Selective Metallization on CFRP Composites by Laser Radiation and Electroless Plating

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Abstract. Selective metallization of carbon fiber-reinforced polymer composites (CFRP) was conducted by laser ablation with 1064 nm laser radiation and electroless plating in nickel solution. A rough caterpillar-like structure and polar surface with high property of absorption and anchoring for active seeds were produced by laser ablation. The laser treatment produce had a pronounced influence on nickel deposition. After immersed in nickel solution for 150s, a homogeneous and dense nickel film was selectively deposited on the laser treatment area of CFRP by electroless plating successfully. The Ni plating exhibited excellent adhesion on the CFRP. The technique in this study would widespread the application of CFRP in the area of spacecraft microwave components and waveguide antenna.

Keywords. Selective metallization, carbon fiber-reinforced polymer composites, laser ablation, Electroless plating.

1. Introduction
Polymeric matrix reinforced with carbon fibers (CFRP) have a wide application in spacecraft microwave components and waveguide antenna for their superiority such as high strength-to-weight ratio, high modulus, high stiffness, dimensional stability, and low thermal expansion coefficient [1, 2]. However, due to the low conductivity of polymeric matrix, the CFRP cannot meet the needs of electromagnetic wave transmission [3, 4]. As a result, in is urgent to develop surface metallization technology on CFRP.

Electroless plating has been widely developed due to various advantages such as high density, large thickness and easily implement. However, the metal plating has low adhesion on CFRP because of the inert surface of the substrate. Various efforts have been made to improve adhesion of plated metals on CFRP surfaces such as chemical treatments, abrading, and spraying organic transition layer [5, 6]. However, these conventional methods have low accuracy and low selectivity. Under the shock by the rigorous low (-196°C) and high (100°C) temperature space environment, the plated metals on CFRP surfaces are easily to de-bonded and raise blisters [7].

Laser-assisted selective activation of polymer for consecutive metal plating has received extensive concerns in the past years due to its simple, flexible, and effective [8-11]. By means of laser radiation activation, the physical and chemical characteristics of the polymer surface can be changed, which is beneficial to the deposition of active metal atoms [10, 11]. Miyamaru F [10] fabricated Cu coating with 15μm thickness on polyethylene terephthalate (PET) film by laser radiation and electroless plating. Catalyzed by laser-induced deposition of Ag particles, copper can be selectively deposited on PI surface [11]. At the laser ablated region, the active ion can be reduced to active atom, which could
serve as seeds for electroless copper deposition. In contrast, up to now, there have not relative reports about selective metallization on CFRP composites by laser-assisted method.

In this paper, the Ni plating on CFRP composites has been produced by laser radiation and electroless plating. And the detailed surface analyses were carried out to investigate the physical and chemical change caused by laser radiation. Then, the process of electroless plating was analyzed. The study in this paper can speed up the application of CFRP in the area of spacecraft microwave components and waveguide antenna.

2. Experimental

2.1. Substrate
In our experiments, carbon fiber-reinforced cyanate ester resins of 2 mm thickness were used as substrates. And the substrates were cleaned ultrasonically in ultrapure water beforehand.

2.2. Laser Source and Irradiation Condition
A pulsed (λ= 1064 nm) fiber laser was used in this paper to perform the laser processing. The repetition rate of the laser was 10 kHz~200 kHz and the pulse duration was 8μs. The focused spot size on the CFRP substrate was 50 μm. The scanning velocity, scanning spacing, repetition rate and output power were precisely controlled by computer.

2.3. Electroless Plating
The laser active samples were immersed into active PdCl₂ solution and NaH₂PO₂ solution for 3 min sequentially. Then, the laser treated samples were immersed into an electroless Ni plating solution with the deposition temperature of 353 K. The electroless Ni plating solution is composited with 35 g/L Ni₂SO₄, 35 g/L NaH₂PO₂, 20 g/L sodium citrate, 20 g/L sodium acetate and 18 g/L MgSO₄. The PH of the solution was adjusted by acetate to 4.4~4.6. After that, the samples were rinsed in deionized water. Then, the selective Ni metal plating on the surface of CFRP was achieved.

