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Preparation, characterization and millimetre wave attenuation performance of carbon fibers coated with nickel-wolfram-phosphorus and nickel-cobalt-wolfram- phosphorus

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ABSTRACT

Carbon fibers (CFs) coated with Ni–X–P (X = W, Co–W or none) alloys were prepared by electroless plating. The morphology, crystal structure, and element composition of alloy-coated CFs were characterized by scanning electron microscopy, X-ray diffractometry, energy-dispersive spectrometry and microwave attenuation. The results showed that CFs were coated with a layer of alloy particles. P content in Ni–Co–W–P or Ni–W–P alloys was lower than that in Ni–P alloy, and coating alloy Ni–P was amorphous. After W or Co introduction, coating alloys exhibited crystal characteristics. MMW-attenuation performance analysis showed that the 3 mm wave attenuation performance of CFs/Ni–Co–W–P, CFs/Ni–W–P and CFs/Ni–P increased by 7.27 dBm, 4.88 dBm and 3.55 dBm, and the 8 mm wave attenuation effects increased by 11.61 dBm, 6.11 dBm, and 4.06 dBm respectively, compared with those of CFs. MMW-attenuation performance is attributable to the sample bulk resistivity and P content in the alloy. Moreover, an optimal weight gain value existed for the MMW-attenuation performance of alloy-coated CFs.

1. Introduction

Facing with the growing international military competition, millimetre wave (MMW) technology has been growing quickly in the past decades [1]. Military targets need to be protected against the monitoring and tracking of MMW radars, and is of critical importance for military specialists and scientists. The MMW energy can be attenuated by scattering or absorption, which are closely related to the electromagnetic properties of attenuation materials. Carbon fibers (CFs) are a widely-used MMW attenuation material because of their lower density, high tenacity and superior conductivity. However, the electromagnetic properties, especially the MMW-attenuation performance of CFs, are not as good as metal or alloy. Metal and alloy, when used as small chaffs and slices in the hiding smokescreen, are too heavy to keep floating for longer time compared with CFs. For the sake of the above two points, metal or alloy can be electroless-plated on the surface of carbon fibers (CFs) to improve their conductivities due to the skin effect [2] and decrease the whole weight of chaffs in the unit volume. So coating CFs with metal or alloy is an excellent way to improve the attenuation properties of CFs. Although metal- or alloy-coated CFs are rarely applied to millimetre-wave attenuation, they have been applied to centimeter-wave attenuation. De Rosa et al. [3] studied the microwave absorbing properties of polyester composites containing Ni coated carbon fibers. The results showed that multiphase composite materials filled with multiwall carbon nanotubes (MWCNTs), short nickel-coated carbon fibers and millimetre-long CFs with various weight fractions and compositions are developed and used for the design of wide-band thin radar-absorbing screens. Park et al. [4] investigated the microwave absorbing hybrid composites containing alloy-coated carbon nanomaterials for wider absorption bandwidth (BW) with thinner thickness in X-band. When Ni–Fe coated carbon nanofibers were prepared and added into epoxy, optimally designed Ni–Fe coated CNFs/epoxy composites had 10 dB absorbing bandwidth of 3.7 GHz (8.3–12.0 GHz) in the X-band with the content of 40.0 wt.% (2.40 mm thickness). Akman et al. [5] reported the Polyacrylonitrile (PAN) textiles coated with magnetic nanoparticles in coating baths with Ni, Co and their alloys via an electroless metal deposition method. The microwave absorption of the composites have been carried out in the frequency range of 12.4–18 GHz, and one absorption peak was observed between 14.3 and 15.8 GHz. The reflection loss (R_L) can be achieved between −30 and −50 dB for

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PAN textiles coated with Ni–Co alloy. Wang et al. [6] reported microwave absorbents with "tree-like" structures, which were composed of hollow porous carbon fibers (HPCFs) acting as "trunk" structure, carbon nanotubes (CNTs) as "branch" structure and magnetite (Fe_3O_4) nanoparticles playing the role of "fruit" structure. Microwave reflection loss, permittivity and permeability of Fe_3O_4-CNTs-HPCFs composites were investigated in the frequency range of 2–18 GHz. It was proven that the prepared absorbents possessed the excellent electromagnetic wave absorbing performance. The bandwidth with a reflection loss less than −15 dB covers a wide frequency range from 10.2 to 18 GHz with the thickness of 1.5–3.0 mm, and the minimum reflection loss is −50.9 dB at 14.03 GHz with a 2.5 mm thickness. Qiu et al. [7] reported a new kind of magnetic CFs with nickel/Fe_3O_4 nanoparticles (Ni/Fe_3O_4-NPs) composite coatings. Electromagnetic interference (EMI) shielding test showed that the prepared magnetic CFs exhibit excellent EMI shielding effectiveness. Based on Schelkunoff electromagnetic shielding theory, the high permeability in the prepared carbon fiber can bring about the co-effect of reflection and absorption mechanisms and thus obviously improve its EMI shielding effectiveness. Che et al. [8] studied the microwave absorption enhancement and complex permittivity and permeability of Fe encapsulated within carbon nanotubes.

