Preparation of tin coating on the surface of copper-coated carbon fiber and its effect on the microstructures and properties of the composite coating

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Abstract

In order to prevent the copper coating on the carbon fiber surface from oxidizing and falling off, the tin coating is plated on the surface of copper-coated carbon fiber. In this paper, the copper–tin composite coating with different thicknesses of tin coatings were successfully prepared by electroless plating. The results show that with the increasing of electroless tin plating time, the thickness of the copper–tin composite coating increases. The test results of the bonding force between the composite coating and the carbon fiber show that the coating bonding force is the best when the thickness of composite coating is between 1.31 μm and 1.55 μm. This is due to the formation of copper–tin intermetallic compounds prevents direct contact between the copper coating and oxygen, which can effectively inhibit the oxidation of the copper plating layer, thereby making the plating layer less likely to fall off. However, the excessively thick tin coating would increase the internal stress of the coating, and promote the generation of cracks on the surface of the composite coating, which would cause the composite coating to fall off. This research will provide new ideas for the preparation of high-performance copper plating on the surface of carbon fiber, and provide an important theoretical and practical basis for the application of copper coatings.

1. Introduction

Carbon fiber reinforced aluminum matrix (Cf/Al) composites are widely used in automotive industry, aircraft, aerospace and other fields because of its excellent comprehensive properties [1–3]. However, the interfacial binding characteristics between carbon fiber and aluminum matrix seriously affect the properties of Cf/Al composites, and also limit its further application and development [4–6]. At present, regulating the wettability and reaction degree between the carbon fiber and the aluminum matrix are key to improving the interface bonding. Li et al regulated the wettability between the carbon fiber and aluminum matrix by Ni-coated carbon fiber, and successfully prepared a composite material in which the carbon fiber was completely impregnated [7–9]. Liu et al found that the presence of copper coating would hinder the diffusion of carbon elements into aluminum matrix, which can effectively inhibit the interface reaction between carbon fiber and aluminum matrix [10]. Therefore, the coating was prepared on the carbon fiber surface has an important influence on the properties of Cf/Al composites.

In recent years, copper coating has attracted more attention to the preparation of carbon fiber surface coating due to its low thermal expansion coefficient and good ductility. Duguet et al successfully prepared the copper coating with uniform, continuous and strong adhesion by vapor deposition, but the in-situ water vapor in the preparation process was easy to oxidize the deposited copper coating [11]. The study of copper plating was coated on carbon fiber surface by Varentsova et al [12] showed that the electrode potential change during the electroplating process can easily lead to uneven coating and poor bonding force between carbon fiber and metal matrix. Zhou et al prepared a copper coating with uniform, good gloss, high strength and good adhesion on the
carbon fiber surface by electroless plating \[13, 14\]. However, Huang et al \[15\] found that the thermostability of copper coating was poor, and it was easily oxidized during the preparation of composites. The copper coating was easily fall off after oxidation. In order to improved the oxidation resistance of the pure copper coating. The Cu-Ni double coatings was prepared and the adhesion was stronger than the single copper coating. At the same time, the Cu-Ni coating was used to improve carbon fiber conductivity and higher than non-copper-coated carbon fibers \[13\]. However, the nickel coating is easy to fall off and produce brittle phases in the matrix \[16, 17\]. Therefore, improving the oxidation resistance of the pure copper coating by a suitable method is important for the preparation of Cf/Al composites.

As is known that copper-tin alloy has excellent mechanical properties, and the addition of tin can increase the passivation rate and realize the improvement of oxidation resistance \[18\]. In this paper, copper-tin composite coating was prepared by electroless on carbon fiber surface. The effect of tin coating on the microstructure and bonding properties of the copper-tin composite coating has been studied in detail. This research will provide new ideas for preparing high-performance copper coating on carbon fiber surface, and provide significant theoretical and practical basis for the application of copper coatings.

2. Experimental procedure and mathematical models

2.1. Experimental material

The polyacrylonitrile-based carbon fiber (T-300) were produced in the Institute of Coal Chemistry Academy of Sciences in chinese, and the diameter of carbon fiber is 8 μm. In the electroless plating process, high-purity chemical reagents used in each stage are shown in figure 1.

2.2. Coating fabrication

The process of preparing a copper coating by electroless plating on carbon fiber surface is shown in figure 1. The carbon fiber was pretreated before electroless copper plating to improve surface catalytic activity, which consists of five stages: removing, coarsing, neutralization, sensitization and activation. The carbon fiber was cleaned with deionized water in every stage. Then, the carbon fiber was immersed in an electroless plating solution for 12 min. Before electroless tin plating, the copper-plated carbon fiber needs to be cleaned to prevent contamination of the electroless tin plating solution. The tin coating was obtained at different time (0 min, 15 min, 20 min, 25 min, 30 min).

