

CHEMICAL DEPOSITION OF COPPER AS A NOVEL SOLUTION FOR LIGHTNING STRIKE PROTECTION OF CARBON FIBRE REINFORCED POLYMER PARTS

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Abstract

In this research, electroless chemical deposition of copper is proposed as a novel competitor for lightning strike protection (LSP) of carbon fibre reinforced polymer (CFRP) structures. Specimens were cut off from flat epoxy/carbon fibre panels manufactured by resin transfer moulding (RTM) and auto-catalysed copper deposition was produced by immersion via aqueous solution. The sequence of baths was prepared with cheap and readily available chemicals and metallization was carried out at normal laboratory conditions. Plating was conducted for different times and a thin layer of copper slowly formed onto samples surfaces.

1. Introduction

One of the biggest drivers of the aircraft industry has been the weight reduction of the flying elements since the use of lightweight elements can suppose huge savings in terms of fuel consumption during flight. Thus, the substitution of metallic parts by carbon fibre reinforced polymer (CFRP) materials has been the focus of a great number of industrial developments, led among others by the outstanding specific mechanical performance, chemical stability and reduced density that these materials exhibit. In contrast, the low electrical and thermal conductivity of CFRP has been a big concern for manufacturers when manufacturing aircraft outer skin parts which requirements in terms of electrical properties and lightning strike protection (LSP) are major.

For safety of the flight, most of fuselage, tail or head skin parts must present the ability to either receive or drive away the energy of a lightning impact with the minimum of damage. In conventional aircrafts in which most exterior structures are metallic the electrical paths are naturally occurring and thus no additional measures must be taken. In the other hand, CFRP structures must be protected by LSP solutions such as metal foils, expanded copper foils (ECF) and metallic meshes attached to the surface of components. These elements contribute significantly to enhance the surficial electrical conductivity of parts, and thus to release the high levels of current produced when a lightning strikes [1].

Despite the very good performance of common LSP based on metallic attachments, these solutions are expensive, difficult to apply and heavy as compared to CFRP elements which main advantage is the low weight. Thus, there is a trend in the effort of finding new systems to protect non-conductive

components by other means [1-2]. The use of alternatives such as modified resins containing metal/carbonaceous particles is attractive, but very often presents drawbacks. Modified resins either do not show appropriate conditions for processing or cannot achieve good results under lightning event. In the other hand, most metallic coating techniques such as physical vapour deposition (PVD) involve the use of high vacuum chambers which is not eligible in terms of costs for large components.

In this work, a novel approach for the metallization of the surface of CFRP based on surface treatment is proposed. The feasibility of chemical deposition of copper was studied for the application of the resulting coatings as LSP of CFRP. This technique of surficial metallization is widely employed in industry for aesthetic finishing of non-conductive parts, and presents objective advantages over physical deposition since no vacuum process is involved [3]. Also, the use of chemical process instead of manual attachment of LSP solutions would have high industrial interest in aeronautics sector due to the high automation degree of the process and would lead to lower personal and material costs.

2. Materials and methods

Samples used as substrates subjected to study were extracted from a flat panel of carbon fibre reinforced epoxy laminate manufactured by RTM. The thickness of the laminate was 2 mm and the squared specimens were prepared by rotatory disk cutting 40x40 mm width and length parts. Samples were cleaned and degreased in three steps with liquid soap, acetone and NaOH solution in advance to surface treatment. Prior to copper plating, non-conductive substrates were pre-activated to increase its surficial energy and form a catalytic surface in order to be sensitive to subsequent coating process. Specimens were subjected to pre-treatment by immersion in a series of aqueous baths composed of acid etch (sulfuric acid solution), mordant (NaCl, SnCl₂ and HCl) and activation bath (AgNO₃). The immersion was carried for 15 min at room temperature into each bath under moderate stirring and abundant rinsing between stages in order to protect the baths from contamination. During pre-treatment, the appearance of surface of samples changed from original dark black until they presented an slight blue shine and enhanced hydrophilicity which was interpreted as a change in morphology and chemical characteristics of the surface, and thus the surface activation was obtained. Pre-treated samples were subjected to chemical deposition of copper by immersion in aqueous solution containing CuSO₄, EDTA and KOH to adjust the pH. The reaction of copper reduction was forced to begin by the addition of HCHO. Samples were extracted from metallizing bath at 15, 30, 45 and 60 min, rinsed with deionized water and left to dry at room conditions before sealing in zip-lock bags to avoid possible further oxidation.

