Supercritical Fluid-assisted Electroless Copper Plating of Aramid Film : The Influence of Surface Treatment

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Abstract: A process of metalizing aramid fibers using supercritical CO₂ (sc-CO₂) followed by electroless copper plating has been developed recently. However, some applications require larger conductive surfaces without losing any of aramid fibers qualities (heat and chemical resistance, high strength, high flexibility). In response to such requirements, we developed in our present study a method of plating aramid film after impregnating it with organometallic complexes using sc-CO₂ as a medium. In order to achieve uniform plating coupled with a high adhesiveness of the plated layer, two factors were examined. The impregnated Pd was reduced by two agents, NaBH₄ in aqueous solution and H₂ gas, in order to increase the amount of Pd metal present on the film surface. We found that the reduction of Pd did improve the plating of the aramid film. In spite of this, the adhesion of the shiny copper-colored layer had low strength.

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1. Introduction

For over 50 years, plastic materials have been replacing metals in many different fields (automobiles, housing, safety and computers). Indeed, polymers are more versatile and can thus be modeled to exactly fit their new specific usages such as intelligent fibers or nano fibers. However, until recently, scientists faced the problem of the non-conductivity of polymers. Hence, they developed various metallization processes 1-3 to create smaller and lighter electrical devices.

With the realization that industrial waste leads to environmental problems 4, new techniques have been developed to comply with new ecological legislation 5, 6. Supercritical carbon dioxide (sc-CO₂) is a widely used medium because of its intrinsic properties. Sc-CO₂ is completely recyclable, does not generate waste water and is an efficient replacement for many organic solvents 7. Moreover, it has high diffusivity, low viscosity and high thermal conductivity, and is available at low cost. Sc-CO₂ addresses safety considerations as well, since it is non-flammable and non-reactive under most conditions. Due to those properties, sc-CO₂ is a valuable medium in the fields of extraction 8, dyeing 9 and impregnation 10. In the case of polymer impregnation, sc-CO₂ plasticizes the matrix and swells it, thereby providing the room necessary to for the impregnation of solutes with relatively large molecular weights, such as organometallic

complexes 11.

In this study, aramid film was impregnated with a palladium complex as a pre-treatment for electroless copper plating. This pre-treatment ensured the presence of Pd metal on the surface of the film and its action as catalyst during the plating. Pd ions and Pd complexes were also impregnated, but they did not have the ability to accelerate the plating. Hence, the reduction of Pd²⁺ into Pd(0) was investigated using an aqueous solution of NaBH₄ 12 or using H₂ gas 13. NaBH₄ was also used before impregnation to smooth the surface of the film and thus avoid the clustering of Pd. These two approaches were adopted with the purpose of rendering uniform the plated metal layer as well as improving its adhesive property.

2. Experimental

2.1 Materials

Aramid film (thickness : 16 μm) was provided by Teijin Advanced Films, Ltd. CO₂ (purity : +99.99%) was purchased from Uno Oxygen Co. and used as received. Palladium (II) acetylacetonate (Pd(acac)₂) was purchased from Tokyo Chemical Industry, and palladium(II) hexafluoroacetylacetonate (Pd(hfa)₂) was purchased from Sigma-Aldrich ; both were used without further purification.

Sodium tetrahydroborate (NaBH₄) was acquired

Fig. 1 Organometallic complexes : 1) $\text{Pd}(\text{acac})_2$ and 2) $\text{Pd}(\text{hfa})_2$.

from Wako Pure Chemical Industries, Ltd. and used as received. The electroless copper plating solutions were ATS-ADDCOPPER IW-A, ATS-ADDCOPPER IW-M and ATS-ADDCOPPER IW-C (Okuno Chemical Industry Co., Ltd.)

2.2 Methods

Figure 2 illustrates the $\text{sc}\text{-CO}_2$ apparatus, in which each sample was impregnated with one of the organometallic complexes as a pre-treatment.