2.3. Microstructures and mechanical properties

The microstructures of the copper coating and copper-tin composite coating on the carbon fiber surface and transversal sections were detected by Hitachi (TM3030 and SU8010) scanning electron microscope (SEM). The
The carbon fiber coating thickness was measured by the line-intercept method from at least five SEM micrographs and the average value was the final thickness of the coating. The bonding properties was tested between composite coatings and carbon fiber by a water quenching method. The specimens were heated at 473K (8 K/min) for 60 min, afterwards, which were removed from the furnace and immersed in ice water for 3 min. Lastly, in order to obtain the plating weight change (measurement accuracy 0.00001 g) that the carbon fiber was desiccated. The process was repeated until the coating suddenly appears weight loss. The microstructures and the fracture characteristics of copper-tin composite coating were examined using SEM.

3. Results and discussion

3.1. Effect of electroless tin plating time on carbon fiber surface coating

Figure 2 shows the microstructures of copper plating and copper-tin composite plating on carbon fiber surface that prepared by electroless. The plating surface morphology of carbon fiber with copper plating are shown in figure 2(a), it can be seen all carbon fibers are evenly covered with the copper coating, and the coating surface becomes rough due to chemical deposition. The increase of carbon fiber surface roughness is beneficial to the bonding between copper and tin coatings. The morphology of the copper-tin composite coatings coated with tin coatings at different time (15 min, 20 min, 25 min, 30 min) are shown in figures 2(b)–(e). When the electroless tin plating time is 15 min, it can be clearly observed that the surface of the coating becomes smooth, so it can be determined that the process can plate the tin coating on the copper coating and shown in figure 2(b). The surface roughness of the composites coating increases with the electroless plating time increases, and tiny island-like particles are gradually formed in figures 2(c) and (d).

When the increase of the electroless tin plating time to 30 min, although the tin coating can still completely cover the copper-coated carbon fiber, cracks and coarse grains are found on the surface of the copper-tin composite coating, as shown in figure 2(e). This is because the continuous copper coating can provide a favorable deposition sites for the tin coating, which is beneficial for the tin coating to deposit and cover the copper-coated carbon fiber surface [15]. However, the increase of the electroless tin plating time not only promotes the growth of crystal grains, but also causes the internal stress of the tin coating to increase. The internal stress accumulates to a constant value that cracks will appear on the coating surface. This phenomena not only destroys the integrity of the coating, but also severely reduces the bonding effect between the coating and the carbon fiber [13]. As shown in figure 2(e).

In addition, with the electroless tin plating time increasing, the thickness of the tin plating also increases. The weight versus with time of copper-tin composite coating was show in figure 3. It can be seen that the slope of the curve is decreases when the deposition time between 25 min-30 min the coating weight and time were not linear and consistent with the results of previous studies [20]. Ions self-catalysis and energetically favoured sites are the main factor to influence of deposition ratio. The cross-section image of the carbon fiber after electroless plating shows in figure 4. It can be seen that the plating binds well with the carbon fiber and the copper coating thickness in this process is 0.95 μm in figure 4(a). With the increasing of the electroless tin plating time, the composite coating thickness increases significantly, as shown in figure 4(b)–(e). This can indicate that the tin coating was successfully deposited at copper-coated carbon fiber surface by electroless plating. Figure 4(b) shows the
cross-section of the composite coating after electroless tin plating for 15 min. At this time, the composite coating thickness has increased to 1.12 μm. The line scanning energy spectrum analysis result of the copper-tin composite coating is shown in figure 4(f), which indicates the coating contained only copper and tin elements and also proved that the tin coating has been successfully deposited at copper-coated carbon fiber surface. With the increase of electroless tin plating time to 20 min, 25 min and 30 min, the total thickness of the composite coating reached 1.31 μm, 1.55 μm, and 1.58 μm, respectively.

3.2. Effect of electroless tin plating on the binding properties
In this paper, the bonding force was tested between composite coating and carbon fiber by thermal shock method. The weight change curves with copper-tin composite coating at different tin plating time (0 min, 15 min, 20 min, 25 min, 30 min) are shown in figure 5. The weight changes first to increases and then decreases rapidly was observed for pure copper plating. This is because copper was easily oxidized at 200 °C and a large number of CuO brittle phase is generated [21]. In this case, the copper coating begins to fall off and fracture from the second...
thermal cycles, and terminate at five thermal cycles. When the tin plating thickness was addition on the copper-coated carbon fiber surface, the weight change is not significantly increase compared to pure copper plating, which can be indicates that the thermal shock resistance of the composite coating has been obviously improved. When the electroless tin plating time was increased to different times (15 min, 20 min, 25 min, 30 min), the thermal cycles was 7, 12, 12 and 11 respectively. The thickness of tin coating can be thought of as the main factor as describing increase the number of thermal shock cycles. At the same time, the intact tin coating deposite on copper coating was conducive to improve the bonding strength. In particular, the coating has the best performance when the electroless plating time is 20 to 25 min.