3. Results and discussion

After the whole process, the samples presented a visible layer of copper with decreasing levels of gloss with the time of treatment as shown in Fig. 1. The coating was uniform in colour, with no visible defects or detachment of the layer.

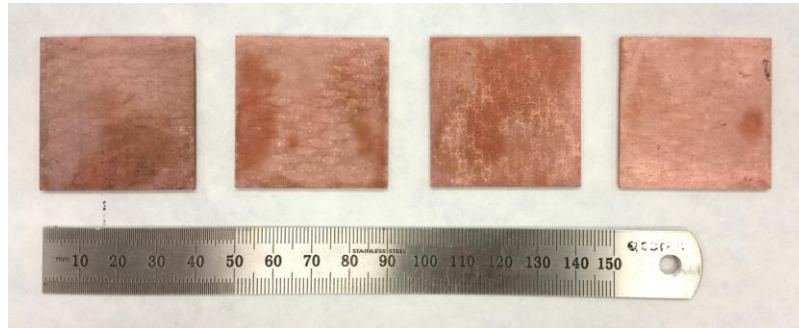


Figure 1. Samples extracted from metallization bath at 15, 30, 45 and 60 min respectively.

Scanning electron microscopy (SEM) technique was used in order to investigate the microstructure of the coatings achieved. In addition, the energy dispersive x-ray spectrometer (EDS) instrument attached to SEM equipment was also employed to analyse the chemical composition of the samples. EDS inspection showed a high concentration of copper atoms, but also low presence of tin and silver which is in accordance with the pre-treatment performed on the samples.

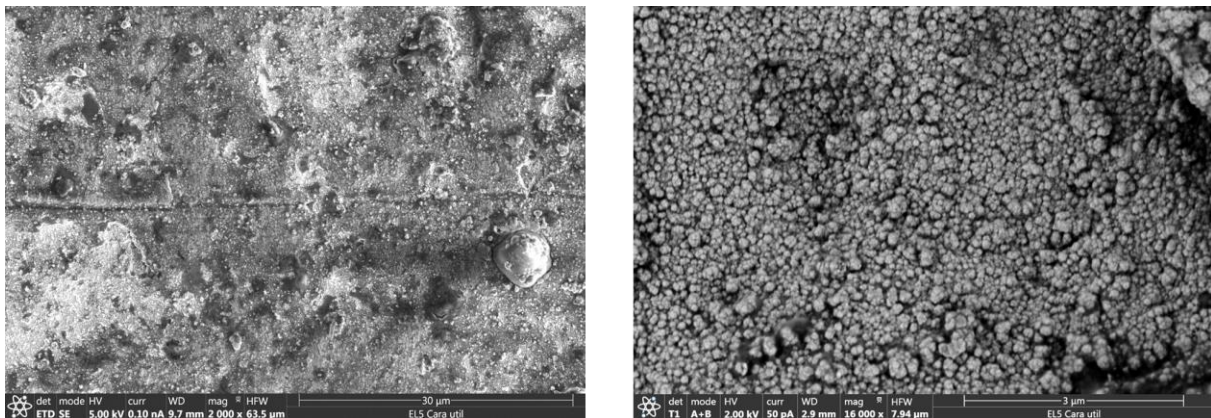


Figure 2. SEM micrographs of a 30 min coated piece at 2000X (left) and 16000X (right).

