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A STUDY ON CARBON FIBER (LONG FIBER) REINFORCED COPPER MATRIX COMPOSITE

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A STUDY ON CARBON FIBER (LONG FIBER) REINFORCED COPPER MATRIX COMPOSITE

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Abstract: Based on the characteristics of carbon fiber, this paper describes the technology of continuous multi-step electrodeposition and a self-made special installation for continuous three-step electrodeposition. The carbon fiber (long fiber) reinforced copper matrix composites produced has a longitudinal tensile strength of 590 MPa by continuous three-step electrodeposition and vacuum hot pressing. Experiments show that this method has the following advantages: low operating temperature, easy adjustment of fibervolume fraction, uniform arrangement of fiber, ready achievement of continuous operation, low cost and high quality of carbon fiber reinforced copper composites.

Key words: carbon fiber, copper matrix, composite material, continuous electrodeposition, hot press, property, fabrication,

I. INTRODUCTION

Carbon fiber reinforced metal composite is a new type of material developed since 1950 [1]. Its excellent property has made it the focus of world attention. However, the development of this material is not as rapid as people expect it to be. The main reason is in the fabrication process of metal matrix composite which is much

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more complicated and difficult than that of plastic and resin matrix composite. The difficult point of fabrication of carbon fiber reinforced metal matrix composite can be summarized as the following: 1. The melting point of metal is high so effective way to prevent fiber from chemical and physical damage is necessary in fabrication process. 2. The difference between the properties of carbon fiber and metal is significant. In the view of application, more the properties of two constituents differ from each other, more likely they can supplement and coordinate with each other thus to form a composite of better property. However, in the view of fabrication, more the properties of two constituents differ from each other, more difficult to produce a composite it would be because the first point in fabrication is to solve the problem of inclusion between two constituents [2] for good binding of their interfaces and for their uniform distribution. The fact that current fabrication technology has problem of complicated processing and high cost makes the development of this new type of composite slow down. Therefore, people are investigating on new fabrication technology in order to simplify the processing and to lower its cost. Electrodeposition is one from that [3].

Carbon fiber reinforced copper matrix (for simplicity, use carbon-copper in the remaining part of this text) composite is in the ascendant as a set of carbon-metal composite [4]. Its strength and modulus are much higher than those of any copper and copper alloys. Besides, it has higher electrical and thermal conductivity, good combination of low friction coefficient and high wear-resisting as well as stable property and size at higher temperatures. Carbon-copper composite is attractive in making electronic material, wear-resisting material and material used at a certain temperature and environment. The United States are also involved in the research of carbon-copper composite for making brush in strong-current pulse electrical machinery [5]. However, copper has high melting point and low infiltration with carbon fiber. So the methods of infiltration using molten liquid and press casting are very complicated in fabrication technology.
This paper describes the technology of continuous three-step electrodeposition and a self-made special installation of continuous electrodeposition processing series and vacuum hot press machinery, studies on carbon-copper composite fabrication technology and control of fibervolume fraction, also analyzes of the binding condition of matrix with carbon. It discusses a simple, direct and economical method which is also easy to be applied to industrial manufacture of carbon-copper composite.

II. EXPERIMENTAL MATERIALS AND EXPERIMENTAL SCHEME

The materials used in this experiment:

Reinforced material uses medium-strong type polyacrylonitrile matrix carbon fiber made in our country. It has the tensile strength of about 2,000 MPa, elastic modulus of about 200 GPa, specific weight of 1.74 g/cm\(^3\) and concentration of copper being greater than 94%. The surface condition and the cross section of carbon fiber are shown in Figures 1 and 2.

Matrix material is electrolyte copper. It contains 99.9% of copper and its tensile strength is 232 MPa.