Fig. 2 Illustration of the reaction apparatus. (A) Syringe pump, (B) cleaning pump, (C) heater and high-pressure stainless-steel vessel, (D) organometallic complex, (E) sample, (F) sample cartridge, (G) washing solvent, (H) thermometer, (I) glass filter, (1, 2, 3, 4, 6, 7, 9, 10) valves, and (5, 8) pressure gauges.

2.2.1 Supercritical pretreatment

All experiments were performed in a batch-type supercritical extractor (SFE System 2000 ; ISCO, USA). A simplified scheme of the experimental procedure is shown in Figure 3. The aramid film was cut into 1.5 cm 5.0 cm or 5.0 cm 5.0 cm pieces. Sample impregnation was conducted in a 10- cm^3 cartridge that was sealed with two plugs, one at the entrance for $\text{sc}\text{-CO}_2$ and the other at a high-pressure needle valve. The cartridge was set up as follows : a glass filter was placed at the bottom ; the sample was placed above it, followed by two glass filters with a specific amount of organometallic complex between the filters. The complex was introduced in excess relative to the average solubility of the metal complex and the amount absorbed by the aramid film. The amount depended on the duration of impregnation. When the thermoregulated heater reached 150°C , the

Fig. 3 Schematic diagram illustrating the processes of supercritical pre-treatment (impregnation, thermal treatment, decomposition).

cartridge was inserted, and the pre-treatment was conducted from 30 minutes to 7 hours for $\text{Pd}(\text{acac})_2$ and for 3 hours or 30 minutes for $\text{Pd}(\text{hfa})_2$. The temperature and pressure of impregnation were kept constant for the duration of the treatment. When the impregnation was finished, the cartridge was decompressed by releasing the CO_2 , then the cartridge was extracted from the heater.

2.2.2 Treatment with NaBH_4

The pre-treatment consisted in dipping the aramid film sample into a 1 mol/L water solution of NaBH_4 for 10 or 20 minutes under manual stirring. For the reduction treatment, aramid film impregnated with palladium complex was dipped into a solution with the same concentration for 1, 5 or 10 minutes.

2.2.3 Treatment with H_2

Aramid film impregnated with one organometallic complex was reduced by H_2 gas for 1, 5 or 10 minutes at 150°C and 0.5 bar. The H_2 gas was in large excess.

2.2.4 Electroless copper plating

The electroless plating method was used for the metal plating process (Fig. 4). The electroless copper plating solution was created by adding 10 mL of ATS-ADDCOPPER IW-A to 172 mL of deionized water, followed by the addition of 16 mL of ATS-ADDCOPPER IW-M and 2 mL of ATS-ADDCOPPER C. The impregnated aramid film was dipped into the electroless copper plating solution at $42^\circ\text{C} \pm 2^\circ\text{C}$ until a homogeneous metal layer was formed on its surface or until the metal layer began to peel off. To achieve proper mixing and to avoid damaging the sample, the solution was stirred manually.

2.3 Analyses

The adhesive strength of the plated metal layer after

Fig. 4 Schematic diagram of the electroless deposition of copper onto aramid film by manual stirring.

electroless copper plating was evaluated by the cellophane tape method. A piece of cellophane tape was stuck on the plated metal layer. The pressure applied to stick the tape was the same for each test. Then, the piece of tape was pulled off. The adhesive strength of metal layer was evaluated visually according to the scale shown in Table 1.

Table 1 Evaluation scale for the adhesive strength of the plated metal layer.

○○	○	×	×
No metal on the tape: adhesion is strong.	Few small specks of metal on the tape: adhesion is not strong enough.	Large specks of metal on the tape: adhesion is low.	All the plated metal is on the tape: no adhesion.

X-ray photoelectron spectroscopy (XPS) was conducted on a ULVAC 5500 spectrometer with Mg-K α excitation. The settings were 100 μ m, 300 W and 15 kV under a vacuum pressure of 110^{-8} Pa. Before the XPS analysis, each sample was placed in a vacuum oven at 40°C for a minimum of 12 hours. Scanning electron microscopy (SEM) was carried out on a Hitachi S-2600H microscope at an accelerating voltage of 15 kV.