In Fig. 2 it is shown the coated area of a sample under low and high magnifications. It can be observed in the image at the left that the coating is uninterrupted and does not present any cracks or defects. Anyway, it can be seen a region with an elevated structure, not clear if it is due to a punctual increased growth of the layer or by contrast there is a drop-like defect of the resin underneath the coating.

Right image presents a detailed view of the structure of the layer at high magnification. When using higher magnification, SEM reveals the actual microstructure of the coating. The copper layer is composed of small (80-120 nm) rounded globular structures that agree with the theoretical structure of nucleation-growth of copper nuclei in chemical deposition [4].

The electrical conductivity of the all coatings produced was evaluated using a Keithley 2400 SMU instrument by the four probe method. Since the specimens were coated in all surfaces exposed to baths the coating was removed from all faces except one for a proper electrical investigation. A level of current of 1 A was injected on two opposite edges of samples and the measurement of resistance was carried out by placing the probes on the surface with spacing of 25 mm. The electrical resistance expressed in ohms was recorded and converted into sheet resistance by the following equation (Eq. 1):

$$R_{square} = R \cdot w / l. \quad (1)$$

Where $l = 25 \text{ mm}$, $w = 40 \text{ mm}$ and R_{square} is expressed in $[\Omega/\square]$.

Values obtained are presented in Figure 3.:

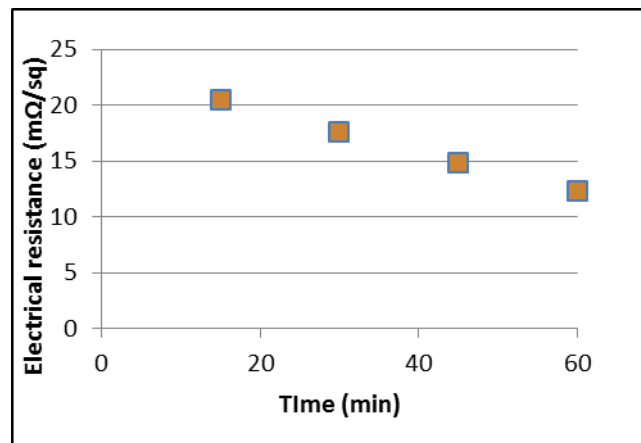


Figure 3. Sheet resistance of different coatings expressed in $m\Omega/\square$ versus time of deposition.

Sheet resistance of coatings presents a linear downtrend with the time of deposition. The samples coated for 15 min show near $21 \text{ m}\Omega/\square$ whilst samples coated for 60 min showed a decrease of almost 45% in this value, near $12 \text{ m}\Omega/\square$. There is a direct relationship between the time of deposition and the electrical performance of the coatings most likely due to an increased amount of deposited material. Furthermore, values obtained for 40 and 60 min are compliant with the requirements of LSP for indirect effects of some areas of current aircrafts which threshold is $15 \text{ m}\Omega/\square$.

By paying attention to the visual appearance of the coatings and also noticing the downtrend in sheet resistance with the increasing time of deposition, it can be inferred that the layer of copper may be thicker for more prolonged times of metallization. Thus, according to Eq. 2, it can be easily related the theoretical thickness of a layer with the sheet resistance that it presents whenever the resistivity of the material is known.

$$R_{square} = \rho / t. \quad (2)$$

Where ρ is resistivity in $\Omega \cdot \text{mm}$ of the material and t is thickness of the layer in mm.

Table 1. Calculated thicknesses of the coatings

Time of deposition	R_{square} ($\text{m}\Omega/\square$)	Calculated thickness (μm)
15 min	21	0.81
30 min	17	1.00
45 min	15	1.15
60 min	12	1.42

It was assumed for calculations that the layer deposited is fully composed by pure copper which resistivity is $\rho = 1.71 \cdot 10^{-8} \Omega \cdot \text{m}$. Values obtained for coated samples vary from near 0.8 μm to 1.4 μm which are at the beginning of the bulk growing stage according to former studies of this kind of coatings [5]. Paunovic stated that coatings produced with absence of electricity present a thin film stage until 1 μm of thickness and subsequently it is formed a thick film structure of greater grain size.

