Crank, *The Mathematics of Diffusion* Second Edition. Oxford; 1975.