3. Results and discussion

3.1 Optimal impregnation time for Pd(acac) $_2$

Since no literature could be found on the impregnation of Pd(acac) $_2$ into aramid film, it was necessary to determine the time of impregnation for that complex. Our study focused on the time only, in order to be able to compare the efficiency of aramid film plating after impregnation of Pd(hfa) $_2$ and Pd(acac) $_2$. Aramid film was impregnated with Pd(acac) $_2$ in large excess relative to the average solubility of the metal complex and the amount absorbed by the aramid film, so that the time of impregnation would not be influenced by a lack of complex during the process. The process lasted from 30 minutes to 7 hours. The efficiency of the impregnation was checked by performing electroless copper plating in the conditions explained in Section 2.2.3.

From the 3-hour impregnation, it was possible to obtain a shiny copper-colored plated layer on the aramid

film. Therefore, it was possible to conclude that the impregnation of Pd(acac) $_2$ is optimal when it lasts for 3 hours at 150°C and 15 MPa. The second part of this study focused on the improvement of the adhesive property of the plated copper layer based on these optimal impregnation conditions. The cellophane tape method applied to the films after plating revealed that the plating was indeed homogeneous but that the adhesion strength was lower than the standard industrial requirements.

3.2 Improvement of the metal plating

Once it was possible to plate aramid films homogeneously, it was necessary to focus on the improvement of the copper layer adhesion.

Aramid film was subjected to a two- or three-step treatment. The optional treatment was the reaction with the reducing agent, NaBH $_4$.

Both complexes were impregnated for 3 hours at 150°C and 15 MPa.

The film's aspect was not changed by any of the treatments (treatment with NaBH $_4$ or impregnation of a metal complex). It retained its shiny yellow color and flexibility.

In the first trial, the samples were plated for 40 seconds and acquired a homogeneous copper layer. Even if 15 minutes is the recommended time for the electroless plating process, quick plating can endow the metal layer with properties more suitable for industrial application (homogeneity, high adhesive strength). Hence, the next samples were subjected to electroless copper plating until a uniform copper layer was formed on both sides or until the first signs of metal peeling off appeared.

3.2.1 Surface treatment with NaBH $_4$

Charbonnier and co-workers¹⁴ described that the surface of a polymer became smooth and regular after reduction using NaBH $_4$. Our idea was to use NaBH $_4$ to smooth the surface of aramid film in order to avoid the formation of Pd clusters during the metal complex impregnation. In this way, the plating might start after a shorter time lag and at the same time everywhere on the surface of the film, thus leading to the formation of a homogeneous metal layer. So, we tried this method on aramid film treated with NaBH $_4$ for 10 and 20 minutes. Images of the surface obtained with an electronic microscope are shown in Figure 5.

The NaBH $_4$ treatment retarded the start of the electroless plating process. In addition, copper was deposited on random spots of the surface, and even after 15 minutes of plating, it was not possible to obtain a homogeneous layer on both sides of the aramid film. Moreover, the adhesion of the plated copper on the

Fig. 5 Microscope images of the surface of aramid film before and after treatment with NaBH_4 .

surface of the film did not improve, and in some cases the adhesion deteriorated. The percentage of copper coverage of the aramid film after impregnation is also interesting. Even if the plating is not homogeneous on the film treated with NaBH_4 , the percentage of copper coverage is more important. The SEM images (Fig. 6) show cracks of the copper layer plated on the aramid film treated with NaBH_4 . Clusters of copper are also present on the surface of the metal. Therefore, it is reasonable to assume that the copper was continuously deposited on the same spots, and because the copper layer at those spots became too thick, the interaction between the film and the layer was not strong enough to keep the copper attached to the film. Thus, cracks appeared when the tension between the polymer and the metal layer became too strong.

Based on these findings, it might be thought that the auto-catalysis reaction occurring in the electroless plating solution starts with difficulty due to the lack of Pd catalyst. Indeed, the pre-treatment with NaBH_4 might interfere with the impregnation of the organometallic complex and prevent the penetration of the catalyst into the aramid film. These comments are valid for both complexes, $\text{Pd}(\text{acac})_2$ and $\text{Pd}(\text{hfa})_2$.