Experimental scheme:

Carbon fiber has electrical conductivity so it can be used as cathode in electrodeposition while copper plate containing phosphorus serves as an anode. Insert both poles in the solution in the meantime. The electrodeposition reaction happens at the cathode with the action of a certain current density causing a layer of metal coated on the surface of carbon fiber. However, carbon fiber has the higher electrical resistance (resistivity is 0.0016 \(\Omega\)cm) compared with that of metal. Besides, carbon fiber is supplied in the form of a batch, each batch incudes one thousand peices of fiber and each peice has the diameter of about only 6 \(\mu\)m, so its surface area ratio is large (about \(3 \times 10^4\) m\(^2\)/kg). The behavior of higher electrical resistance and larger surface area of carbon fiber causes difficulty in electrodeposition. At cathode electrodeposition the so-called "agglomeration" readily happens, that is, at electrodeposition the
outer layer of a batch of carbon fiber gets more deposit of metal while some pieces of fiber inside the batch can not get deposit of metal at all. The phenomenon of nonuniform distribution of metal coating on fiber surface makes poor binding of part of fiber with metal matrix. Not only it makes the reinforcement inefficient, but also produces hollows inside matrix thus affecting material property. Therefore, avoidance of "agglomeration" is the key objective in electrodeposition technology.

![Figure 1: The surface condition of carbon fiber (× 5,000)](image1)

![Figure 2: The cross section of carbon fiber (× 10,000)](image2)

Our experiment has used the scheme of continuous multi-step electrodeposition. Considering the change of the carbon fiber properties from before its surface gets deposit of metal layer to after that, we let fiber go continuously through three electrodeposition trough. The solution contents and the technological parameters in each trough can be adjusted independently according to the technology requirements. The metal deposition layer on fiber surface gets thickened gradually thus preventing from "agglomeration" phenomenon due to deposition in a single trough thus resulting in uniform distribution of matrix on fiber.

The detailed experimental procedures are as the following:

1. Preprocessing of carbon fiber

In order to reinforce the binding with matrix, carbon fiber needs preprocessing of surface purification before continuous electrodeposition. This preprocessing includes deresin, deoil, water rinsing, drying up, etc. The preprocessing on carbon fiber has to be
done beforehand which is not covered in continuous operation equipments.

2. Continuous multi-step electrodeposition of metal layer on carbon fiber surface

At the drive of mechanical equipment, preprocessed carbon fiber goes through three electrodeposition troughs in order. Not only its surface is coated by a copper layer of a certain thickness, but also it winds on reel in a given shape at deposition. The effect of each step in continuous deposition can be summarized as the following:

The first step is predeposition. After gone through this electrodeposition trough each piece of carbon fiber can be coated uniformly by a thin layer of copper. High compactedness of texture is required in order to form good interface for binding with fiber. The thickness reaches about 1 μm.

The second step is thickening deposition. In the second deposition trough predeposited copper layer on carbon fiber surface gets thickened gradually resulting in its thickness of about 2 μm. Uniform distribution of carbon fiber in copper matrix is also ensured.

The third step is wind deposition and shaping. Finishing the first two steps of electrodeposition, the composite fiber is uniformly arranged on reel at deposition and shaping. Proper adjusting solution contents and technological parameters can control volume fraction of fiber to copper matrix.

The raw composite after three-step electrodeposition is taken off from reel followed by water rinsing, inactivation, stoving, the processing to prevent it from surface oxidation. After that it is preserved in drier containers.

3. Vacuum hot press diffusion processing

The raw composite made by continuous multi-step electrodeposition does not have compactedness of inner texture, so vacuum hot press diffusion processing is necessary in order to eliminate hollows and to make matrix density reaching true value for good binding of carbon fiber with copper for producing carbon-copper composite.

4. Texture analysis and property test
Both optical and scanning electron microscopes were used in analysis of texture of carbon-copper composite. In the meantime its electric and mechanical properties were tested.

III. EXPERIMENTAL INSTALLATION AND DETERMINATION OF TECHNOLOGICAL PARAMETER

Experimental equipments include mainly continuous electrodeposition equipments and vacuum hot press diffusion machinery.

3.1 Continuous three-step electrodeposition equipments

The series of continuous three-step electrodeposition technological process includes:

Carbon fiber → first-step predeposition trough → water rinsing trough → neutralization trough → second-step thickening deposition trough → third-step deposition and shaping trough.

