Influence of Ni-Cu-La-B-coated Glass Fiber on Conductivity and Electromagnetic Shielding Performance of Coatings

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Abstract. A novel electromagnetic environmental pollution protective coating with high performance was prepared with Ni-Cu-La-B-coated glass fiber and nickel powder as composite fillers. Its conductivity, shielding effectiveness was discussed. The results showed that the coatings with a thickness of 300 μm containing 6 wt% of Ni-Cu-La-B-coated glass fibers had the lowest resistivity of 0.58 Ω•cm and best shielding effectiveness ranging from 51.45 dB to 62.18 dB in 0.3-1 000 MHz frequency band.

1. Introduction
With the rapid development of science and technology, a colorless, tasteless, invisible electromagnetic radiation pollution which is known as the “invisible killer” has been increasingly concerned by all walks of life. The harm of electromagnetic radiation pollution on economic construction, national defense security and social production and living is more and more serious\cite{1-2}. To research and develop all kinds of high cost performance of electromagnetic shielding materials has become one of the important research topics in the field of materials science and engineering. In recent years, electromagnetic environmental pollution protective coatings have become a kind of important electromagnetic shielding materials because of their low cost, simple technology, flexible application and strong adaptability\cite{3-4}. However, the cost and conductivity of fillers in the coatings have become two key factors restricting the coatings cost performance. So, the study for cost performance of conductive filler on preparation, characterization, the effect on electrical conductivity and electromagnetic wave shielding performance of shielding coating has important practical significance.

As an energy-saving and environment-friendly surface metallization treatment technology, electroless plating plays an increasingly important role in the preparation of cost-effective conductive composite filler due to its low cost, simple process and good coating quality\cite{5-6}. A low density, low cost, conductive and Ni-Cu-La-B-coated glass fiber was developed by electroless plating\cite{7}. In this paper, a novel electromagnetic environmental pollution protective coating with high performance was prepared using the fibers and nickel powders as composite fillers and Epoxy resin as binders. Furthermore, its conductivity, shielding effectiveness was discussed. This study is helpful to improve the added value and utilization of the glass fiber. This also provides a new idea and method for the development of low-cost electromagnetic environmental pollution protective coatings.
2. Experimental

2.1 Materials
Nickel powder (Chengdu Nuclear 857 New Materials co., LTD) with grain diameter of 0.2 to 0.4 microns contained 99.50 wt % nickel. Ni-Cu-La-B-coated glass fibers contained 41.36 wt % nickel, 2.32 wt % copper, 0.5 wt % lanthanum and 0.5 wt % boron. The length of fiber glass was 10-200 microns, the diameter was 2-30 microns, and the length diameter ratio was 5-100. Moreover, glass fibers, epoxy resin, dedicated thinner, additive etc. were all homemade. The basic composition of electromagnetic wave shielding composite coating was shown in table 1.

Table 1. Basic formula of electromagnetic shielding coatings.

| Coating ingredient | Composite filler content | Epoxy resin content | Coating thinner | Coating additive |
|--------------------|--------------------------|---------------------|----------------|-----------------|
| Mass fraction      | 70-90                    | 10-30               | Add according to coating viscosity | Micro-addition |

2.2 Coating preparation
The coating with high performance was prepared with Ni-Cu-La-B-coated glass fiber and nickel powder as composite fillers, and epoxy resin as binder. Secondly, the fibers and nickel powders were coupled by 2.5 wt % of titanate coupling agent in order to improve the filler dispersion in the resin. Thirdly, the fiber content in the filler was respectively 0 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt% and 8 wt%. Then, the filler was respectively mixed evenly and added to the epoxy resin, and a small amount of solvent was added to dilute it to a viscous state. The mixture was ground 2-4 times with a three-roller grinder. And then, the thinner and other additives were put into the mixture and mixed evenly. The amount of thinner was added according to the coating viscosity. It was measured with the coated-4 cup viscosity tester. The viscosity of the coating was 10-30 seconds. The coating was encapsulated for later use.

2.3 Spraying coating
The preparation method of the coating was by spray method. The outer diameter of the plate was 115 mm, the inner diameter was 10 mm and the thickness was 2mm. The above prepared coating was sprayed over the surface of PVC plastic substrate.