The phase composition of copper coating and copper-tin composite coating after the first heating in the thermal shock experiment was investigated using XRD-7000 as shown in figure 6. It can be found that pure copper coating was very easy to oxidize and generate CuO at 473 K. With the addition of electroless tin plating, the CuO phase is significantly reduced. When the electroless tin plating time is increased to 20 min, the oxidation of the copper coating can be effectively inhibited. This is due to the formation of copper-tin intermetallic compounds prevented direct contact between the copper coating and oxygen. At the same time, the formation of SnO2 also enhance the oxidation resistance of the coating. Otherwise, the copper-tin
intermetallic compounds are crucial to improve bonding force between copper-tin composite coating and carbon fiber.

Based on the microstructures of copper coating and copper-tin composite coating after thermal shock test in figure 7. The microstructures of copper-coated carbon fiber after thermal shock test are shown in figure 7(a), the copper coating fall from carbon fiber surface formation a large area due to the generation of the CuO brittle phase. With the thickness of the tin coating increased, the phenomenon that the detach coating was improved. The presence of tin coating can slow down the rapid oxidation and shedding of pure copper coating. However, the presence of tin coating would increase the internal stress of the coating, and promoted the generation of cracks after multiple cooling and heating cycles, which would cause the composite coating to fall off. As shown in figure 7(b)–(e). The effect of different times between 20 min and 25 min with electroless tin plating improved the detach coating is optimal, the Copper-tin intermetallic compounds isolated the oxygen is the main factor to improve the thermal stability of composite coating.

During the thermal shock experiment, the formation process of the copper-tin intermetallic compound and the interface reaction are shown in figure 8.

Interface I: from the C-Cu binary phase diagram, it can be found that carbon and copper have good thermal stability.

Interface II:

\[ 3\text{Cu} + [\text{Sn}] \rightarrow 4\text{Cu}_{3/4}\text{Sn}_{1/4} \]  \hspace{1cm} (1)

Interface III:

\[ 22\text{Cu}_{6/11}\text{Sn}_{5/11} + 9[\text{Cu}] \leftrightarrow 28\text{Cu}_{3/4}\text{Sn}_{1/4} + 3[\text{Sn}] \]  \hspace{1cm} (2)

Interface IV:

\[ 5\text{Sn} + 6[\text{Cu}] \rightarrow 11\text{Cu}_{6/11}\text{Sn}_{5/11} \]  \hspace{1cm} (3)

With the increase of temperature, the copper-tin intermetallic compound was generated during the thermal shock test, which was due to the interdiffusion of copper and tin atoms in copper-tin composite coating. The diffusion rate of copper in tin was greater than that of tin in copper [22]. Therefore, \( \text{Cu}_6\text{Sn}_5 \) phase was initiated generation at the interface IV, because the copper atoms were continuously enriched. Diffusion reaction front
advances toward the copper coating was beneficial to formation Cu₆Sn₅ phase. The diffusion rate of copper in the Cu₆Sn₅ phase was faster than that of tin have been confirmed [23]. This could provide favorable conditions for the transition from Cu₆Sn₅ phase to Cu₃Sn phase at the interface III. Cu₃Sn phase was grew at the expense of Cu₆Sn₅ phase and it will be accompanied by tin atoms shifting to left [24]. When the tin atoms reached at the interface II, Cu₃Sn phase was generated again. The copper–tin intermetallic compounds was generated not only improves the bonding force, but also further ensures the stability of the copper–tin composite coating.

4. Conclusion

(1) The tin plating is successfully performed on copper-plated carbon fiber surface to obtain different thicknesses of copper–tin composite coatings. With the increase of the electroless tin plating time, the thickness of the tin plating also increases. The most suitable electroless tin time was between 20 min and 25 min to inhibit oxidation of copper coating.

(2) The thermal shock test indicate that the coating thickness between 1.31 μm and 1.55 μm, the bonding force between the copper–tin composite coating and carbon fiber is the best, because the formation of copper–tin intermetallic compounds prevented direct contact between the copper coating and oxygen achieve optimal.

(3) The mechanism that increase thermal shock resistance of copper–tin composite coatings is related to Cu₆Sn₅ and Cu₃Sn formed by diffusion during heating of the C/Cu/Sn system.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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