The schematic diagram of experimental equipments are shown as the following:

1. fiber 2. power source 3. filter pump 4. gear 5. fiber supplying wheel 6. predeposition trough 7. water rinsing trough 8. neutralization trough 9. thickening deposition trough 10. shaping deposition trough 11. fiber arrangement device 12. shaping model wheel

Figure 3 The series of continuous three-step electrodeposition technological process
(1) Mechanical gear:

The conveyance of carbon fiber is performed by two pairs of rolling transmission shafts installed at the two ends of trough. The contact pressure between two shafts is adjustable. One shaft is made of metal so it can be plugged to cathode of the source to connect carbon fiber with cathode. The surface of driving shafts and that of reel are running at the same linear velocity in the first and second steps deposition troughs thus ensuring continuous and uniform supply of carbon fiber under the loose state without tension.

(2) Solution mixing:

Solution is being processed by cyclic filtering in the first and second deposition troughs. This has two purposes: the first one is to make solution uniform mixed and to reduce the polarization of concentration difference while the second one is to facilitate the spreading of fiber in solution.

3.2 Vacuum (or protection atmosphere) hot press diffusion machinery

Vacuum hot press diffusion machinery was made by using one hundred tonnages universal hydraulic press and equipped with a vacuum furnace. Generally vacuum value less than 10^{-1} Pa is needed in vacuum heating. Protection atmosphere can be supplied if necessary.

3.3 Selection of electrodeposition solution

Multi-step electrodeposition of metal layer on carbon fiber surface depends on change of carbon fiber property in electrodeposition process. Contents of solution in each deposition trough can be adjusted independently according to technological requirements in order to ensure uniform deposition of metal on carbon fiber surface and to prevent it from "agglomeration".

The surface of carbon fiber before being coated by metal layer has relatively high resistance so metal ions readily store up on the surface of fiber pieces causing "agglomeration". The property of solution in predeposition troughs is of significant importance. Basicity cyanogen-free complex solution has been selected after many tests. The candidates of complex may be coke phosphate,
EDTA, NTA, tartrate, citrate, etc. added by proper amount of op series activating agent. It has the following property:

(1) Predeposition solution has good infiltration with fiber. After entering solution, a batch of preprocessed fiber spreads out immediately so that each piece of fiber can get infiltrated by solution.

(2) Solution can facilitate some side reactions. Adjusting technological parameters enhances cathode polarization which facilitates the reaction of $2H^+ + 2e = H_2 \uparrow$ producing lots of hydrogen which further breaks fiber up and leads the way for copper ion to reach the inner part of fiber batch.

(3) Basacity solution has low efficiency of electric current resulting in slow deposition which meets the technological requirements of first step deposition. In the meantime basacity solution with the optimal contents makes fine grains of crystalline metal with high compactedness and strong adhesion onto fiber surface thus ensuring binding strength of interfaces.

The surface of each fiber piece has been coated with a copper layer after the first-step predeposition so that its electrical resistance got decreased while the electrical conductivity got significantly improved. Discharge with large current is proper in order to reduce the time of electrodeposition, so acidity cupric sulphate solution is used for the second-step and third-step electrodeposition troughs. Direction for producing solution varies according to technological requirements for two troughs.

3.4 Adjusting distribution of electric current in predeposition trough

Going along the moving direction of batch in the first-step predeposition trough, the resistance of carbon fiber is getting down due to continuous deposition of copper. Because the cathode electric current is not in uniform distribution the current density at the end of the trough is higher than that at the inlet of the trough, copper deposition is accelerated at the end of the trough which may readily cause nonuniform metal deposition on fiber surface. This problem has been solved by adjusting the distribution of anode technologically. Larger anode area and closer arrangement is needed
at the inlet of the trough while smaller anode and sparse arrangement is needed at the end of the trough. Adjustment of anode distribution has a good effect.