2.4. Characterization
The microstructure of CFRP was observed by scanning electron microscope (SEM, ZEOSS SIGMA 500). The surfaces chemical states CFRP before and after laser activation were analyzed by X-ray photoelectron spectroscopy (XPS, Model Axis Supra).

3. Results and Discussion

3.1. Surface Microstructures of CFRP Composites after Treated by Laser
Two main processing parameters affecting the interaction between the laser beam and the substrate were laser power intensity and pulse overlap, all of which can be adjusted by scanning velocity, scanning spacing, repetition rate and output power. In order to investigate the influence of the power intensity and the pulse overlap on the microstructures of CFRP composites respectively, the power intensity was adjusted in the range of 6 J· cm⁻² to 90 J· cm⁻² at the overlap of 0%. And then, the pulse overlap was varied from -50% to 100% with the power intensity of 60 J· cm⁻². The relevant results are illustrated in figure 1 and figure 2.

When treated with 0% overlap, the surface roughness of CFRP increased with an increase of the laser power intensity (as shown in figure 1 (a-c)). At low laser power intensity of 6 J· cm⁻², the surface of the carbon fibers is slippery. Conversely, many irregular nanoscale particles distributed on the surface of the carbon fibers at the laser power intensity of 30 J· cm⁻² and 60 J· cm⁻². The morphology of carbon fibers wrapped nanoparticles can be termed as caterpillar-like structure. However, with the laser power intensity increasing to 90 J· cm⁻², the surface of the carbon fibers changed back to slippery with ablation stripe hole at the middle position (as shown in figure 1 (d)). The similar trend of topographies can be observed with pulse overlap increasing. As illustrate in figure 2, the slippery
surface of carbon fibers at the overlap of -50% changes into caterpillar-like structure when the overlap increased to 50%, and changed back to slippery at the overlap of 100%. Also, the ablation stripe hole were generated when the pulse overlap were at 50% and 100%.

Figure 1. SEM photographs of CFRP composites with laser power intensity of 6 J·cm⁻²(a), 30 J·cm⁻²(b), 60 J·cm⁻²(c), 90 J·cm⁻²(d) and pulse overlaps of 0%.

Figure 2. SEM photographs of CFRP composites with laser power intensity of 60 J·cm⁻² and pulse overlaps of -50% (a), 0% (b), 50% (c), 100% (d)

Under the pulsed laser beam radiation with the wave length of 1064 nm, a cumulative thermal effect could be induced on the surface of CFRP [12]. When radiated by 1064 nm laser, multi-photon energy was absorbed by CFRP, lots of molecules and atoms were vibrated, and thus, caused the rise of local temperature. Once the temperature increased to a certain threshold, the resin wrapping around the carbon fibers was degraded and volatilized from the surface. And as the laser beam moves away, parts of the ablated fragments were deposited and re-coagulated to the nanoparticles on the surface. A simple schematic diagram of the thermal degraded-deposition process for CFRP under laser radiation was shown in figure 3. Either increasing the laser power intensity or the pulse overlap can enhance the thermal effects. And then more resin was ejected and redeposited, which resulted in the increase roughness and more re-coagulated nanoparticles, as shown in figure 1(b, c) and figure 2(b, c). With further enhancing the thermal effect, the temperature on the surface of CFRP was high enough to inhibit the ablated fragments to be deposited. As a result, the caterpillar-like structure was changed back to slippery and the carbon fiber could be ablated to form stripe hole (as shown in figure 1(d) and figure 2(d)). The rough caterpillar-like structure could make the active metallic atoms be anchored firmly to the surface of CFRP, and the deposit adhesion could be increased sequentially.