When spraying, firstly, the base board was fixed. Secondly, air compressor pressure was adjusted to 3 ~ 6 Mpa, and the distance between the nozzle and the workpiece was adjusted to 20 ~ 40 cm. And then, the electromagnetic environmental pollution protective coating was evenly sprayed on the substrate. The film thickness was 300 microns.

2.4 Coating curing
After the coating surface drying, coating curing was divided into two stages. The first stage was the artificial drying curing processing. The substrate whose spraying coating has been completed was put into the oven drying 30 minutes at 80-100 °C, and then took out. The second stage was curing at room temperature for 24-48 hours.

2.5 Performance testing and analysis
Resistivity test of the coating was carried out with a digital multimeter after the film was completely cured.

The shielding effectiveness of the coatings was tested by coaxial flange method in accordance with Chinese standard of SJ20524-95, i.e., “Measuring Methods for Shielding Effectiveness of Materials”. Schematic diagram of the coaxial flange test device of shielding effectiveness of the shielding coating was shown in Figure 1. The operating frequency of coaxial testing device is in the range of 0.3~1500 MHz, and its impedance is 50 Ω. The value of tested shielding effectiveness was higher than 100 dB dynamic range.
Figure 1. Schematic diagram of shielding effectiveness test device of the shielding coating.

Adhesion test of the coating was performed according to Chinese standard of GB/T 9286-1988, i.e., “Paints and Varnishes-cross Cut Test for Films”. Pencil hardness of the coating was tested according to Chinese standard of GB/T 6739-1996, i.e., “Determination of Film Hardness by Pencil Test”. Impact resistance determination of the coating was conducted according to Chinese standard of GB/T 1732-1993, i.e., “Determination of Impact Resistance of Film”. Wear resistance of the coating was tested following Chinese standard of GB/ GB1768-1979, i.e., “Method of Test for Abrasion Resistance of Paint Films”. Drying time test of the coating was conducted according to Chinese standard of GB/T 1728-1979, i.e., “Methods of Test for Drying Time of Coatings of Paints and Putties”.

3 Result analysis and discussion

3.1 Coating resistivity

The coating resistivity test results are shown in Figure 2.

In Figure 2, for the flake nickel powder/ acrylic resin electromagnetic shielding composite coating, the coating resistivity achieves the minimum of 1.77 Ω•cm with a thickness of 300 μm. However, for the Ni-Cu-La-B-coated glass fibers/flake nickel powder/ acrylic resin electromagnetic shielding composite coating, the coating resistivity decreases first and then rises with the increase of Ni-Cu-La-B-coated glass fibers content. The resistivity achieves the minimum when the fibers content is 6 wt% in the composite fillers. At this time, the minimum resistivity of the composite coating is 0.58 Ω•cm with a thickness of 300 μm.

According to the conductive theory of this kind of filled conductive composite coating, the coating conductivity mainly depends on the quality of conductive network formed in the coating by composite fillers and polymer[8-10]. The composite particle's physical contact with each other and electron tunneling effects are the two major factors for the conductive coating. The effects between conductive filler particles in the coating is promoted when the content of Ni-Cu-La-B-coated glass fibers is 6 wt% in the composite fillers. This is beneficial to form relatively dense conductive network structure because of the bridge filling effect of different length of the conductive glass fibre, so as to improve
the electrical conductivity of the coating. Thus, the right adding amount of Ni-Cu-La-B-coated glass fibers has a significant effect on the conductivity of the coating.

3.2 Shielding effectiveness

The electrical conductivity of composite coatings have important effects on electromagnetic shielding performance. For this kind of filled conductive electromagnetic shielding coating, the better the conductivity, the greater the electromagnetic shielding effectiveness. So, the shielding effectiveness of two kinds of coatings with or without 6 wt% Ni-Cu-La-B-coated glass fibers are tested by coaxial flange method in accordance with Chinese standard of SJ20524-95. The test results are shown in table 2.

| Frequency /MHz | Coating without Ni-Cu-La-B-coated glass fibers | Coating with 6 wt% Ni-Cu-La-B-coated glass fibers |
|---------------|-----------------------------------------------|-----------------------------------------------|
| 0.3           | 48.92                                         | 60.63                                         |
| 5             | 50.85                                         | 62.18                                         |
| 30            | 49.74                                         | 61.07                                         |
| 50            | 51.24                                         | 56.61                                         |
| 100           | 49.87                                         | 56.57                                         |
| 200           | 49.72                                         | 52.24                                         |
| 300           | 45.89                                         | 54.36                                         |
| 500           | 40.55                                         | 52.73                                         |
| 800           | 40.76                                         | 51.45                                         |
| 1000          | 40.13                                         | 52.40                                         |

