Multimetallic Electrodeposition on Carbon Fibers

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Abstract. Efficient lightweight design requires intelligent materials that meet versatile functions. One approach is to extend the range of properties of carbon fiber reinforced plastics (CFRP) by plating the fiber component. Electroplating leads to metalized layers on carbon fibers. Herein only cyanide-free electrolytes were used. Until now dendrite-free layers were only obtained using current densities below 1.0 A dm⁻². In this work, dendrite-free tin and copper coatings were achieved by pre-metalizing the carbon fiber substrates. Furthermore, applying a combination of two metals with different sized thermal expansion coefficient lead to a bimetallic coating on carbon fiber rovings, which show an actuator effect.

1. Introduction

The substitution of classic materials by carbon fiber reinforced polymers (CFRPs) provides advantages in materials properties. Impressive arguments for their use are high strength and flexibility, very low weight, positive behavior in important application criteria such as energy consumption, vibration resistance and damping, corrosion and aging. CFRPs show disadvantages like insufficient electrical and thermal conductivity. Furthermore, damages in CRFP parts are difficult to detect [1].

To overcome those weaknesses, several strategies which allow the functionalization of CFRP are under investigation. Therefore, three different strategies are preferred. On one hand it is possible to metalize the CFRP at its surface [2]. This way efforts consuming pre-treatment steps and the use of harmful chemicals. Furthermore, the layer is exposed to the environment what can cause contamination or oxidation. On the other hand it is possible to integrate the functionalization into the CFRP structure using metal wires [3]. In this case the millimeter thick metal wires forward weakness. In addition, metal wires are getting more and more expensive the smaller their diameters are.

The third preferred strategy is the production of metalized carbon fibers which are economic, environmentally friendly producible but currently not commercially available, except for nickelized carbon fibers [4–6]. A viable commercial transfer of metalized carbon fibers efforts the use of cyanide-free electrolytes and high current densities. In contrast to this requierements dendrites mainly grow while plating in example tin or copper at current densities above 1.0 A dm⁻² [4]. According to the plating metal, the coatings show more or less dendrites [7]. In this work, a conductive basic layer was used to prevent the formation of dendrites. Furthermore, two metals with different thermal expansion coefficients were combined to produce a bimetallic coating with actuator effect for the first time.
2. Methods

2.1. Equipment and Materials

The investigation of dendrite-free tin and copper coatings at carbon fibers were examined on carbon fiber woven fabrics (type Aero 160 from R&G Verbundwerkstoffe GmbH containing Toho Teijin Tenax HTA 40 E13 3K fibers). The woven fabrics were cut into segments of 40 mm x 60 mm to metalize the top layer.

Initial tests for the development of carbon fibers with an actuatory effect were examined on carbon fiber rovings of the type HTA 40 E 13 3 K (Toho Teijin Tenax). The fibers were cut into segments of approximately 70 mm length and fixed in a polypropylene holder.

The prepared substrates were immersed in a cyanide-free electrolyte for nickel, tin or copper at a temperature 25±1 °C. Electroplating experiments were examined by a laboratory power supply Beha Uniwat NG 304. Tempering and circulation of the electrolyte were ensured by using a laboratory stirrer IKA C MAG HS. The anodes were purchased from Galva-Metall GmbH.

Metallographic cross-sections were prepared to analyze the metal layers. Those samples were examined via optical microscope Olympus GX51 with Olympus XC30 camera.

2.2. Equipment and Materials

Desizing of the substrates was carried out by immersing the carbon fibers for 60 minutes in an ultrasonic bath filled with acetone. The temperature was held at 60 °C during desizing.

The electrodeposition on carbon fiber rovings was carried out under variation of the process parameters like current density between 0.25 and 1.5 A dm\(^{-2}\) and a plating time in a range from 5 to 60 minutes. The coated samples were rinsed with distilled water and ethanol. A subsequent drying process at 60 °C for 4 hours in a vacuum compartment dryer finalized the coating process of each layer.

The bi-metallic coating with an aspired actuatory effect requires an one-sided metal deposition at the carbon fiber surface. Thus, only one anode was used. In addition, it is necessary to protect the opposite side of the carbon fibers to prevent undesired metal deposition. Therefore, the bottom half of the rovings was embedded in an epoxy resin. After the successful metal deposition at the upper half, the samples were placed in acetone for 24 hours, to remove the protection layer.

3. Results

3.1. Dendrite-free copper plating

Initially, the carbon fibers were nickelized in order to increase their conductivity and prevent the formation of dendrites. The coating process was observed by measuring the voltage in dependence of time. The resulting diagrams are similar to each other. Here, we present the deposition of the basic layer and a copper layer as representative example.