Figure 3. Schematic diagram of the thermal degraded-deposition process for CFRP under laser radiation
3.2. Surface Chemistry of CFRP Composites by Laser Ablation

In order to analyse the surface chemical changes, XPS was applied to characterize the CFRP surfaces before and after laser activation. The relative atomic ratio of carbon (C), oxygen (O) and nitrogen (N) before and after laser activation were listed in Table 1. It can be observed that the C/O atomic ratio increased from 4.8 to 6.1 after laser activation. However, the C/N atomic ratio decreased from 68.1 to 27.8 by laser activation. The reason might be that there are plentiful O atoms were released as gas or volatilized from the cyanate ester resins, and leaving carbon fiber exposed on the surface. Then the active groups on CFRP surface reacted with the ionized nitrogen and oxygen elements in air, which result in the content of N and O increasing slightly. A same trend has been found in polyimide treated by nanosecond pulsed UV laser [13].

Table 1. Surface composition (at%) of CFRP before and after laser activation as measured by XPS.

| CFRP             | C (at%) | O (at%) | N (at%) | C/O  | C/N |
|------------------|---------|---------|---------|------|-----|
| Before activation| 81.7    | 17.1    | 1.2     | 4.8  | 68.1|
| After activation | 83.3    | 13.7    | 3.0     | 6.1  | 27.8|

Figure 4 shows the High-resolution C1s, O1s and N1s XPS spectra obtained from the pristine surface (a, b and c) of CFRP and the laser activated surface (d, e and f) at 60 J-cm² power intensity and 0% overlap. The relative component ratios of CFRP before and after laser activation are shown in Table 2. The prominent peak presented in 284.8 eV was attributed to C-C and C-H bonds. XPS spectra of the C 1s peak were shown in figure 4(a, d). The peak at 286.3 eV was assigned to C=O bond. And the peak at around 288.8 eV was related to C-N-C bonds [14, 15]. After laser ablation, the ratio of the C/C-C/H bonds and C-N-C bonds decreased. However, the ratio of C=O bond increased. These results indicated that the C-C/C-H bonds and C-N-C bonds bond were broken and leaving the surface with dangling bonds. These dangling bonds would react with oxygen in the air to form C-O group. XPS spectra of the O 1s peak were shown in figure 4(b, e). After laser irradiation, the relative ratios of C=O bond at 531.6 eV and C-O bond presented in 532.7 eV became smaller. A new component was observed at 533.5 eV after laser activation, which was attributed to O-C=O group. This further indicated that the C=O and C-O grounds were incorporation of oxygen in the air to form the O-C=O group. Figure 4(c, f) showed the high resolution spectra of N 1s. The ratio of C=N bond at 400.5 eV decreased and the C-N bond increased. The probable reason might be that the decomposition of C=N bonds rising from triazine structure in cyanate ester resins and rearrangement of nitrogen in the form of C-N bonds. It can be indicated from the above analysis that under laser irradiation, more polar groups such as C-O, O-C=O and C-N had generated due to reacting with oxygen and nitrogen in the air, which would be benefit to increase the adhesion of active metal atoms on the surface.

Table 2. Component ratio of CFRP before and after laser activation as measured by XPS.

| Binding energy (eV) | Functional group | Relative content (at. %) | Before activation | After activation |
|---------------------|------------------|--------------------------|------------------|-----------------|
| C1s                 |                  |                          |                  |                 |
| 284.8±0.2           | C-C/C-H          | 88.9                     | 62.7             |                 |
| 286.3±0.2           | C-O              | 8.4                      | 35.8             |                 |
| 288.8±0.2           | C-N-C            | 2.7                      | 1.5              |                 |
| 531.6±0.2           | C=O              | 44.1                     | 14.9             |                 |
| O1s                 |                  |                          |                  |                 |
| 532.7±0.2           | C-O              | 55.9                     | 41.5             |                 |
| 533.5±0.2           | O-C=O            | 0                        | 43.6             |                 |
| N1s                 |                  |                          |                  |                 |
| 599.7±0.2           | C-N              | 28.7                     | 41.8             |                 |
| 400.5±0.2           | C=N              | 71.3                     | 58.2             |                 |
3.3. Generation of Active Seeds
It is well known that electroless plating process cannot be initiated on CFRP surface when lacking catalytically active centers. Due to the excellent catalytic activity, metal palladium (Pd) was usually used as the active seeds to trigger the reduction reaction of the plating [16]. To obtain more active seeds on the surface, the laser treated CFRP were rinsed in PdCl₂ solution and reductive NaH₂PO₃ solution for 3 min sequentially.