Only four samples achieved strong adhesion. All of them were impregnated with $\text{Pd}(\text{acac})_2$. In addition, those samples had a short electroless plating time due to a homogeneous and fast start. Hence, the results of our study agree with those obtained by Charbonnier *et al.* 14, who mentioned that a short time lag is the main factor for obtaining a homogeneous metal layer with a strong adhesion. Nevertheless, if the dipping time in the

Fig. 6 SEM images of the copper layer on aramid film pre-treated with NaBH_4 (a : $\text{Pd}(\text{acac})_2$ at 12% w.o.f. ; b : $\text{Pd}(\text{acac})_2$ at 8% w.o.f. ; c) $\text{Pd}(\text{hfa})_2$ at 12% w.o.f impregnated for 3 hours ; d) $\text{Pd}(\text{hfa})_2$ at 20% w.o.f impregnated for 3 hours ; e) $\text{Pd}(\text{hfa})_2$ at 12% w.o.f impregnated for 30 minutes ; f) $\text{Pd}(\text{hfa})_2$ at 20% w.o.f impregnated for 30 minutes).

electroless solution is too short, the layer is almost translucent and therefore cannot confer useful properties (conductivity, electromagnetic shield) to the film. According to these observations, a balance has to be struck between the adhesion strength and the thickness of the plated layer. In this study, we found the optimal dipping time to be around 1 to 2 minutes. Regarding the samples treated by $\text{Pd}(\text{hfa})_2$, the plating was not efficient under the same conditions (12% w.o.f. of complex for 3 hours at 150°C and 15 MPa) of impregnation. Even if the amount of complex was increased to 20% weight of fabric (w.o.f), the plating was still not efficient, and it was not possible to obtain a homogeneous metal layer on the aramid film. However, it has been observed that $\text{Pd}(\text{hfa})_2$ is less stable than $\text{Pd}(\text{acac})_2$ in a sc-CO_2 environment, so we tried to impregnate it for 30 minutes under the same conditions of temperature (150°C) and pressure (15 MPa). Those changes led to a more uniform plating, but the dipping time was still too long to ensure a strong adhesion of the plated layer.

3.2.2 Reduction reaction

During sc-CO_2 treatment, the organometallic complex undergoes thermal decomposition and Pd is impregnated into the aramid film. Pd is the main catalyst for the electroless copper plating. However, not only Pd metal is impregnated, but also Pd(II), which does not

catalyze the plating. By reducing the Pd ions, the amount of Pd(0) might be increased, which would enable the electroless copper plating to start faster and thus lead to the formation of a more homogeneous metal layer with a greater adhesion strength. Regarding the conclusions drawn in the previous section, Pd(hfa)₂ was impregnated for 30 minutes.

3.2.2.1 Reduction agent : NaBH₄

NaBH₄ is a strong reduction agent that has been used to reduce ions into metals, which then react with Cu ions in the electroless plating process 15. The nature of its reduction of Pd has been described by Zhao, X. 16. NaBH₄ in aqueous solution liberates Na⁺ and BH₄⁻, which belongs to the redox couple B(OH)₄⁻/BH₄⁻ (E₀=-1.24V at pH=14). Its decomposition reaction is as follows :

Combined with the half-reaction equations of the redox couple of Pd (Pd/Pd²⁺ ; E₀ = 0.915V) and BH₄⁻, the reaction occurring in the reduction solution could be represented as follows :

According to Ma *et al.* 17, the XPS Pd 3d core-level is a doublet (Pd 3d_{5/2} and Pd 3d_{3/2}) lying at about 338 and 343eV. Moreover, they observed that the doublet at that energy ensures the presence of Pd(II). As shown by the XPS spectra (Fig. 7), the aramid film impregnated with Pd(hfa)₂ was impregnated with Pd(0) and Pd(II) as well, with a predominance of Pd(II) (spectrum (a), blue curve). The reduction treatment of the aramid film led to a decrease in the amount of Pd(II) and an increase in the amount of Pd(0) (spectrum (a), yellow, pink and turquoise curves). Regarding the XPS spectra of Pd(acac)₂ (spectrum (c)), the amount of Pd species impregnated, Pd(0) and Pd(II), was around three time higher than the amount of Pd(hfa)₂. Nevertheless, it was more difficult to determine the main species impregnated. In the case of Pd(acac)₂ (spectrum (c)), a small doublet is observed at around 332 and 336eV. It might correspond to PdO and PdO₂, respectively, which might be due to the oxidation of Pd after reduction.