Nickel (Ni) and cobalt (Co), as members of the eighth subgroup with iron (Fe), are important candidates for MMW-attenuation applications. The strong magnetism of Ni or Ni–Co alloy can increase the magnetic loss to enhance the MMW-attenuation performance of Ni or Ni–Co alloy-coated CFs. However, if Ni or Ni–Co alloy is used as coating alloy on CFs, disadvantages like non-abrasion and non-corrosion resistances will be exposed. Wolfram (W) is a high hardness and high melting point metal, with high temperature strength, high creep resistance, good thermal and electrical conductivity, and high electron emission performance. When wolfram was introduced into the alloys, the hardness and wear resistance of the alloys will be improved effectually. Therefore, Ni–W–P and Ni–Co–W–P alloys coated CFs could have excellent abrasion resistance, higher high-temp oxidation resistance and better corrosion resistance, compared with Ni–P alloy-coated CFs, and could be applied in microwave electromagnetic interference under special extreme environments.

Throughout previous research works, metal or alloy can be deposited on CFs by electroless deposition [9,10,4], electroplating [11–16], vapor deposition [17–21], and electromagnetic sputtering [22,23]. Electroless deposition is a mature and widely used method, in which silver or palladium is often used as the catalyst core [24,4,25–28]. However, these heavy metals are expensive and harmful to humans and the environment. Therefore, it will be an interest to avoid the use of precious metal salt as the sensitizing activator in deposition.

In this work, Ni–P, Ni–W–P and Ni–Co–W–P were coated on CFs by electroless plating, without using precious metal ions for the sensitization and activation of CFs. The morphology, crystal structure, constituent, and MMW-attenuation properties of these alloy-coated CFs were studied.

2. Experimental

2.1. Reagents and materials

Carbon fibers, made from polyacrylonitrile (PAN), were manufactured by Shanghai Carbon Group Co. Ltd. and in the form of continuous bundle revolving around a bobbin. Each bundle consisted of 12,000 filaments with an average diameter of 7 μm stuck together by an organic binder. The tensile strength, elastic modulus and ultimate elongation of CFs were 3100 MPa, 345 GPa and 1.2%. CFs used in this work were cut to 1.5 mm and 4 mm lengths. Ammonium chloride (NH_4Cl), nickel sulfate ($NiSO_4$), cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), sodium tungstate dihydrate ($Na_2WO_4·2H_2O$), potassium tartrate ($KC_4H_5O_6$), dihydrated trisodium citrate ($Na_3C_6H_5O_7·2H_2O$), sodium hypophosphite (NaH_2PO_2) and sodium hydroxide (NaOH) were all of analytical grade, purchased from Sinopharm Chemical Reagent Co. Ltd., China.

2.2. Pretreatment of carbon fibers without precious metal

To obtain complete and continuous alloy coating, CFs were pretreated before electroless plating without using silver or palladium for the sensitization and activation. The pretreatment started with CF heat treatment at 400 °C in an oven for 30 min to remove the organic binder, then the heat-treated CFs were immersed in 50 wt.% HNO_3 aqueous solution for 24 h, washed with deionized water and dried under −0.1 MPa vacuum for 3 h.

2.3. Chemical plating solution composition

The composition of chemical plating solution is shown in Table 1, in which sodium hypophosphite (NaH_2PO_2) were used as reducing agent, potassium tartrate ($KC_4H_5O_6$) and dihydrated trisodium citrate ($Na_3C_6H_5O_7·2H_2O$) were used as complexing agent, and ammonium chloride (NH_4Cl) was used as regulator.

2.4. Electroless plating procedure

Electroless plating solution was prepared according to the formula in Table 1. Pretreated CFs were added to the solution under ultrasonication for 30 min, then pH was adjusted to 9 with NaOH solution, and the mixture solution was heated to 80 °C with stirring, maintained for 30 min and filtered. Products were washed with deionized water, and dried under −0.1 MPa vacuum for 5 h.

2.5. Surface characterization

Surface morphologies and elemental compositions of the coated CFs were characterized by scanning electronic microscope

Table 1
Composition of chemical plating solution.

Composition of coating alloy	Ni–W–P	Ni–Co–W–P	Ni–P
Nickel sulfate ($NiSO_4$) (g/L)	10	8	16
Cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$) (g/L)	0	8	0
Sodium tungstate dihydrate ($Na_2WO_4·2H_2O$) (g/L)	2	4	0
Sodium hypophosphite (NaH_2PO_2) (g/L)	12	12	12
Two hydrated trisodium citrate ($Na_3C_6H_5O_7·2H_2O$) (g/L)	20	20	20
Potassium tartrate ($KC_4H_5O_6$) (g/L)	0	20	0
Ammonium chloride (NH_4Cl) (g/L)	12	12	12
pH	9	9	9
Temperature (°C)	80	80	80