Figure 5 shows the Pd3d XPS spectra of laser treated CFRP after rinsed in PdCl₂ solution (a) and NaH₂PO₃ solution (b) sequentially. The peaks at around 337.9 eV and 342.5 eV were attributed to PdCl₂ group. As well as the peaks at around 343.5 eV and 336.0 eV were assigned to metallic Pd. The results suggested that parts of the Pd²⁺ had been reduced by NaH₂PO₃ solution. The metallic Pd obtained by reduction reaction acting as active seeds played a critical role in the following electroless plating process. As exhibited in figure 6, metallic Pd could accelerate the adsorption of H₂PO₂⁻ and OH⁻ on the surface, which was the committed step in coating deposition [17].
The absorption schematic diagram of metallic Pd in electroless plating process.

The absorption and anchoring of active seeds on the surface of CFRP were the critical factors for the adhesion of planting. The rough caterpillar-like structure and polar surface initiated by laser radiation could absorb and fasten more Pd atoms on the surface, which were benefit to improve the planting adhesion. The phenomenon could be proved by SEM detection, the results of which were illustrated in figure 7. There are more Pd elements can be detected in laser treated area than pristine surface. Furthermore, it can be seen from the amplification images that the Pd elements are uniformly distributed around the carbon fiber. It was another evidence that laser radiation process could improve the adhesion of active seeds.

3.4. The Progress of Electroless Plating
Figure 8 shows the SEM images of the laser treated CFRP after electroless Ni plating for 0s, 30s, 60s, 90s, 120s and 150s. Initiated by active Pd seeds, the Ni$^{2+}$ was absorbed and deposited quickly. When immersed into the electroless Ni plating solution for 30s, several Ni particles with hundred nanometers were detected on the surface of CFRP (figure 8(b)). Owing to the scattered Pd deposition, Ni was deposited on the surface of CFRP in scattered manner. Then the scattered Ni particles began to propagate, enlarge, and interconnect (figure 8(c-f)). At the plating time for 150 s, the carbon fibers were wrapped by Ni particles completely (figure 8(f)). The Ni particles are connected with each other closely to form the homogeneous and dense plating film. It can be further verified by SEM element mapping and EDX images (figure 9). Ni element and P element are homogeneous distrusted on the surface of CFRP, and there was no C element and O element from carbon fiber could be detected by EDX.
Figure 8. SEM images of the laser treated CFRP after electroless Ni plating for different time

Figure 10 gives the images of CFRP after electroless plating for 30 min, which showed good selectivity. In the area of laser treatment, uniform Ni plating could be produced. Moreover, the Ni plating exhibited excellent adhesion according the grid test. In contrast, there was no melt coating can be obtained in un-treatment area. The results demonstrated that selective metallization could be realized successfully on CFRP by laser-assisted method.

Figure 9. SEM element mapping (a, b, c) and EDX images (d) of the CFRP after electroless plating for 150 s.

Figure 10. Images of CFRP after electroless plating for 30 min.
4. Conclusion
A simple laser activation pre-treatment based technique for selective metallization on CFRP has been demonstrated in this paper. After laser activation with laser power intensity of 30–60 J·cm⁻² and pulse overlap of 0–50%, a rough caterpillar-like structure and polar surface were synthesized on the surface of CFRP. More active metallic Pd could be absorbed and fastened on the laser treatment area, which were benefit to improve the planting adhesion. After electroless plating procedure, a homogeneous and dense nickel film with excellent adhesion was selectively deposited on the laser treatment area of CFRP. This technique provides a new approach for selective metallization of CFRP on the application of microwave components and waveguide antenna.

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