Even if the XPS analyses confirm the efficiency of the reduction of Pd(II) into Pd(0), which is the catalyst of electroless copper plating, the plating was not accelerated, and therefore the amount of copper deposited on the surface of the film was still excessive, making it impossible to achieve the adhesive strength required by the industry standard. Moreover, the SEM pictures (Fig. 8) show that the surface of the copper layer has major defaults, especially scratches and cracks.

3.2.2.2 Reduction agent : H₂ gas

Another way of reducing Pd(II) before electroless copper plating is to use H₂ gas. Indeed, the redox couple H₂/H⁺ has a redox potential equal to 0 V ; therefore, H₂ can react with Pd²⁺ (E⁰=0.915 V), as shown by the following reactions :

The XPS spectra (Fig. 7) show that the characteristic doublet corresponding to the Pd 3d core-level (Pd 3d_{5/2} and Pd 3d_{3/2}) was present at about 338 and 343eV. Moreover, the reduction of both complexes, Pd(hfa)₂ and Pd(acac)₂, occurred. The Pd(II) peak decreased as the peak corresponding to Pd(0) was increasing. As observed previously, the amount of Pd(0) and Pd(II) was larger in the case of Pd(acac)₂. This might be explained by the fact that Pd(hfa)₂ has a high solubility in sc-CO₂ and therefore a lower partition into the aramid film. Consequently, the polymer cannot absorb as much Pd(hfa)₂ as it can absorb Pd(acac)₂. The XPS analyses demonstrate that a lower rate of reduction was obtained in the 5-minute treatment for Pd(hfa)₂ and the 10-minute treatment for Pd(acac)₂, with both reduction agents. Regarding the impact of the reduction on the electroless copper plating, it has to be performed to the end of the conventional time of 15 minutes. Therefore, in the case of H₂ as well, the amount of copper plated on the surface of the aramid film was too great for the adhesive property to be satisfactory. In addition, the SEM images (Fig. 9) show scratches, cracks and clusters of copper at the surface of the plated layer. Nevertheless, the reduction achieved with H₂ might be gentler than the one with NaBH₄, considering that the surface of aramid film treated with H₂ was less faulty after plating.

4. Conclusion

As a first step, this study determined the ideal impregnation conditions for Pd(acac)₂ and optimized those for Pd(hfa)₂. It was then possible to establish the influence of three treatments on the adhesive property of the plated copper layer. The surface of the aramid film was smoothed to prevent the formation of catalyst cluters during the impregnation of the organometallic complex. Next, NaBH₄ and H₂ were utilized as reduction agents to the Pd catalyst at the surface of the film, to improve the adhesion of the metal layer of electroless copper. Both

Fig. 7 XPS spectra of the Pd peaks of aramid film impregnated with Pd(hfa)₂ and reduced by NaBH₄ (a) or H₂ (b) and aramid films impregnated with Pd(acac)₂ and reduced by NaBH₄ (c) or H₂ (d).

Fig. 8 SEM images of copper-plated aramid film reduced by NaBH₄.

Fig. 9 SEM images of copper-plated aramid film reduced by H₂.

agents improved the plating ; indeed, it was possible to deposit a uniform copper layer on the film. Nevertheless, the layer did not reach the industrial standard regarding the adhesive property.

In future studies, it is necessary to investigate the influence of thermal treatment on the impregnated Pd catalyst and on the plated metal layer. The idea is to try to increase the amount of catalyst by having a second thermal decomposition and also to observe the influence of the water present in the aramid film.

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