IV EXPERIMENTAL RESULTS AND ANALYSIS

Direction of producing deposition solution and technological parameters in each step trough in the series of continuous three-step electrodeposition technological process has been optimized independently by orthogonal tests. It has been determined by further adjustment in continuous tests. The application of continuous electrodeposition equipments is assured to be stable after many tests. The results of experiments are as the following:

4.1 Result and analysis of predeposition (first step)

Preprocessed carbon fiber runs through solution in first step predeposition trough for 15 minutes. After getting out from the trough the surface of each fiber piece gets a thin and uniform layer of deposited copper with metal lustre without causing "agglomeration". It is as shown in Figure 4. The thickness of copper layer is determined by both weighing calculation and micrometer measurement. The average value of these two methods is taken. The result of these two methods is close, such as the predeposited copper has the thickness of 1.13 μm by weighing calculation and 1.25 μm by micrometer measurement. The average thickness is then about 1.19 μm as shown in Figure 5.

4.2 Result and analysis of thickening deposition (second step)

Copper layer on fiber by the first-step predeposition gets rapidly thickened in acidity solution in the second-step deposition trough. It runs for 10 minutes in the second-step thickening deposition trough causing the average thickness of copper layer on fiber surface to increase till 2.30 μm as shown in Figures 6 and 7.

4.3 Result of winding deposition and shaping (third step)

Inside the third-step deposition trough there is equipped with a reel in the shape of regular hexagonal prism which surface has been attached by a copper foil connected to cathode. Auto fiber
Figure 4 There is a uniform copper layer on the surface of each fiber piece after pre-deposition (×1,500)

Figure 5 The thickness of predeposited copper layer on the surface of carbon fiber (×10,000)

Figure 6 Result of thickening deposition (×800)

Figure 7 The thickness of copper layer on the surface of carbon fiber after thickening deposition (×5,000)

arrangement device makes composite fibre pieces after the previous two-step deposition uniformly distributed on reel. Adjusting contents of electrodeposition solution, through electric voltage and the width of winding on reel can control volume fraction of fibre to
matrix. The number of winding layers varies according to requirements.

4.4 Vacuum hot press diffusion and property tests

The raw fiber after the third-step shaping deposition has uniform distribution but loose texture so vacuum hot press diffusion is necessary to eliminate hollows. In tests vacuum value is less than $10^{-1} \text{Pa}$. Hot press parameters can be taken within the following range. The temperature is kept constant for 20-90 minutes. The pressure is 5 to 20 MPa. The experimental result shows that the property of composite is closely related to hot press condition. Composite of higher property can form at optimum hot press temperature, optimum constant temperature time and optimum pressure. This test shows that when fiber volume fraction is about 35% its longitudinal tensile strength reaches 590 MPa. The ratio of longitudinal tensile strength to transverse one is 5:1. Longitudinal conductivity is 90% of $\text{CS}$. Hot press eliminates hollows resulting in good binding of carbon/copper composite as shown in Figure 8.

Figure 9 shows photo of longitudinal cross section of carbon-copper composite by scanning electronic microscope which shows good binding of carbon with matrix with part of fiber off. Matrix appears to be like tough hollow.

Figure 8  Hot press has eliminated hollows in carbon/copper composite ($\times300$)

Figure 9  Tensile cross section of carbon/copper ($\times2,000$)
V. CONCLUSION

1. Electrodeposition method has low operating temperature thus effectively prevents fiber from damage. It is also advantageous of continuous operation, easy and simple fabrication process and low cost so is a good way to develop and apply some sets of carbon fiber reinforced metal matrix composite.

2. Continuous three-step electrodeposition makes fiber be uniformly distributed in matrix and its reasonable arrangement. The experiments have shown that this method is feasible for fabrication of carbon-copper composite. It can furthermore be extended into the application to some sets of carbon fiber reinforced metal matrix composite.

3. The composite shaped by electrodeposition has loose texture and relatively low compactedness so vacuum (or protection atmosphere) hot press diffusion processing is necessary to eliminate its hollows for good binding of carbon fiber with metal matrix.

4. It is promising to use the method of electrodeposition combined with vacuum hot press diffusion processing to produce carbon fiber reinforced copper matrix composite of high property.

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