With the aim of validating the calculus, samples were cut and polished with 1 μm diamond powder fluid in order to prepare the surface for observation with optical microscope.

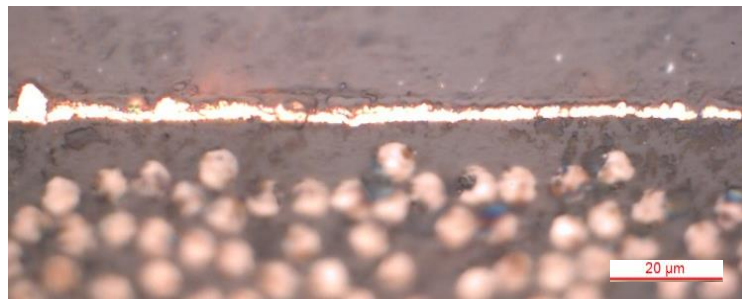


Figure 4. Transversal micrograph of a 60 min coating.

Values obtained from images of the thickness of coatings were obtained employing specialized measurement software attached to the microscope. The transversal size of the copper layer was investigated and was revealed similar to the values thrown by the calculations based on the sheet resistance of the coatings. In Fig. 4 it can be seen a micrograph of the samples coated for 60 min. In this particular case the measured average thickness was 1.45 μm , very close to the value indicated by Eq. 2 (1.42 μm).

For comparison, in former works related with copper plating such as that carried out by Smith et al. [6], the values obtained by simulation for a 0.45 μm thickness interconnect of rectangular section produced by PVD/CVD were calculated to be near 37 $\text{m}\Omega/\square$. In this case, the foreseen performance of the copper interconnector is lower than that presented in this study, since for a similar copper coating the expected sheet resistance would be near 26 $\text{m}\Omega/\square$ according to the linear trend presented in Fig. 3. In the other hand, Lagrange et al. [7] performed annealing of copper layers of near 1 μm thickness obtained by electrodeposition onto silicon oxide substrates achieving a sheet resistance drop of 20% from 20 $\text{m}\Omega/\square$ to 16 $\text{m}\Omega/\square$. The final value is comparable to that obtained in our study for a 30 min copper plating which exhibits 17 $\text{m}\Omega/\square$ with no extra thermal treatment.

The study on the coatings produced included resistance to separation test according to cross-cut test procedure under ISO 2409. Results revealed that the coatings have outstanding adherence to substrate showing best rating of the standard scale. In the other hand, samples were also immersed for 96h in most common aeronautic contaminants (i.e. acetone, MEK, JP-8 and de-icing fluid) and only the samples immersed in MEK showed a significant damage in electrical properties.

4. Conclusions

Basic properties of coatings produced by chemical deposition of copper onto epoxy-based CFRP were studied as a preliminary work for assessing the feasibility of this technology to be eligible as lightning strike protection of parts. A thick and continuous layer of copper was attached to the surface of the specimens which presented a globular-like structure. Samples exhibited sheet resistance levels increasing with the time of deposition and in some cases the values reached the compliance threshold for indirect effects of lightning strike in aircraft. The thickness of the coatings was measured indirectly by calculations involving electrical parameters but also experimentally by optical microscope. Both methods threw results congruent with each other and the thicknesses were observed to be in the range of 0.8-1.4 μm . Furthermore the coatings showed outstanding resistance to separation and good chemical stability under common aeronautic contaminants.

The preliminary works carried out in this technology brought attractive results for further investigation. The novel approach presented for lightning strike protection of CFRP by the use of chemical deposition of copper shows promising characteristics which will lead to future works involving bigger coupons and under artificial lightning event conditions.

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