In table 2, electromagnetic shielding effectiveness of flake nickel powder/acrylic resin composite coating is only 40.55 ~ 51.24 dB, the whole shielding effectiveness is low in the scope of 0.3 to 1000 MHz band. When the content of Ni-Cu-La-B-coated glass fibers is 6 wt% in the composite fillers, the composite coating has the highest electromagnetic shielding effectiveness, its value reach 51.45 ~ 62.18 dB in the same frequency range. Thus it can be seen its shielding efficiency increases significantly and are generally better than that of no adding Ni-Cu-La-B-coated glass fibers.

From above analysis, to add 6 wt% of Ni-Cu-La-B-coated glass fibers helps to form high quality conductive network in the coating, and this makes the electric performance of coating to achieve the best. This is mainly because the coating containing 6 wt% of Ni-Cu-La-B-coated glass fibers has a more dense conductive network, better conductivity and stronger electromagnetic wave loss capacity. This is mainly because the electromagnetic energy is loss by electromagnetic wave absorption, reflection and diffuse reflection effect after the incident electromagnetic wave acts on the coating. So, the right adding amount of Ni-Cu-La-B-coated glass fibers also has a significant effect on electromagnetic shielding effectiveness of the coating.

3.3. Environmental properties

The test results of main environmental properties of the coatings containing 6 wt% of Ni-Cu-La-B-coated glass fibers are shown in Table 3.

| Test items               | Test standard                 | Test results |
|-------------------------|-------------------------------|--------------|
| Adhesion / level        | GB/T9286-1988                 | 1            |
| Pencil hardness /H      | GB6739-1986                   | 5            |
| Impact strength /(kg·cm)| GB/T1732-1993                 | 50           |
In table 3, the main environmental properties of the electromagnetic shielding coatings containing 6 wt% of Ni-Cu-La-B-coated glass fibers are as follows: the adhesion force is level 1, the pencil hardness is 5 h, the impact strength is 50 kg·cm, the wear resistance (gravity) is 0.001 g/cm², the surface dry time (25 ℃) is 30 min, and the actual drying time (25 ℃) is 12 h. The main environmental properties of the coatings indicators have reached Chinese army standard GJB 2604-1996, i.e., “military electromagnetic shielding coatings general specification of the relevant provisions”.

4. Conclusion
A novel electromagnetic environmental pollution protective coating with high performance is developed with Ni-Cu-La-B-coated glass fiber and Nickel powder as composite fillers. Its conductivity, shielding effectiveness and main environmental properties are discussed. The study results showed that the right adding amount of Ni-Cu-La-B-coated glass fibers has a significant effect on conductivity and electromagnetic shielding effectiveness of the coating.

For flake nickel powder/acrylic resin electromagnetic shielding composite coating, the coating resistivity achieves the minimum of 1.77 Ω·cm with a thickness of 300 μm. For Ni-Cu-La-B-coated glass fibersflake nickel powder/acrylic resin electromagnetic shielding composite coating with a thickness of 300 μm, the best addition amount of Ni-Cu-La-B-coated glass fibers is 6 wt%, and the coating resistivity achieves the minimum of 0.58 Ω·cm.

The electromagnetic shielding effectiveness of flake nickel powder/acrylic resin composite coating is low and only reaches 40.55~51.24 dB in the scope of 0.3 to 1000 MHz band. When the content of Ni-Cu-La-B-coated glass fibers is 6 wt% in the composite fillers, the electromagnetic shielding effectiveness of Ni-Cu-La-B-coated glass fibersflake nickel powder/acrylic resin electromagnetic shielding composite coating has significantly increased to 51.45 ~ 62.18 dB in the same frequency rang.

The main environmental properties of the coatings have reached Chinese army standard of military electromagnetic shielding coatings general specification of the relevant provisions (GJB 2604-1996).

This offers a new idea for the development of low-cost electromagnetic environmental pollution protective coatings. This study is helpful to enhance the added value of the glass fiber and utilization, and raise the level of electromagnetic environmental pollution protection.

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