The initial voltage of the nickelization amounts 3.2 V and decreases to a constant value of 2.1 V after one minute deposition time (Figure 1). Copper plating takes place at a lower nearly constant voltage, which amounts to approximately 0.5 V.
Figure 1. Time-voltage diagram recorded during the electroplating of a nickel basic layer deposited at a pure carbon fiber woven fabric and a copper layer deposited at a nickelized carbon fiber woven fabric.

The results of the coating processes can be observed by microscopy of cross-sectional views. The conductive basic layer is 1 µm thick and homogeneously distributed. Furthermore, the nickel layer shows a good penetration depth (Figure 2).

Figure 2: Cross sectional views of nickelized carbon fibers with a dendrite-free copper coating in different magnifications.

The electrodeposition of copper was carried out at a current density of 1.5 dm⁻² (Figure 1). The achieved copper layer covers the outer surface of the carbon fiber roving completely. In contrast to former coating experiments, it is possible to achieve very thin dendrite-free copper layers using the conductive basic layer (compare Figure 2 and [5]). The thickness of the copper layer amounts to approximately 2 µm.

3.2. Dendrite-free copper plating

For the electrodeposition of dendrite-free tin layers, the carbon fibers were nickel plated too. The nickel-coating is 1 µm thick and homogeneously distributed and comparable to the conductive basis layer for dendrite-free copper. The penetration depth is as good as observed above (Figure 3).
The tin layer was deposited at a current density of 1.5 A dm$^{-2}$ (Figure 3). The layer is located at the outer surface of the carbon fiber rovings and it does nearly cover their whole surface. The deposition of tin at a conductive basic layer leads to layers with an average thickness of approximately 7 µm. The coating is also dendrite-free.

3.3. Bi-metallic coating with actuatory effect

Two metals with preferably different expansion coefficients were chosen to create a bi-metallic coating with actuatory effect at a carbon fiber roving (Table 1). In the following example copper was plated as first and zinc as second layer.

| Material   | $\alpha$ in $10^{-6}$ K$^{-1}$ |
|------------|-------------------------------|
| copper     | 16,5                          |
| nickel     | 13,4                          |
| zinc       | 36                            |
| tin        | 27                            |
| carbon fibers | –0,1                    |

Due to the before applied protection layer using an epoxy resin, the coating is located at only one side of the carbon fiber roving. The protection layer could easily be removed after the electroplating processes.

The semi coated rovings show an actuatory effect (Figure 4).
Figure 4. Macro image of semi-coated carbon fiber rovings with a copper-zinc bi-metallic layer, showing an actuator effect.

The samples are slightly deformed in the ground state (25 °C) due to residual stress. This deformation was completely removed by thermal post-treatment of the coated fibers up to 400 °C. Thus, the system is able to overcome a length of 6 mm.

4. Discussion
The carbon fiber woven could be nickelized easily, as known from literature [2]. This reproducible procedure can be used to create a conductive basic layer for further metallization. Due to the low current density a thin nickel layer was deposited. This shows a good penetration depth and coverage according to the greater convection and electrolyte used.

The voltage curve of the application of further layers is much lower than in case of direct carbon fiber metallization [see 2, 4–6,9], because an increasing conductivity of the layer leads to a decrease of voltage. The homogeneously conductive nickel layer provides a very good basis for the next layers. In case of copper, no additional seed is necessary and very thin coatings are possible while high current densities are applied. Caused by the nickel layer, the deposited copper layer is homogeneously distributed as well. Furthermore, the copper layer is located at the outer surface. The nickel layer shields the carbon fibers and prevents a further coating.

The conductive basic layer enables the dendrite-free deposition of tin, too. Remarkably, in comparison to literature (i.e. [5,9]), thick dendrite-free tin layers at carbon fibers could be described for the first time. In this work, a dendrite-free layer was obtained at a current density of 1.9 A dm$^{-2}$ while the tin deposition in [9] was no longer possible at current density of 1.0 A dm$^{-2}$.

Furthermore, a bi-metallic coating with actuator effect was applied by the means of copper and zinc deposition. Both metals were chosen according to their coefficient of expansion. The one-sided coating provided a good opportunity to give the fibers actuatorary elements. The deformation by heat reaction occurred relatively quickly. Just as quickly, the rebound occurred when removing the heat source. This is due to the small coating thickness, which also has only a small heat capacity. Figures Each figure should have a brief caption describing it and, if necessary, a key to interpret the various lines and symbols on the figure.

5. Conclusion
In this work, dendrite-free copper and tin coatings at high current densities were achieved by pre-metalizing the carbon fiber substrates. Furthermore, applying a combination of two metals with different sized thermal expansion coefficients lead to a bimetallic coating on carbon fiber bundles, which shows an actuator effect. To the best of our knowledge such results haven’t been published yet. Structure-property relationships and cycling tests of the bi-metallic coating with actuator effect are currently under investigation.
6. References

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